

Dual Nanoresonators for Ultrasensitive Chiral Detection

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Dual Nanoresonators for Ultrasensitive Chiral Detection

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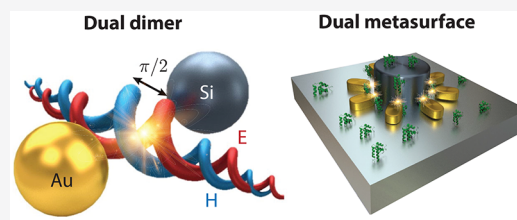
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Supporting Information

ABSTRACT: The discrimination of enantiomers is crucial in biochemistry. However, chiral sensing faces significant limitations due to inherently weak chiroptical signals. Nanophotonics is a promising solution to enhance sensitivity thanks to increased optical chirality maximized by strong electric and magnetic fields. Metallic and dielectric nanoparticles can separately provide electric and magnetic resonances. Here we propose their synergistic combination in hybrid metal–dielectric nanostructures to exploit their dual character for superchiral fields beyond the limits of single particles. For optimal optical chirality, in addition to maximization of the resonance strength, the resonances must spectrally coincide. Simultaneously, their electric and magnetic fields must be parallel and $\pi/2$ out of phase and spatially overlap. We demonstrate that the interplay between the strength of the resonances and these optimal conditions constrains the attainable optical chirality in resonant systems. Starting from a simple symmetric nanodimer, we derive closed-form expressions elucidating its fundamental limits of optical chirality. Building on the trade-offs of different classes of dimers, we then suggest an asymmetric dual dimer based on realistic materials. These dual nanoresonators provide strong and decoupled electric and magnetic resonances together with optimal conditions for chiral fields. Finally, we introduce more complex dual building blocks for a metasurface with a record 300-fold enhancement of local optical chirality in nanoscale gaps, enabling circular dichroism enhancement by a factor of 20. By combining analytical insight and practical designs, our results put forward hybrid resonators to increase chiral sensitivity, particularly for small molecular quantities.

KEYWORDS: chiral sensing, optical chirality, circular dichroism, duality, gap antennas, hybrid metal–dielectric metasurfaces



INTRODUCTION

Chirality plays a vital role in the functionality of biomolecules such as proteins, amino acids, and carbohydrates.^{1,2} It also determines the interactions of chiral drugs within the human body in terms of their healing potency and toxicity.^{3,4} Furthermore, chirality could be one of the microscopic origins of Alzheimer's, Parkinson's, and chronic kidney diseases.^{5–7} Therefore, the detection and differentiation of chiral molecules is of great interest in chemistry, biomedicine, and the food and pharmaceutical industries.

Chiral molecules reveal their handedness through interaction with another chiral entity such as circularly polarized light. Circular dichroism (CD) spectroscopy exploits the difference in light absorption for right- and left-handed circular polarizations.⁸ The differential absorbed power of a small volume of a chiral sample with respect to right and left circularly polarized light can be expressed as⁹

$$P_R^{\text{abs}} - P_L^{\text{abs}} = 4c_0 \text{Im}(\kappa) C_R V_s \quad (1)$$

where c_0 , κ , and V_s are the speed of light, the Pasteur parameter of the chiral sample,¹⁰ and the sample volume, respectively, and C_R is the optical chirality under illumination with right-handed circularly polarized light, which is assumed to be uniform inside the sample. Optical chirality is defined as¹¹

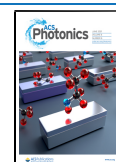
$$C = -\frac{k_0}{2c_0} \text{Im}(\mathbf{E} \cdot \mathbf{H}^*) \quad (2)$$

where k_0 is the free-space wavevector and \mathbf{E} and \mathbf{H} are the complex electric and magnetic fields. For small volumes of biomolecules, the differential absorbed power (eq 1) is exceptionally weak because both the chiral sample volume and the Pasteur parameter are extremely small ($\text{Im}(\kappa) \sim 10^{-4} - 10^{-7}$).¹² To push down the detection limit, these weak chiroptical signals can be compensated by an increase in optical chirality even above that of a circularly polarized plane wave, motivating a quest to find nanophotonic platforms for improved chiral sensitivity.^{13–20}

To increase optical chirality, we need both electric and magnetic resonances to be as strong as possible. Their resonant peaks should spectrally match to exploit the capability of such resonances for optimal superchiral fields. Additionally, the corresponding electric and magnetic fields in eq 2 must be parallel and $\pi/2$ out of phase and spatially overlap. We refer to this set of requirements as *optimal conditions for optical chirality*. As we shall demonstrate, however, the combination of these optimal conditions with maximal strength of the

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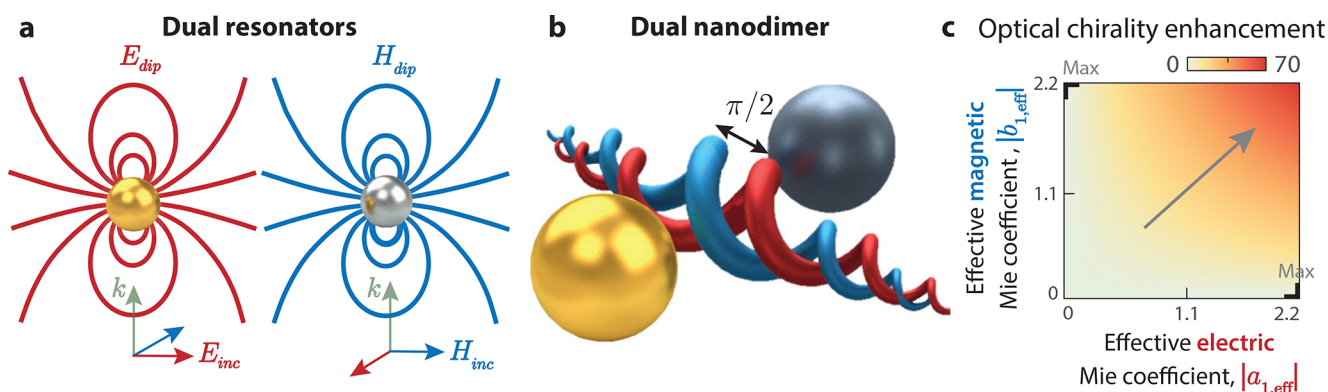


Figure 1. Dual nanoresonators for enhanced optical chirality. (a) Dual character of the fields in individual electric and magnetic resonators. E_{dip} (red) and H_{dip} (blue) indicate the analogous dipolar fields associated with electric and magnetic resonators (yellow and gray spheres, respectively). (b) A dimer of dual nanoresonators illuminated by circularly polarized light provides strong resonances with the optimal conditions for optical chirality. Red and blue indicate electric and magnetic fields, respectively. (c) Optical chirality enhancement at the center of a symmetric dimer (eq 3) vs the magnitudes of the effective Mie coefficients, which are constrained to a maximum value of 2.2. The dimer is made of two nanospheres with a center-to-center distance of 160 nm. The optical chirality is calculated at the wavelength $\lambda = 560$ nm and increases along the diagonal.

resonances restricts the maximum attainable optical chirality in nanophotonic structures.

To date, efforts have focused on exploiting either metallic^{21–23} or dielectric particles,^{16,24,25} for which the magnetic or electric field enhancement is comparatively weak. Metallic nanostructures can create intense electric dipole fields thanks to localized surface plasmons.^{26,27} On the other hand, high-refractive-index dielectric nanoparticles offer strong magnetic dipole response through Mie resonances^{28–32} (Figure 1a). Dielectric nanostructures can create high optical chirality close to the Kerker condition, where the electric and magnetic dipoles have equal strengths.^{9,33} However, the peaks of the two resonances do not spectrally match, thus reducing the maximum optical chirality. On the other hand, tuned resonant peaks destroy the phase condition, resulting again in suboptimal optical chirality.^{9,34}

Here we exploit the complementary strengths of metal and dielectric nanostructures to obtain strong chiral hotspots. To understand the general mechanism of chiral field formation in resonant structures, we first focus on simple nanodimers and derive analytical expressions describing the optical chirality at the center of the dimer. Through this analysis, we classify the resonant systems into two categories: incident-dipolar and fully dipolar. Then we find the fundamental limits of optical chirality for each class of resonant systems, with the highest value obtained for resonant dimers sustaining both electric and magnetic resonances. On this basis, we introduce an idealized dimer satisfying perfect duality symmetry.

To harness this insight with realistic materials, we propose a hybrid dimer consisting of a metallic particle next to a high-refractive-index dielectric particle (Figure 1b). In such a system, our theoretical results reveal strong and decoupled electric and magnetic resonances, which are separately tunable while meeting all of the other requirements to maximize optical chirality. Finally, on the basis of the mechanisms identified in simple nanodimers, we introduce a metal–dielectric metasurface for practical chiral detection. The proposed structure creates optical chirality hotspots 300 times stronger than the incident field, which is a significant enhancement compared with state-of-the-art dielectric nanostructures. These chiral hotspots are also able to enhance the average value of optical

chirality, resulting in an enhancement of CD signals by a factor of 20.

■ NANODIMERS IN THE ELECTRIC–MAGNETIC DIPOLE APPROXIMATION

To recognize the different mechanisms governing the formation of chiral fields in resonant systems, we first analyze a typical dimer composed of two identical spheres of diameter D separated by a center-to-center distance l along the y axis (Figure 2). The dimer is illuminated by circularly polarized light propagating along the z axis. For practical applications, the spherical particles could be replaced by disks on top of a substrate.^{35,36} The optical response of this system can be described by replacing each particle by an electric dipole and a magnetic dipole.³⁷ This electric–magnetic dipole approximation is valid as long as the particle dimensions are much smaller than the wavelength ($k_0 D \ll 1$) and the interparticle distance l is larger than the particle dimensions.^{38–40} The electromagnetic interaction of these dipoles is then given by a self-consistent system of coupled equations. Solving this system yields the dipole moments induced in each particle (Supporting Section S1).

The dominant dipole components producing chiral fields are those along the dimer axis. Therefore, we consider only the y components of the dipoles in our analysis (Supporting Section S2). Similarly to conventional gap antennas for electric field enhancement alone, such parallel dipoles ensure the existence of parallel field components in the gap as well as their spatial overlap. The optimal conditions for chiral fields then reduce to achieving spectral overlap of the resonances and $\pi/2$ dephasing of the electric and magnetic fields. As shown in Supporting Section S1, the optical chirality at the center of the nanodimer normalized to that of the incident field is

$$\frac{C_{\text{center}}}{C_{\text{inc}}} = \frac{1}{2} + 3\pi \operatorname{Im} \left[\zeta \left(\frac{k_0 l}{2} \right) a_{1,\text{eff}} - \zeta^* \left(\frac{k_0 l}{2} \right) b_{1,\text{eff}}^* \right] + 18\pi^2 \left| \zeta \left(\frac{k_0 l}{2} \right) \right|^2 \operatorname{Re} [a_{1,\text{eff}} b_{1,\text{eff}}^*] \quad (3)$$

where $C_{\text{inc}} = k_0/c_0\eta_0$, in which η_0 is the free-space wave impedance; $\zeta(x) = \exp(-ix)(ix^{-2} + x^{-3})/2\pi$ is related to the yy component of the dyadic Green's function of dipole radiation

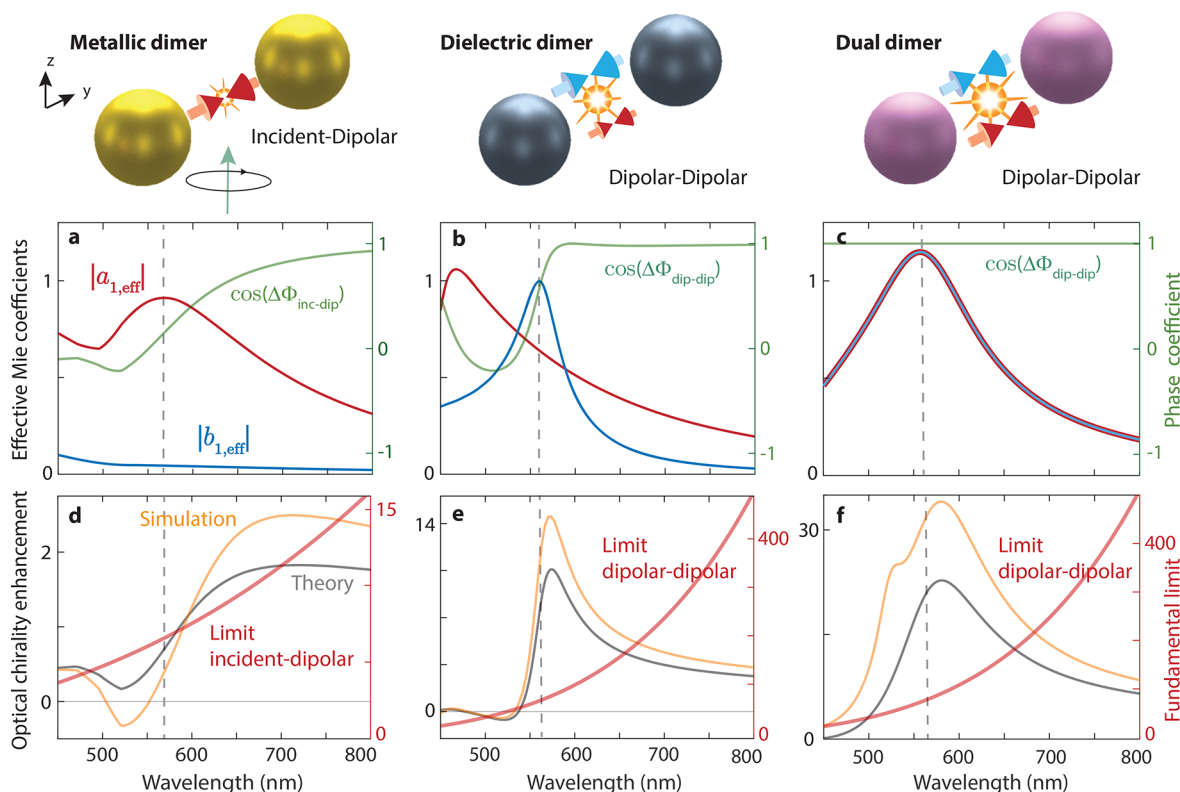


Figure 2. The optical chirality at the gap of symmetric dimers is controlled by the strength and phase of the effective Mie coefficients. We compare metallic (gold), dielectric (silicon), and ideal dual dimers with the same particle diameters of 130 nm and interparticle distance of 160 nm, corresponding to a gap of 30 nm. (a–c) Magnitudes of the effective electric (red) and magnetic (blue) dipolar Mie coefficients and the phase coefficient (green). (d–f) Optical chirality enhancement calculated using eq 3 (black) and full-wave numerical simulations (orange) along with the fundamental limit for each dimer (red).

in free space; and the effective electric and magnetic dipolar Mie coefficients for the nanodimer are

$$a_{1,\text{eff}} = \frac{2a_1}{1 + i6\pi\zeta(k_0l)a_1} \quad (4)$$

$$b_{1,\text{eff}} = \frac{2b_1}{1 + i6\pi\zeta(k_0l)b_1} \quad (5)$$

where a_1 and b_1 are the electric and magnetic dipolar Mie coefficients of the individual particles, respectively.⁴¹

The optical chirality enhancement at the center of a general nanodimer is given analytically by eq 3 in the electric–magnetic dipole approximation. We represent it as a function of the effective Mie coefficients in Figure 1c. First, we consider purely real values for the effective Mie coefficients and later investigate the effect of a phase difference between them. The diagonal increase in the optical chirality confirms the capability of dual electric and magnetic resonances to achieve strong superchiral fields. To understand how such resonances give rise to optical chirality, we return to eq 3 to find the origin of its different terms (Supporting Section S3). The first constant term comes from the y components of the incident fields. The second term corresponds to the interaction of incident and dipolar fields, for which $\zeta(k_0l/2)a_{1,\text{eff}}$ and $\zeta^*(k_0l/2)b_{1,\text{eff}}^*$ express the interaction of the incident magnetic field with the dipolar electric field and the incident electric field with the dipolar magnetic field, respectively. Finally, the last term provides the optical chirality due to the interaction of the dipolar electric and magnetic fields.

On this foundation, we can classify dimer resonators on the basis of the origin of optical chirality from incident-dipolar fields or fully dipolar fields (Supporting Section S3). This classification helps us to find a fundamental upper limit of optical chirality for different types of resonant systems. For resonators supporting only electric resonances, such as metallic dimers, the dominant part of optical chirality in eq 3 is $3\pi\zeta(k_0l/2)\|a_{1,\text{eff}}\| \cos(\Delta\Phi_{\text{inc-dip}})$, where $\Delta\Phi_{\text{inc-dip}} = \angle[\zeta(k_0l/2)a_{1,\text{eff}}] - \pi/2$. The phase coefficient $\cos(\Delta\Phi_{\text{inc-dip}})$ indicates the dephasing of the dipolar electric and incident magnetic fields, where $\cos(\Delta\Phi_{\text{inc-dip}}) = \pm 1$ is the perfect phase condition. On the other hand, for resonators with both electric and magnetic resonances, such as dielectric dimers, the dominant term is

$$\frac{C_{\text{center}}}{C_{\text{inc}}} = 18\pi^2 \left| \zeta\left(\frac{k_0l}{2}\right) \right|^2 \|a_{1,\text{eff}}\| \|b_{1,\text{eff}}\| \cos(\Delta\Phi_{\text{dip-dip}}) \quad (6)$$

where $\Delta\Phi_{\text{dip-dip}} = \angle a_{1,\text{eff}} - \angle b_{1,\text{eff}}$. A unity phase coefficient (i.e., $\cos(\Delta\Phi_{\text{dip-dip}}) = 1$) guarantees $\pi/2$ out of phase dipolar electric and magnetic fields.

For particles without gain, there is an upper limit of unity to the Mie coefficients of the individual resonators,⁴² which sets a limit of 2.2 on the effective Mie coefficients of dimers (Figure 1c and Supporting Section S4). Accordingly, the fundamental limit of optical chirality is $6.6\pi\zeta(k_0l/2)$ for a metallic dimer and the significantly higher value of $87.12\pi^2|\zeta(k_0l/2)|^2$ for a dielectric dimer. These strikingly different limits prove the promise of electric–magnetic resonant systems for strong chiral fields, for which $\|a_{1,\text{eff}}\| \|b_{1,\text{eff}}\| \cos(\Delta\Phi_{\text{dip-dip}})$ should be

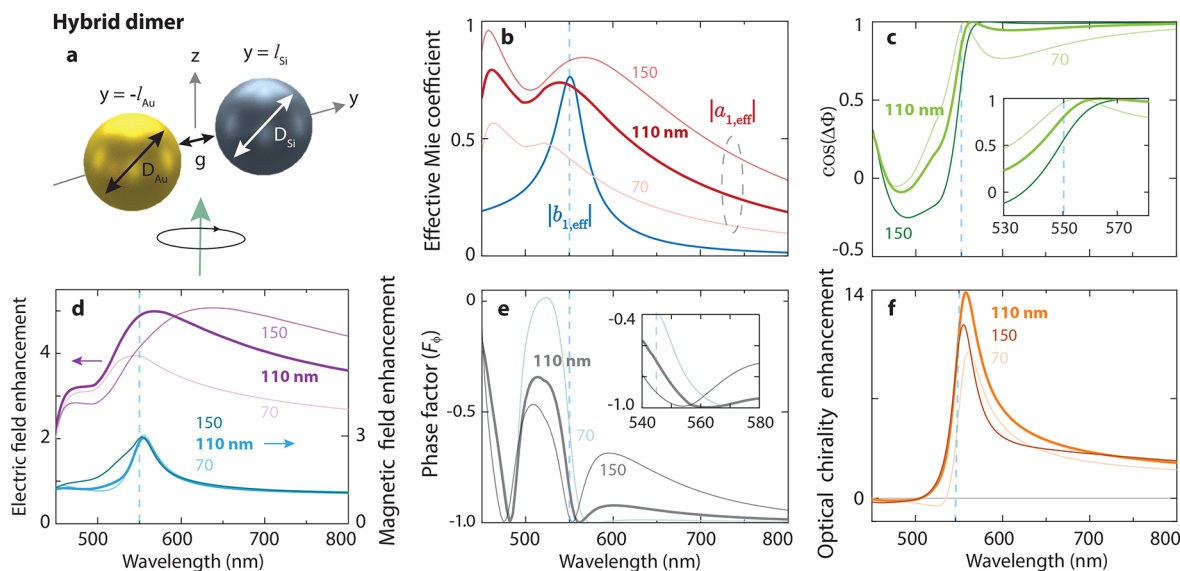


Figure 3. Hybrid metal–dielectric dimers. (a) A dimer consisting of a metallic sphere and a dielectric sphere separated by a distance $l = l_{\text{Au}} + l_{\text{Si}}$ is illuminated with a circularly polarized plane wave propagating along the z axis. (b, c) Investigation of resonance strength and optimal conditions for optical chirality by comparison of the magnitudes (red and blue) and the phase coefficient (green) of the effective electric and magnetic dipolar Mie coefficients in eqs 7 and 8. We fix the diameter of the dielectric particle at 130 nm and sweep the size of the metallic sphere to maximize $|a_{1,\text{eff}}||b_{1,\text{eff}}| \cos(\Delta\Phi)$ for the highest optical chirality. (d) Simulated electric and magnetic field enhancements (purple and blue), (e) phase factor, and (f) optical chirality enhancement at the center of the hybrid dimer for different diameters of the metallic particle. The vertical dashed line indicates the magnetic resonance of the dimer. The thickest line in each panel highlights the diameter with the highest optical chirality.

maximized. Analogously, we can classify the individual nanoresonators and find the fundamental limits in each class (Supporting Section S5). Our analysis shows that the fundamental limits are 2.2 and 2.2^2 times higher for the dimers compared with individual nanoparticles for the incident-dipolar and fully dipolar classes, respectively. We note that the fundamental limits derived above using the dipolar approximation for dimers could be generalized to multipolar resonators and higher numbers of nanoparticles.

To investigate the interplay between the resonance strength and the optimal conditions for optical chirality, we compare metallic and dielectric dimers with a hypothetical dimer fulfilling dipolar duality symmetry (Figure 2).^{43,44} Such an ideal dual dimer consists of particles with equal electric and magnetic dipolar responses ($a_1 = b_1$). In all three cases, the diameter of the spherical particles is $D = 130$ nm and the gap is $g = 30$ nm (interparticle distance $l = 160$ nm). For a fair comparison, we set the resonance wavelengths of the three systems to the same spectral range to take into account the increase in the fundamental limit of optical chirality at longer wavelengths (see eq 6 and red lines in Figures 2d–f). Hence, for the ideal dual dimer, we choose the permittivity and the permeability as $\epsilon = \mu = 4.75 - 0.01i$, resulting in a resonance at around $\lambda = 560$ nm. It should be noted that we use the time-harmonic convention $\exp(i\omega t)$ throughout this article, which determines the sign of the imaginary part of the permittivity.

First, we calculate the magnitude of the effective dipolar Mie coefficients and the phase coefficients for metallic, dielectric, and dual dimers (Figure 2a–c). The negligible effective magnetic Mie coefficient (blue) in the metallic dimer results in an electric-resonant system. Consequently, it has a much lower fundamental limit of optical chirality than the dielectric and dual dimers (red curves in Figure 2d–f). Furthermore, the small phase coefficient around the peak of its effective electric Mie coefficient (vertical dashed line) prevents using the full

strength of the electric resonance for chirality. In contrast, the dielectric dimer provides a larger value of $a_{1,\text{eff}}$ close to the resonance peak of $b_{1,\text{eff}}$. Nevertheless, the phase coefficient is still suboptimal, with $\cos(\Delta\Phi_{\text{dip-dip}}) = 0.5$.

The ideal dual symmetric dimer removes the main drawbacks of the metallic dimer (small fundamental limit) and the dielectric dimer (imperfect phase coefficient). Duality symmetry provides spectrally matched effective Mie coefficients higher than 1. The phase coefficient is also perfect as a consequence of preserving the helicity of the incident field, which ensures that the scattered light has a $\pi/2$ phase difference between the electric and magnetic field components. The dual symmetric dimer thus offers stronger chiral fields than the dielectric and plasmonic dimers as a result of optimal utilization of the fundamental limit. To conclude the study of eq 3, we calculate the optical chirality for the three cases both analytically and through full-wave numerical simulations (Figures 2d–f, black and orange curves). The good agreement proves the validity of the approximations.

■ HYBRID METAL–DIELECTRIC NANODIMERS

To tap into the insight gained so far from symmetric dimers, we propose asymmetric metal–dielectric dimers with realistic materials as a new type of electric–magnetic resonator. Such systems offer a fundamental limit of optical chirality that is as high as that of the dielectric and dual dimers while leveraging the stronger effective electric Mie coefficients of plasmonic dimers. Furthermore, this hybrid route allows a simple approach to obtain decoupled electric and magnetic resonances with controllable spectral matching and a perfect phase condition.

To understand the physical origin of these unique opportunities, we study a hybrid dimer composed of gold and silicon nanospheres (Figure 3a). They have diameters D_{Au} and D_{Si} and are placed at $y = -l_{\text{Au}} = -(g + D_{\text{Au}})/2$ and $y = l_{\text{Si}} =$

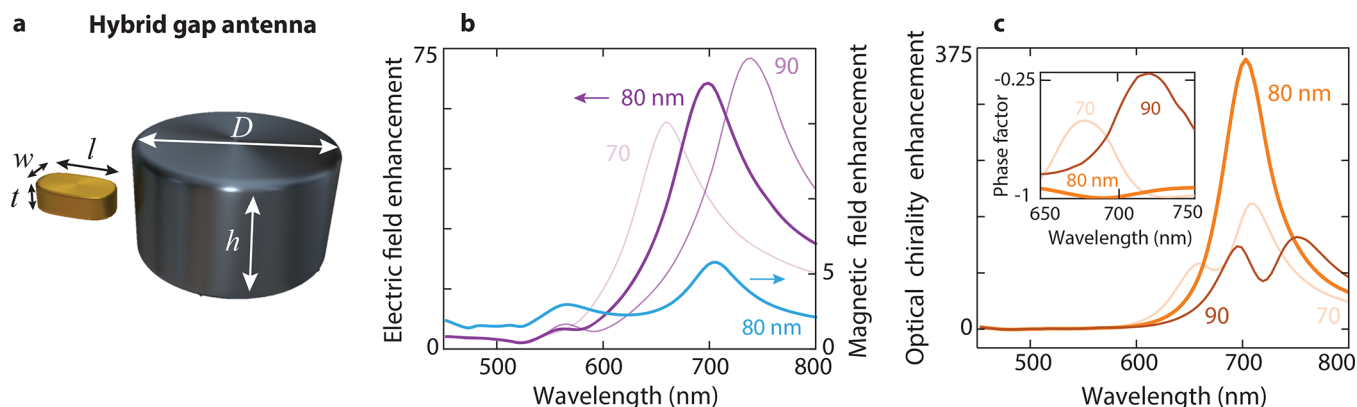


Figure 4. Basic building block for a realistic metasurface exploiting dual resonators. (a) A gold nanorod next to a silicon disk. The diameter D and height h of the silicon disk are both 160 nm. The width and the thickness of the nanorod are $w = 30$ and $t = 15$ nm, respectively, and its length l is varied to tune the electric resonance independently of the magnetic resonance of the silicon disk. (b) Electric and magnetic field enhancements and (c) optical chirality enhancement at the center of the gap under illumination with circularly polarized light propagating along the disk axis. The inset in (c) shows the corresponding phase factors.

$(g + D_{\text{Si}})/2$, respectively, where g is the gap. The resulting self-consistent system is similar to that of the symmetric dimer, but now the metal particle sustains only an electric dipole. Solving this system of equations yields the effective electric and magnetic dipolar Mie coefficients of the hybrid dimer (Supporting Section S6):

$$a_{1,\text{eff}} = \{ \zeta(k_0 l_{\text{Au}}) [1 - i6\pi\zeta(k_0 l) a_1^{\text{Si}}] a_1^{\text{Au}} + \zeta(k_0 l_{\text{Si}}) [1 - i6\pi\zeta(k_0 l) a_1^{\text{Au}}] a_1^{\text{Si}} \} / \{ \zeta(k_0 l/2) [1 + 36\pi^2 \zeta^2(k_0 l) a_1^{\text{Au}} a_1^{\text{Si}}] \} \quad (7)$$

$$b_{1,\text{eff}} = b_1^{\text{Si}} \quad (8)$$

where $l = l_{\text{Au}} + l_{\text{Si}}$, a_1^{Au} and a_1^{Si} are the electric dipolar Mie coefficients of the single plasmonic and dielectric particles, respectively, and b_1^{Si} is the magnetic dipolar Mie coefficient of the dielectric particle.

The electric resonances of the metallic and dielectric particles are thus coupled and form an effective electric resonance (eq 7). Remarkably, the effective magnetic resonance of the system is determined only by the dielectric particle and is decoupled from the effective electric resonance (eq 8). As a result, we can maximize the product $|a_{1,\text{eff}}| |b_{1,\text{eff}}|$ by tailoring the effective electric dipolar Mie coefficient to be as strong as possible while spectrally matching the magnetic resonance. However, the phase coefficient should also be taken into account for optimal optical chirality.

To demonstrate such tunability, we consider a hybrid metal–dielectric system with a fixed diameter of the dielectric particle providing a magnetic resonance at $\lambda = 550$ nm (Figure 3b, blue). We sweep the diameter of the metallic particle to control the effective electric dipolar Mie coefficient of the hybrid dimer (red). The metal–dielectric system can be engineered to provide high values of $|a_{1,\text{eff}}|$, comparable to that of metallic dimers (Figure 2a), and spectrally coincide with the magnetic resonance. The phase coefficient $\cos(\Delta\Phi_{\text{dip-dip}})$ is also close to unity around the magnetic resonance of the dimer (Figure 3c).

We examine next the electromagnetic fields, the phase condition, and the optical chirality enhancement at the center of the hybrid dimer using numerical simulations (Figure 3d–f). To evaluate the phase condition, we define the phase factor

$F_\phi = \sin(\Delta\phi)$, where $\Delta\phi = \angle E_y - \angle H_z$, is the phase difference between dominant field components. The strongest electric field that overlaps with the magnetic resonance occurs for $D_{\text{Au}} = 110$ nm (Figure 3d, thicker purple line). For this diameter, the phase factor F_ϕ vanishes 10 nm away from the magnetic resonance (Figure 3e inset). This perfect phase condition cannot be found in metallic or dielectric dimers, but it is realized by a hybrid nanodimer. The optical chirality is thus maximized at the wavelength $\lambda = 560$ nm, yielding a 14-fold enhancement (Figure 3f). For smaller gaps, the attainable optical chirality can be even higher as a result of enhanced electric hotspots (Supporting Section S7).

■ HYBRID METASURFACE FOR CHIRAL SENSING

In nanophotonics-enhanced chiral sensing, the sample is usually uniformly dispersed over the nanostructures. The CD signal is then proportional to the optical chirality averaged over the volume of the chiral sample.^{9,14} It is therefore highly desirable to increase the average value of the optical chirality, which is restricted by the small volume of the chiral hotspots. To remedy this limitation of simple nanodimers, we propose a hybrid metal–dielectric metasurface for practical chiral sensing by leveraging multiple chiral hotspots.

The basic constituent element of the proposed metasurface is a metallic nanorod next to a silicon disk (Figure 4a). Similar to our analysis above for spherical dimers, the strategy is to realize a strong electric hotspot with perfect phase close to a fixed magnetic resonance of the silicon disk ($\lambda = 710$ nm in Figure 4b). We vary the nanorod length to control the electric resonances and to achieve a phase factor of unity. Under illumination with circularly polarized light, we calculate the electric and magnetic field enhancements at the center of the gap (Figure 4b). The magnetic field enhancement is constant for different nanorod lengths (Figure 4b, all shown by a single blue curve), which confirms the decoupling of the magnetic resonance from the electric resonance. Furthermore, there is a strong electric hotspot that spectrally overlaps with the magnetic resonance for an optimal length of 80 nm. In this case, the phase factor is close to perfect around the magnetic resonance (Figure 4c inset, orange), resulting in a 375-fold enhancement of the optical chirality. To the best of our knowledge, this is the highest enhancement of local optical chirality in the visible and near-infrared reported to date.⁴⁵

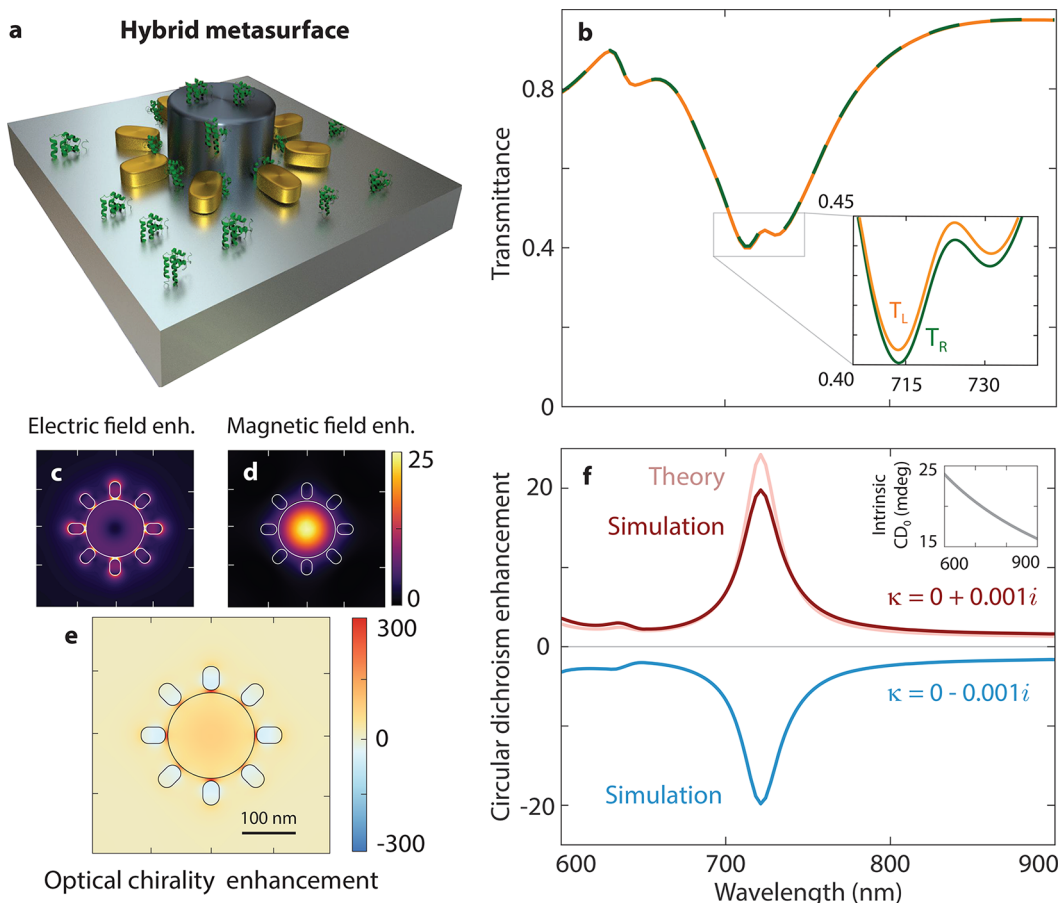


Figure 5. Hybrid metal–dielectric metasurface for enhanced chiral molecular detection. (a) Unit cell with a silicon disk surrounded by gold nanorods. Above the substrate, there is a buffer solution with a refractive index of 1.33. A planar chiral layer with a thickness of 20 nm covers the metasurface. The refractive index and the Pasteur parameter of the chiral sample are $1.46 - 0.01i$ and $\kappa = 0 \pm 0.001i$, respectively. (b) Transmission spectra for right and left circularly polarized light. The inset shows the difference in transmission around the resonance. (c–e) Electric field, magnetic field, and optical chirality enhancements at resonance ($\lambda = 720$ nm) on a plane at the center of the nanorods. (f) Enhanced circular dichroism signals for positive (red) and negative (blue) Pasteur parameters as retrieved from the transmission spectra in (b), compared with the theoretical prediction obtained using eq 9. The inset shows the CD of the chiral layer alone.

To increase the total volume of the chiral hotspots, we use multiple nanorods arranged as a hybrid oligomer. This approach is suitable as long as the coupling between nanorods does not disturb the main mechanism of chiral field formation. We surround a central silicon disk by eight identical gold nanorods equally spaced around the disk equator (see the metasurface unit cell in Figure 5a). The metasurface is covered by a chiral thin film with a thickness of 20 nm that coats the substrate and the outer surfaces of the structures. Because of the presence of a glass substrate and a buffer superstrate, we adjust the dimensions of the nanorods to an optimal length of 60 nm. The chiral sample on the metasurface displays a small difference in the transmission spectra for illumination with right- and left-handed circularly polarized light, I_R and I_L (Figure 5b, including a close-up around the resonance). The coupled electric resonances in the nanorods and the disk provide strong electric hotspots at the magnetic resonance wavelength of the disk (Figure 5c,d). These spectrally overlapping resonances provide electric and magnetic fields that are dephased by $\pi/2$, leading to a 300-fold enhancement in optical chirality in every nanogap (Figure 5e).

From the transmission spectra, we calculate the CD as a function of differential transmittance as $\tan^{-1}[(T_R - T_L)/(T_R$

$+ T_L)]$ (Figure 5f).⁴⁶ The CD enhancement¹⁴ can be expressed as

$$\frac{\text{CD}}{\text{CD}_0} = \frac{C_{\text{av}}/C_{\text{inc}}}{T} \quad (9)$$

where CD_0 is the CD of the chiral film without nanostructures and T and C_{av} denote the transmittance and the average optical chirality over the sample, respectively, when the system is illuminated with either right- or left-handed circularly polarized light (Supporting Section S8). Apart from the average optical chirality, the CD depends on the transmission in a similar way as the dissymmetry factor for chiral molecules, which is inversely proportional to the electric energy density.¹¹ In most relevant studies exploiting transmission (absorption), the circular dichroism (dissymmetry factor) enhancement is achieved by suppressing the transmittance (electric energy density), which degrades the signal-to-noise ratio. In contrast, our hybrid metasurface retains 40% of the transmission near the resonance. The CD enhancement predicted by eq 9 shows good agreement with numerical simulations (Figure 5f, pink and red). The hybrid metasurface creates a 20-fold enhancement of CD compared with the chiral layer without nanostructures. The enhanced CD is due to the higher average value of chiral fields over the volume of the chiral sample aided

by the stronger local optical chirality in the hotspots (Figure 5e). Reversing the handedness of the chiral molecules reverses the CD as well, confirming that the structure does not introduce any chiroptical background.

CONCLUSIONS

We have presented metal–dielectric nanostructures as dual electric–magnetic resonators for achieving strong chiral fields. We derived closed-form expressions for the optical chirality in a symmetric nanodimer. On the basis of the dominant term, we classified the resonant systems into distinct incident-dipolar and fully dipolar categories. We then extracted the fundamental upper limits of optical chirality for each class, demonstrating values for dimers beyond those of single nanoparticles. Through our analytical treatment, we merged different requirements for the optical chirality into only two conditions: the magnitude and the phase retardation of the effective Mie coefficients of the dimers. On the basis of these observations for symmetric dimers, we exploited a combination of the electric and magnetic resonances found in metallic and high-index dielectric nanoparticles. We showed that hybrid nanosphere dimers can provide larger values of the effective Mie coefficients. Together with spectral overlap of the resonances and a perfect phase, the asymmetric dual dimers result in superchiral light in nanoscale gaps.

To obtain a practical metasurface for chiral sensing, we adapted the spherical nanodimers into an array of disk–rod oligomers sustaining two strong but decoupled electric and magnetic resonances. The decoupling of the resonances provides design flexibility and enables a straightforward realization of maximal electric hotspots at the same wavelength as the magnetic resonance of the dielectric particle. We demonstrated that the proposed metasurface improves the CD by a factor of 20 relative to a chiral thin film thanks to the formation of hotspots with extreme local optical chirality. The possibility of obtaining strong fields for enhanced circular dichroism in metal–dielectric nanogap antennas will push the sensitivity of chiral molecular detection to the few- and single-molecule regimes.

METHODS

We perform full-wave numerical simulations using the finite element method in COMSOL Multiphysics 5.5. To incorporate the Pasteur parameter into the simulations, we modified the built-in default wave equations in COMSOL according to the constitutive relations for a chiral medium.¹⁴ In Figures 4 and 5, the width and height of the nanorods are 30 and 15 nm, respectively. The diameter and the height of the silicon disk are both 160 nm. The ends of the nanorods are rounded with a radius of 15 nm for a realistic geometry and to avoid numerical errors.⁴⁷ For maximum access to the magnetic fields outside of the dielectric particle, the nanorods should be aligned around the equator of the silicon disk. The gap between the each nanorod and the disk is 5 nm. The metallic and dielectric nanostructures are made of gold and silicon with realistic permittivities.^{48,49} In Figure 5, the length of the nanorods is 45 nm. The lattice constant of the metasurface is 440 nm, and the refractive index of the glass substrate is 1.5.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsphotonics.1c00311>.

Symmetric nanodimers in the electric–magnetic dipole approximation; dominant dipole moments affecting chiral field formation in a nanodimer; contribution from the incident and dipolar fields to the optical chirality in a nanodimer; upper limit of effective Mie coefficients in a nanodimer; fundamental limit of optical chirality in individual nanoresonators; asymmetric metal–dielectric nanodimer in the electric–magnetic dipole approximation; optical chirality in metal–dielectric nanodimers for small gap distances; CD enhancement for a chiral sample placed on top of a nanophotonic substrate (PDF)

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Notes

The authors declare no competing financial interest.

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