Near-Field Coupling Induced Less Chiral Responses in Chiral Metamaterials for Surface-Enhanced Vibrational Circular Dichroism

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Chiral metamaterials play vital roles in manipulating the circular polarization of electromagnetic waves. Although planar chiral metamaterials are believed to have no true/intrinsic chirality, the design of structural anisotropy can still create enormous circular dichroism, while the mechanism is fully explored. Here, for the first time, it is observed that strong near-field coupling induces less chiral response in chiral metamaterials. Selective exposure methods to manipulate the near-field coupling strength, and experimentally validate the circular dichroism difference from tailored near-field coupling effect are leveraged, which provides strong evidence for the assumption and can be utilized for the structural design framework. Besides, using the enhanced near-field (over 750-fold), surface-enhanced vibrational circular dichroism (SEVCD) for glucose enantiomers, which shows a larger-than-one normalized sensitivity compared with metamaterials with chiral response is demonstrated. Furthermore, The potential of SEVCD by detecting a broadband signal using arrayed metamaterials is explored. These findings pave the way toward chiroptical nanophotonic designs for potential biomedical and healthcare applications.

1. Introduction

Chirality describes objects lacking mirror-reflection symmetry, which means they cannot superimpose with their mirror image.\[1\] In optics, chiral metamaterials are artificially composed nanostructures with designed structural anisotropy, which can behave as asymmetric optical response with different circular polarizations, like circular dichroism (CD) and optical rotatory dispersion (ORD).\[2,3\] To date, there are two types of chiral metamaterials, out-of-plane symmetry-breaking ones, and planar ones. It is believed that only the out-of-plane symmetry-breaking metamaterials have true/intrinsic chirality, while the planar metamaterials can only “mimic” the chiral structure that depends on the illumination direction.\[4\] Hence, tremendous works have studied the way of breaking the out-of-plane symmetry to have a larger CD.\[5–10\] Although there have also been many works exploring the planar chiral metamaterials, like gammadion structures,\[11\] crossing-slit structures,\[12\] asymmetric nanorods, and so on\[13–17\] it is still unclear how the structural anisotropic design affects the far-field circular dichroism. Specifically, there lacks a theoretical framework to investigate the reason why many planarly chiral structures have different CD responses, even zero CD response.

Apart from the far-field CD, near-field chirality has also become a research hotspot, as it can help to characterize the localized enhancement of the optical chirality, which is known as the superchiral field.\[18,19\] Beneficial from the chiral near-field enhancement induced by optical resonators, molecules can experience stronger chiral light-matter interactions, and the molecular signals from the spectroscopies can be amplified.\[20–28\] To enhance the chiroptical activities, theoretical contributions have been made to analyze the relations between dissymmetry factor $g$ and far-field CD.\[29,30\] Recently, many works have used achiral resonators to generate larger optical chiral fields for enantiomer sensing.\[31–34\] Although these works either theoretically or experimentally reported an enhanced molecular signal, there lacks an intuitive comparison of performances between the achiral and chiral sensors. Besides, previous works have studied the near-field interactions between chiral molecules and nanoantennas,\[35\] providing theoretical evidence for the mechanisms of chiral light-matter interactions. However, direct evidence showing the relation between enhanced molecular signal and the chiral near-field enhancement is missing. While previous works have used near-field mapping or microscopic methods to experimentally study the vibrational near-field effect,\[36–38\] it is also desired to experimentally validate the localized chiral near-field enhancement from the resonators with less chiral or achiral response.
In addition, one advantage of using achiral resonators for chiral sensing is the neglected far-field CD from the structures, which will not overshadow the weak molecular chiral signals.[19] This can be important when expanding the wavelength to the mid-infrared range, where the molecular vibrational signal contains valuable structural information and can be fully utilized by signal amplification.[40–57] Together with the optical chirality, multiplexed spectroscopy can provide more information, known as vibrational circular dichroism (VCD).[9,58,59] Besides, compared with infrared absorption or Raman spectroscopy, VCD spectroscopy can also help distinguish optical chirality, which enables the detection of enantiomers. However, VCD spectroscopy suffers from a weak intrinsic signal from the molecules, which is ∼2–3 orders weaker than the CD signal in near-infrared or visible-light wavelengths.[60,61] Therefore, potentials are there to leverage achiral metamaterials for VCD enhancement. Nevertheless, to date, only one group has successfully demonstrated such possibilities with a plasmonic cavity for camphor enantiomers,[19] while the wavelength range is limited from 3.23 to 3.45 μm. As more importance has been attached to the chiral molecules as disease biomarkers, like glucose, protein, and amino acid,[62–65] it is also important to explore potential applications using enhanced VCD spectroscopy for broadband detection of such x biomolecules.

In this work, we start from the fundamental relation between planar chiral metamaterials and chiral response, theoretically raising a presumption that near-field coupling strength can be an essential factor for far-field circular dichroism. Based on this presumption, a quadruple-resonator system is proposed to present less chiral response while maintaining chiral structures, which can help increase the normalized VCD sensitivity of glucose enantiomers to a larger-than-one value. To validate this presumption, we design a selective exposure method to cover the nanogaps of the proposed quadruple-resonator metamaterials to test the relation between the near-field coupling coefficient and far-field CD response. Our experimental results suggest the significance of asymmetric near-field coupling strength, which is also explained and predicted by temporal coupled-mode theory (TCMT). Such observation provides strong evidence for our presumption indicating the near-field coupling effect. Moreover, leveraging the selectively exposed chiral metamaterials, we also experimentally validate the importance of the near-field coupling effect for chiral molecule sensing. Furthermore, we demonstrate broadband VCD sensing of L-glucose and D-glucose with the proposed metamaterial array with different working wavelengths at 1076 and 1216 cm⁻¹. Our sensor has great potential for diabetes diagnosis[66] healthcare[62,67] and chemical processing monitoring applications[68]

2. Results and Discussion

2.1. Observation of Near-Field Coupling Induced Less Chiral Response

The scheme of chiral metamaterials with less chiral responses is shown in Figure 1a. The structure is composed of metal-insulator-metal (MIM) layers (see Experimental Section: Sample fabrication). The incident circularly polarized light is either absorbed or reflected by the metamaterials due to the bottom reflective gold layer. The unit cell design is determined by several parameters, including the periodicity $P_x$ and $P_y$, resonant length $L$, width $w$, and the gap length $g$ (see Figure S1, Supporting Information). Due to the optical chirality of the chiral metamaterials, the reflected light shows asymmetric absorption of the left-handed circular polarization (LCP) and right-handed circular polarization (RCP), resulting in nonzero reflected circular dichroism $R_{CD}$, which is defined by $R_{CD} = R_{LCP}-R_{RCP}$. Our findings originate from the relation between $R_{CD}$ and the near-field coupling strength between a pair of perpendicularly positioned plasmonic resonators, as shown in Figure 1b. The near-field coupling is induced by the evanescent field near the surface of the plasmonic resonant nanostructures, where the coupling coefficient is defined by the parameter $\xi$. In our previous study, the relation between $R_{CD}$ and $\xi$ is determined by the simplified expression[9]:

$$R_{CD} = \frac{a \cdot \xi^2}{|\xi^2 + b|}$$

where $a$ and $b$ are fixed constants, determined by the loss and the resonant wavelength of the coupling system. It should be noted that the coupling coefficient has both positive and negative values, indicating the optical chirality of the chiral metamaterials. According to this simplified equation, we plot the parameters $R_{CD}$ and $\xi$, shown in Figure 1c. From the curve, $R_{CD}$ will first increase (or decrease) to its maximum (or minimum) value, then gradually vanish and get to zero, as the coupling coefficient $\xi$ increase (or decrease) from zero. Our previous study only explained the trend from zero to maximum (or minimum) value using perpendicular-positioned double nanorods with out-of-plane asymmetry.[9] In such a region, the absolute value of $R_{CD}$ is high, however, the near-field coupling strength $\xi$ is still weak. Although such structures can be used for chiral molecule sensors, the molecular signal is inevitably hindered by the CD signal from metamaterials. To solve this problem, we leverage another pair of double nanorods to form a quadruple-resonator system. This quadruple-resonator system has near zero circular dichroism as the near-field coupling strength is enlarged, which can be comprehended by increasing the coupling hotspots between each resonator, as shown in Figure 1d,e. Leveraging such properties, the quadruple-resonator system can present less chiral response but with strong chiral near-field coupling. This is also validated by the near-field simulations in Figure 1d,e. The calculation of optical chirality is defined as:

$$C = -\frac{e_0 \omega}{2} (\mathbf{E} \cdot \mathbf{B})$$

where $e_0$, $\omega$ are the permittivity in free space and the resonant angular frequency, $\mathbf{E}$ and $\mathbf{B}$ are the vector form of the electric field and the magnetic induction field, respectively, $C_0$ is the optical chirality of propagating circular polarized light in free space. We also define the different optical chirality $C = C_{LCP} - C_{RCP}$, which determines the asymmetrically enhanced optical chiral field. Besides, we use an average value $|\Delta C|$ to represent the averaged field enhancement, determined by:

$$|\Delta C| = \iint \frac{|\Delta C|}{c_0} dxdy$$
Figure 1. Near-field induced less chiral response for chiral molecular sensors. a) Schematic drawing of the chiral metamaterials. The metamaterials are composed of MIM structure. The top patterned structures are composed of quadruple resonators. The dimensions are: \( L = 3500 \text{ nm}, \ g = 200 \text{ nm}, \ w = 800 \text{ nm}, \ P_x = P_y = 6300 \text{ nm} \). b) Schematic illustration of the near-field coupling between perpendicularly positioned plasmonic resonators. c) Calculated \( R_{CD} \) as a function of \( \xi \). The double-resonator structure and the quadruple-resonator structures are highlighted as orange and purple dots, respectively. The values of both \( R_{CD} \) and \( \xi \) are normalized from \(-1 \) to \( 1 \). d, e) Simulation of the optical chiral field for both double-resonator and quadruple-resonator structures. f) Measured circular dichroism spectrum for both double-resonator and quadruple-resonator structures coated with L-glucose. The superscript w.o. and w. represent for without and with, respectively. h) Calculated glucose normalized sensitivity of both double-resonator and quadruple-resonator structures.
where S is the size of the total simulated area. As the field distributions in a volumetric layer are similar, we only take an integral through a 2D plane, which is 5 nm above the metamaterial layer (see Figure S19, Supporting Information). The physical meaning of such a parameter is to characterize the averaged chiral field enhancement that a molecule can experience in each unit cell, where we assume the molecules are arbitrarily distributed onto the chiral metamaterials. The calculated \(|\Delta C|\) for the double-resonator and the quadruple-resonator structures are 0.2765 and 0.6588, respectively, indicating a larger field distinguishment and improvement of the chiral metamaterials.

Based on these theoretical discussions, we fabricate both the double-resonator and the quadruple-resonator structures to measure the relevant performances. These two structures have similar q-factors at their resonant wavelengths (see Figure S2, Supporting Information). The measured far-field circular dichroism is shown in Figure 1f. Within the resonant wavelength range, the double-resonator structure shows a negative CD response, while the quadruple-resonator structure has almost zero CD response, which agrees with the calculated results shown in Figure 1c. For sensing demonstration, we use L-glucose and D-glucose in this work. These two glucose enantiomers have vibrational circular dichroism signals at mid-infrared wavelengths. However, the signal is too weak to be detected using our custom-made optical setup (see Figure S12, Supporting Information). Therefore, it is desired to enhance the weak signal of glucose enantiomers using metamaterials with achiral, or less chiral responses, which will not hinder the weak signal of glucose. After being coated with L-glucose at a concentration of 2000 ng μL⁻¹ for both structures, the measured VCD spectra are shown in Figure 1g. The absorption difference \(\Delta A = A_{\text{LCP}} - A_{\text{RCP}}\), where the absorption coefficient is defined as \(A = 1 - R\). The reason for using \(\Delta A\) rather than CD to describe the molecular signal, is to keep consistency with conventional VCD signals. Besides, \(R_{\text{CD}}\) will only be used to denote the reflected CD signal from only the device in this paper. It can be observed that the quadruple-resonator structure has larger signal contrast between the signal with and without molecules. This indicates that the quadruple-resonator chiral metamaterials can enhance the weak glucose VCD signals with reduced interference. We further define this molecular signal contrast as normalized glucose sensing sensitivity, which has an expression of \(\exp(\Delta A_{\text{RCP}} - \Delta A_{\text{LCP}})/\exp(\Delta A_{\text{RCP}})\). This value is to evaluate whether the molecular signal is affected by a chiral sensor. Only when the molecular signal is larger than the chiral response from the sensor, the value is larger than one. This normalized sensitivity is also shown in Figure 1h, where we find that the quadruple-resonator structure can promise a larger-than-one VCD signal of glucose enantiomer compared with the double-resonator structure, meaning a less affected chiral molecular signal.

2.2. Selective Exposure Method for Near-Field Coupling Validation

As our nanostructures only consist of resonators oriented in these two directions, the ports that can provide near-field coupling are only induced by the nanogaps, which are the mentioned hotspot regions between two orthogonal resonators. Therefore, in our assumption, “increasing the hotspots” is considered to increase the coupling coefficient \(\xi\). To experimentally ensure whether this less chiral response is affected by the enlarged near-field coupling strength, we design a selective exposure experiment to provide more evidence for this conclusion. Compared with thin film coating the whole surface with PMMA, selective exposure of each nanogap can provide additional information for us to learn the influence of localized fields separately. Hence, after fabricating the metamaterial device, we further coated another layer of e beam resist PMMA, and selectively exposed the areas in each unit cell. The fabrication process is shown in Figure S3, Supporting Information. The scheme of the selectively exposed metamaterials is shown in Figure 2a, where only the nanogaps between each plasmonic resonator are coated with PMMA, while the other parts are exposed. The AFM and SEM characterized image shows that each PMMA pillar is around the size of 1.2 × 1.2 μm². The thickness of the PMMA pillar is \(\approx\) 190 nm (see Experimental Section: Sample fabrication and Figure S4, Supporting Information). By covering each nanogap region, we assume that the coupling strength between orthogonal modes, is affected. This can be comprehended using temporal coupled mode theory (TCMT) [69,70]:

\[
\begin{pmatrix}
\Delta P_{x1} \\
\Delta P_{x2} \\
\Delta P_{y1} \\
\Delta P_{y2}
\end{pmatrix} =
\begin{pmatrix}
\omega_{x1} & j\omega_{x1} & -j\omega_{y1} & j\omega_{y1} \\
0 & \omega_{x2} & -j\omega_{x2} & -j\omega_{x2} \\
-j\omega_{x1} & -j\omega_{x1} & 0 & \omega_{y2} \\
-j\omega_{y1} & j\omega_{y1} & 0 & \omega_{y2}
\end{pmatrix}
\begin{pmatrix}
\kappa_{x1} & 0 & 0 & 0 \\
0 & \kappa_{x2} & 0 & 0 \\
0 & 0 & \kappa_{y1} & 0 \\
0 & 0 & 0 & \kappa_{y2}
\end{pmatrix}
\begin{pmatrix}
\Delta s_{x1} \\
\Delta s_{x2} \\
\Delta s_{y1} \\
\Delta s_{y2}
\end{pmatrix}
\]

(4)

where \(P_{x1}, P_{x2}, P_{y1},\) and \(P_{y2}\) are the resonant modes oriented along the x and y axis, respectively, as shown in Figure 2b. \(\kappa_{x1},\) \(\kappa_{x2},\) \(\kappa_{y1},\) and \(\kappa_{y2}\) are the far-field coupling coefficients. \(s_i\) represents the amplitude of the incident light. The complex resonant frequency can be further expressed by:

\[
\begin{pmatrix}
\omega_{x1} \\
\omega_{x2} \\
\omega_{y1} \\
\omega_{y2}
\end{pmatrix} =
\begin{pmatrix}
\sqrt{\gamma_x} \sqrt{1 - \kappa_x} & -\sqrt{\gamma_x} & \sqrt{1 - \kappa_x} & -\sqrt{\gamma_x} \\
0 & 0 & 0 & 0 \\
\sqrt{\gamma_x} & \sqrt{\gamma_x} & 0 & \sqrt{1 - \kappa_x} \\
\sqrt{\gamma_x} & \sqrt{\gamma_x} & \sqrt{1 - \kappa_x} & 0
\end{pmatrix}
\begin{pmatrix}
\Delta s_{x1} \\
\Delta s_{x2} \\
\Delta s_{y1} \\
\Delta s_{y2}
\end{pmatrix}
\]

(5)

where \(\gamma_x, 1 - \kappa_x\) are the radiative loss and absorption loss along the x and y axis, respectively. Besides, \(\xi_{x1}, \xi_{x2}, \xi_{y1}, \xi_{y2}\) are the near-field coupling coefficients, which are the most significant factors in our derived model as they describe the coupling between the orthogonal modes. For example, \(\xi_{x1}\) is related to the near-field distribution and intensity of the mode \(x_1\) and \(y_1\), which corresponds to the near-field coupling between these two resonators, as shown in Figure 2b(i). Therefore, when the nanogap between \(x_1\) and \(y_1\) resonators are covered by the PMMA pillar, we assume that the near-field coupling coefficient \(\xi_{x1}\) is also changed. Besides, it should be noticed that there are several zero coupling coefficients in the Hamiltonian of Equation (4). These terms are the near-field coupling coefficients between the parallel modes, which are assumed to be zero due to no near-field overlap (see Figure S5, Supporting Information). Besides, it is also intuitive to learn the influence of the covered PMMA pillar from the near-field simulation results. We simulate the near-field distribution of the filed intensity, as well as the case when all four nanogaps are covered, as shown in Figure 2c. When all the nanogaps are covered, the intensity of the field enhancement shrinks, indicating reduced near-field coupling coefficients. This is also verified by comparing the cross-sectional electric field intensity, as shown in Figure 2d. Similarly, we also calculate the optical chiral field enhancement of the structures, as shown in
Figure 2. Illustration of selectively exposed photoresist for near-field tailoring. a) Schematic drawing shows the selectively exposed PMMA on top of chiral metamaterials. b) Simulated electric field intensity under i) linear polarization along $y$ axis and ii) linear polarization along $x$ axis. c) Simulated electric field enhancement $E/E_0$ under circular polarization when i) all PMMA pillars are exposed and ii) PMMA pillars are selectively exposed. d) Cross-section plot of the electric field intensity $E$ when i) all PMMA pillars are exposed and ii) PMMA pillars are selectively exposed. e) Simulated optical chiral field under circular polarization when i) all PMMA pillars are exposed and ii) PMMA pillars are selectively exposed. f) Cross-section plot of the optical chiral field when i) all PMMA pillars are exposed and ii) PMMA pillars are selectively exposed.

Figure 2e,f, where the PMMA pillars also bring reduced optical chiral field intensities at the nanogap regions.

Before we derive and calculate the result from Equation (4), we make several assumptions to simplify the model. As the four-resonator system contains many miscellaneous parameters, which can be too complicated to extract the critical factors, our first assumption is to reduce the number of resonators. Considering that the near-field distribution of parallel modes is identical, while there is also no near-field coupling between these modes, we merge the separated modes into one. By merging these parallel resonators, we reduce the dimensionality from 4 to 2, where we use $P_x$ to represent $P_{x1}$ and $P_{x2}$, and $P_y$ for $P_{y1}$ and $P_{y2}$. Hence, the next step is to make several assumptions to reduce the dimensionality of the Hamiltonian in Equation (4). For the radiative loss and absorption loss, as all four resonators have identical geometries, while we don’t change their relative position when selectively exposing the PMMA pillars, we can also merge the losses for parallel modes and use $\gamma_{xy}$ to represent $\gamma_{x1y1}$ and $\gamma_{x2y2}$, and similarly, $\gamma_{yx}$ to represent $\gamma_{y1x1}$ and $\gamma_{y2x2}$. After using the same assumptions for the far-field coupling coefficients $\kappa_x$ and $\kappa_y$, we further discuss the near-field coupling coefficients, where different concerns may arise. If all the nanogaps are covered (or not covered) by the PMMA, these near-field coupling coefficients should have identical values, as the near-field coupling through each nanogap is the same. However, if not all the nanogaps are covered, then the near-field coupling coefficient could have different values. For example, covering the nanogap between resonator $x_1$ and $y_1$ will only result in a change of $\xi_{x1y1}$, while the other three coupling coefficients are still identical. In such a case, reducing the dimensionality of the near-field coupling matrix will give an asymmetric coupling coefficient between $P_x$ and $P_y$. Therefore, we use $\xi_{xy}$ and $\xi_{yx}$ to represent the coupling coefficient between two orthogonal modes.

Based on these assumptions, we further simplify the TCMT model by reducing the dimensionality in Equation (4):

$$\frac{d}{dt} \begin{pmatrix} P_x \\ P_y \end{pmatrix} = \begin{pmatrix} j\omega_x - \gamma_x - \gamma_{xy} & -j\xi_{xy} \\ -j\xi_{yx} & j\omega_y - \gamma_y - \gamma_{yx} \end{pmatrix} \begin{pmatrix} P_x \\ P_y \end{pmatrix} + \begin{pmatrix} \kappa_x 0 \\ 0 \kappa_y \end{pmatrix} \begin{pmatrix} \xi_x^{py} \\ \xi_y^{px} \end{pmatrix}$$ (6)
Figure 3. Experimental validation for the asymmetric near-field coupling induced additional far-field circular dichroism. a) Schematic drawing shows how the selectively exposed PMMA cant tune the near-field coupling coefficients. i) and ii) When all the nanogaps are exposed and not exposed, there is no induced CD. iii) and iv) When only parts of the nanogaps are exposed, an induced CD will be observed. b,d) Measured reflection spectra under LCP and RCP incidence of 0 gap exposed, 1 gap exposed, and 2 gaps exposed structures. e,g) Measured VCD spectra of 0 gap exposed, 1 gap exposed, and 2 gaps exposed structures.

besides, we also have the:

\[
\begin{align*}
\begin{pmatrix}
\xi_x^s \\
\xi_y^s
\end{pmatrix}
&= 
\begin{pmatrix}
-1 & 0 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
\xi_x \\
\xi_y
\end{pmatrix}
+ 
\kappa \begin{pmatrix}
0 & 0 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
P_x \\
P_y
\end{pmatrix} \\
\begin{pmatrix}
\xi_x^s \\
\xi_y^s
\end{pmatrix}
&= 
\frac{1}{\sqrt{2}} 
\begin{pmatrix}
1 \\
-j
\end{pmatrix} 
\begin{pmatrix}
\xi_x \\
\xi_y
\end{pmatrix}
\end{align*}
\]

where \( s \) represents the amplitude of the reflected light. The physical meaning of “sx-” and “sy-” are the reflected light with linear polarization with the direction along the x-axis and y-axis, respectively. As our device is reflective, it can be expressed in a one-port model, and the far-field coupling coefficient \( \kappa \) can be expressed as \( \sqrt{2} \gamma \). The derived reflective circular dichroism (R\(_{CD}\)) can be written as (see Note S1, Supporting Information):

\[
R_{CD} = \frac{4(\kappa_x + \kappa_y) \left( \frac{\omega_x - \omega_y}{\gamma} \right) + 4(\kappa_y - \kappa_x) \left[ \frac{\omega_x^2 - \omega_y^2}{\gamma^2} \right] + 4(\kappa_x - \kappa_y) \left[ \frac{\omega_x^2 - \omega_y^2}{\gamma^2} \right]}{(\kappa_x + \kappa_y)^2 \left[ \kappa_x \kappa_y + \left( \frac{\omega_x - \omega_y}{\gamma} \right) \right] + 4(\kappa_x + \kappa_y) \left[ \frac{\omega_x - \omega_y}{\gamma} \right]}
\]

The parameter mapping and calculation results can be found in Note S2 and Figure S8 (Supporting Information). Here we mainly discuss the most important near-field coupling coefficient \( \xi_{xy} \) and \( \xi_{yx} \) for further experimental validation. As indicated by Equation (9), when the near-field coupling coefficients have unequal values, an additional RCD induced by the second term in the numerator will be observed. Our experimental validation steps are shown in Figure 3a. When all the nanogaps are exposed or not exposed, as shown in Figure 3a(i),(ii), these near-field coupling ports are all surrounded by air or PMMA pillars, where we assume the near-field coupling is symmetric, which is \( \xi_{xy} = \xi_{yx} \). In this case, Equation (9) can also be simplified as the form in Equation (1). In contrast, when only part of the nanogaps are covered, as shown in Figure 3a(iii),(iv), the case turns asymmetric coupling, which is \( \xi_{xy} \neq \xi_{yx} \). We fabricated the device and covered the nanogaps accordingly, named 2 gaps exposed, 1 gap exposed, and 0 gap exposed (see Figure S6, Supporting Information). The measured reflection spectra under circularly polarized light are shown in Figure 3d. From the spectra, a clear...
difference between LCP and RCP polarizations can be found for 1 gap exposed and 0 gap exposed metamaterials. As the difference signal is weak, we repeated the experiment five times to avoid influences from the noise. The reflected circular dichroism results are shown in Figure 3e,g. The shaded blue areas are the obtained spots for all five tests, while the lines are averaged from the five measured spectra. For the 0 gap exposed metamaterials, the \( R_{\text{CD}} \) is almost zero, while the 1 gap exposed and 2 gaps exposed metamaterials have an additional \( R_{\text{CD}} \), with a minimum value of \( \approx 0.01 \). Although the \( R_{\text{CD}} \) signal is very weak, the existence of this additional circular dichroism shows evidence of a perturbed far-field spectrum influenced by asymmetric near-field coupling. Besides, the results also agree with the simulation results (see Figure S7, Supporting Information). Moreover, apart from the validated results in Figure 3, we have also experimentally validated our conclusion using thickness-varied metamaterials which also consider a difference in loss ratio (see Note S3 and Figure S9, Supporting Information). Furthermore, we also proposed another validation method with different gap sizes (see Note S4 and Figure S10, Supporting Information). All these results confirm the enlarged circular dichroism induced by asymmetric near-field coupling.

2.3. VCD Sensing Enhancement of Glucose Enantiomers

We use glucose enantiomers, L-glucose, and D-glucose for thin-film sensing demonstrations. The glucose enantiomers have different chirality, which shows opposite circular dichroism signals under the illumination of LCP and RCP light. Therefore, we also design a pair of chiral metamaterials using the quadruple-resonator system. The scheme is shown in Figure 4a,d. The D-glucose and L-glucose are diluted in deionized (DI) water with a concentration of 2000 ng \( \mu \text{L}^{-1} \) for thin-film sensing demonstration (see Experimental Section: Preparation of glucose solution). After coating onto the metamaterials, we first measured the IR absorption signals of glucose enantiomers, as shown in Figure 4b,c. Two vibrational peaks located around the wavenumber 1038 and 1076 cm\(^{-1}\) can be observed for both L-glucose and D-glucose, corresponding to the C–O chemical bond, with the plasmonic enhancement by the metamaterials. However, the vibrational wavelengths for L-glucose and D-glucose are almost identical, where only slight differences can be observed by the vibrational strengths, which however can be easily affected by the concentration error. Fortunately, our platform also enables the detection of enhanced VCD signals, as shown in Figure 4e,f. It can be observed that L-glucose presents a positive VCD signal while D-glucose presents a negative VCD signal, while the strongest vibrational peaks also reveal the IR absorption transition. Besides, the enhancement for this VCD signal can only be observed when the chirality of the molecules matches the optical chirality of the plasmonic metamaterials, where the signal of L-glucose (D-glucose) will only be enhanced when coated on L-ring (R-ring). It is also noticed that the enhanced VCD signal for enantiomers do not show complete mirror symmetry. We have analyzed possible reasons from our custom-made optical setup (see Figure S15 and Note S6, Supporting Information). We have also implemented a control experiment to exclude any possible artifacts from the metamaterials or linear dichroism (see Figures S17,S18, and Note S7, Supporting Information).

After demonstrating the VCD-enhanced signals of the chiral metamaterials, we further try to validate the chiral light-matter interaction using the selectively exposed devices. The scheme is shown in Figure 4g, where the PMMA pillars are exposed before glucose thin film is coated. This measurement is to validate where the enhanced molecular chiral signal is from. We also choose the same wavelength band from 1000 to 1100 cm\(^{-1}\), as the PMMA vibrational signal can be almost neglected which does not interfere with the glucose signals, shown in Figure 4h. Besides, we use chiral metamaterials with different lengths to make sure that all the metamaterials share the same resonant wavelength (see Figure S11, Supporting Information). The sensing results of these selectively exposed structures are shown in Figure 4i. Comparing the performance between all exposed and 0 gap exposed metamaterials, the observed results show the strongest VCD signal only appears when some of the nanogaps are covered by PMMA, indicating that PMMA pillars hinder the interaction between the chiral molecules and the circularly polarized light. This conclusion also agrees with the near-field simulation results shown in Figure 2, as the molecules cannot experience the largest field enhancement when PMMA is covered. Besides, comparing the performance of 1 gap exposed and 2 gaps exposed metamaterials, the results indicate that far-field structural CD does not necessarily help enhance the molecular signal. Hence, we summarize that the near-field intensity plays a more important role in chiral molecule sensing applications, even when the chiral structures themselves do not create a strong circular dichroism.

2.4. Metamaterial Array for Broadband Sensing with Different Concentrations

We further demonstrate a chiral metamaterial array for broadband sensing applications. Apart from the glucose vibrational absorption peaks ranging from 1000 to 1100 cm\(^{-1}\), there are also abundant vibrational modes located at shorter wavelengths (see Figure S12, Supporting Information). Detection of multiple IR absorption peaks could help identify the molecules with higher accuracy. Therefore, we decrease the length \( L \) of each resonator to make an arrayed device, where the resonant wavelength could match the glucose resonant peak at \( \approx 1200 \text{ cm}^{-1} \). The measured reflection spectra of the metamaterial array under linear polarization are shown in Figure 5a. Besides, we also measured the spectra under circularly polarized light, indicating the less chiral response of the quadruple-resonator structure (see Figure S11, Supporting Information). We choose the device with \( L = 2.6 \mu \text{m} \) to measure the glucose vibrational signal around this shorter wavelength band. We use the R-Ring structure coated with D-glucose (concentration: 2000 ng \( \mu \text{L}^{-1} \)) to demonstrate the enhancement of the glucose vibrational peaks, as shown in Figure 5b. The differential blue curve shows the differential reflection, which is the enhanced D-glucose infrared absorption signal. The simulated near-field optical chirality is shown in Figure 5c, where opposite field enhancement can still be observed for L-ring and R-ring structures at the resonant wavelength, indicating their selective enhancement toward left-handed and right-handed molecules. Besides, the average chirality is only slightly
Figure 4. Demonstration of chiral metamaterials enhanced glucose enantiomer sensors. a) Schematic drawing of the glucose-coated chiral metamaterials. b) Measured IR reflection spectrum of the chiral metamaterials with L-glucose and D-glucose. c) Extracted surface enhanced IR absorption spectrum of the L-glucose and D-glucose. The extracted absorption signal has been corrected using baseline correction, which is not a simple subtraction from the reflection spectrum by unity. d) Schematic drawing of the selective enhancement of i) L-glucose on L-ring structure and ii) D-glucose on R-ring structure. e,f) Enhanced VCD spectra of L-glucose and D-glucose on both L-ring and R-ring structures. g) Schematic drawing of the glucose-coated chiral metamaterials with selective exposure. h) Measured IR absorption signal of the substrate with PMMA and without PMMA. i) Measured VCD spectra L-glucose and D-glucose on differently exposed L-ring and R-ring metamaterials.

Weaker than that in longer wavelengths. Furthermore, we diluted the concentration from 2000 to 1000, 500, 250, and 125 ng \( \mu \text{L}^{-1} \), respectively. Besides, we use the chiral metamaterials with two lengths, \( L = 2.6 \text{ \mu m} \), and \( L = 3.7 \text{ \mu m} \) to demonstrate a broadband VCD sensor. As we use a dry film sensing process, all the initial concentrations have been recalculated into the amount of matter when calculating the sensitivity. The results are shown in Figure 5d,e. For both L-glucose and D-glucose, the vibrational peaks at \( \approx 1076 \text{ and } 1216 \text{ cm}^{-1} \) can be enhanced by the plasmonic chiral metamaterials, while the optical chirality is recognized and enhanced by L-ring and R-ring structures, respectively. Moreover, the enhanced VCD signal also agrees with the concentration change. The calculated sensitivity of the concentration of our device according to the concentration is shown in Figure 5f. It can be noticed that the highest sensitivity of concentration at 0.70848%/\( \text{mm} \) is observed for the vibrational peak at 1216 cm\(^{-1}\), which is higher than the vibrational peak at 1076 cm\(^{-1}\). Besides, the lowest detection limit of 0.03 mm is achieved for the vibrational peak at 1076 cm\(^{-1}\) (see Figure S13, Supporting Information). Therefore, the detection wavelength bands need to be carefully chosen considering the trade-off between sensitivity of concentration and the detection limit.

3. Conclusion

In summary, we observe enhanced near-field induced far-field less chiral response in chiral metamaterials. A quadruple-resonator metamaterial with less chiral response is proposed based on such a principle, enabling a larger-than-one normalized sensitivity. Guided by the TCMT model, we use selective ex-
Figure 5. Demonstration of metamaterials array for broadband glucose sensor. a) Measured reflection spectra of arrayed chiral metamaterials with different resonant lengths, ranging from 2.5 to 3.7 μm. b) Measured reflection spectrum of D-glucose coated on R-ring structure. The blue dotted curve shows the differential reflection, which is the enhanced IR absorption signal of D-glucose. c) Simulated optical chiral field of both L-ring and R-ring structures at the wavelength of 1216 cm\(^{-1}\). d) Measured enhanced VCD spectrum of different concentrations of L-glucose on L-ring structures at both 1076 and 1216 cm\(^{-1}\). e) Measured enhanced VCD spectrum of different concentrations of D-glucose on R-ring structures at both 1076 and 1216 cm\(^{-1}\). f) Fitted curve of different concentrations with the enhanced VCD signals. The sensitivity of concentration is marked near each fitted curve.

Exposure methods to cover the nanogaps between each resonator for experimental demonstration of the near-field coupling effect. Our theoretical calculation results indicate that asymmetric near-field coupling between orthogonal modes can induce additional far-field CD, which is validated by experimental results, providing strong evidence for our assertion. We also propose several other methods to support our conclusion (see Notes S3, S4 and Figures S9, S10, Supporting Information). The near-field coupling effect is verified to be responsible, while the detailed interaction mechanism still needs further exploration. Based on these investigated results, we demonstrate thin-film sensing of glucose enantiomers using the proposed chiral metamaterials, which show surface-enhanced VCD signals for both D-glucose and L-glucose. Besides, we also emphasize the importance of near-field enhancement by comparing the sensing performance between selectively exposed metamaterials. With decoupled far-field CD and near-field chiral field, our results indicate that enhanced chiral near-field is the key to molecular signal enhancement, while structural CD is less essential. Furthermore, we have also demonstrated a broadband sensing of glucose enantiomers using a chiral metamaterials array. The multi-wavelength band sensing process can be more promising to identify the fingerprint of molecules. By testing the glucose VCD signal with different concentrations, the VCD signal is enhanced with a sensitivity of concentration ≈0.26%/mm and a detection limit of ≈0.03 mm.

This limit is mainly from our home-made optical setup. A better VCD signal with higher SNR and lower limit of detection (LOD) is expected if conventional VCD instrument is used. Our findings provide a clue for the relevance between chiral near-field tailoring and far-field CD difference, opening a new avenue for chiral metamaterials design toward ultra-small volume and label-free detection of chiral molecules.

4. Experimental Section

Sample Fabrication: Dummy silicon wafer was sonicated in acetone for 3 min and then rinsed in IPA followed by nitrogen drying. After surface cleaning, 5 nm thick Ti, 100 nm thick Au, and 200 nm Al\(_2\)O\(_3\) were deposited onto the Si wafer by e-beam evaporator (AJA Ebeam evaporator). Next, positive e-beam resist PMMA (495K, A5) was coated onto the substrate with a speed of 4000 rpm for 1 min. Since the Al\(_2\)O\(_3\) substrate was insulating, a thin conducting polymer file Espacer was also spin-coated with a speed of 4000 rpm for 40 s. After being exposed by E-beam lithography (JEOL JBX-6300FS, dose: 1350 μC cm\(^{-2}\)) to pattern the chiral metamaterials, the sample was first immersed into DI water for 15 s to remove the Espacer, then developed in a mixture of MIBK/IPA (1:3) for 40 s. After being exposed by E-beam lithography (JEOL JBX-6300FS, dose: 1350 μC cm\(^{-2}\)) to pattern the chiral metamaterials, the sample was first immersed into DI water for 15 s to remove the Espacer, then developed in a mixture of MIBK/IPA (1:3) for 40 s, and finally rinsed in IPA for 30 s. After that, 5 nm thick Cr and 75 nm Au were deposited onto the sample using a thermal evaporator (Lesker NANO36), followed by a lift-off process in acetone at 65 °C for 30 min. After that, another PMMA layer was spin coated on the sample with the same recipe. The PMMA resist was exposed using E-beam lithography with a lower dose.
Optical Characterization: The chiral metamaterial was characterized by Spero Chemical Imaging Microscope (see Figure S14, Supporting Information). Two 1/4 waveplates (4Lasers, 19908, 19904) were used to change the linearly polarized light to circularly polarized light at 8.5 μm (1767 cm⁻¹) and 9.5 μm (1052 cm⁻¹), respectively. Both waveplates have a wavelength bandwidth of 400 nm.

Preparation of Glucose Solution: For the glucose sensing measurement, L-glucose and D-glucose were used (Sigma-Aldrich, product G8270 and G5500). The proteins were dissolved in DI water and formed a solution with different concentrations, ranging from 125 to 2000 ng μL⁻¹. The chiral metamaterials were used for multiple measurements. For each measurement, glucose solution was fetched using a micropipette (±2 μL) and dropped onto the metamaterials. The measurement was conducted after 15 min when the droplet was dried. After each measurement, the sample was immersed in DI water for 30 min and then cleaned by nitrogen drying. There was an error between the labeled concentration and the real concentration of the solutions, the influence of such error between concentration was studied, as shown in Figure S16 (Supporting Information).

Numerical Simulation: The simulation was performed using a 3D finite-difference time-domain (FDTD) method (Lumerical-FDTD). In the simulation, the complex refractive index of Au, Al₂O₃, and Si from Palik et al. was used. The refractive index of PMMA was set to 1.52 for all wavelengths. The thickness of Si was set as infinite. The simulation was performed on a unit cell with periodic conditions.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
chiral metamaterials, chiral near field, chirality sensor, vibrational circular dichroism
