Surface Enhanced Circular Dichroism by Quadrilateral Arranged Nanoholes

Abduwaili. Abudukelimu,1,* Tursunay. Yibibulla,2 Muhammad Ikram,1 and Ziyan Zhang1

1School of Physics and Information Technology, Shaanxi Normal University, Xi’an 710119 China
2School of Physics and Electronics, Central South University Changsha, 410083, P. R. China

Circular dichroism (CD) is absorption difference of right-hand and left-hand circularly polarized light by components. CD spectroscopy technique is an important tool for detecting molecular chirality, but the molecular circular dichroism (MCD) is weak and always appears in the ultraviolet (UV) region that is more noisy than visual range (VR). Induced circular dichroism (ICD) arisen from near-field interaction of plasmonic nanostructures and chiral molecules enhances the detection limit of molecular chirality and usually appears in VR. In this study, quadrilateral arranged nanoholes (QAN) are proposed for enhancing the MCD. The maximum enhancement achieved by the structure is about 200 folds of the MCD. Furthermore, we explained the mechanism of ICD which is generated by symmetry breaking of electric field QAN by molecular dipole. We investigated the effect of surface plasmon resonance (SPR) mode on ICD through analyzing the electric dipole (ED) and magnetic dipole (MD) resonance modes. ICD was found to get enhanced as a result of overlapping of ED and MD resonance around QAN. Besides this investigation, we probed the effects of thickness of structure, length of holes and length of periods on the MCD enhancement.

Keywords: chiral molecules, induced circular dichroism, surface enhancement, plasmonic nanostructure.

* Abduwelee@snnu.edu.cn
I. INTRODUCTION

Circular dichroism (CD) is widely used in detecting handedness, absolute configurations of chiral molecules [1–4] and enantioselective separation of enantiomers [5, 6]. Especially, CD spectroscopy is routinely used to determine the chirality of drug molecules [7], which is strongly associated with their therapeutic effect or toxicity [8, 9]. Circular dichroism of molecules (CDM) is, however, intrinsically weak with peaks located in the ultraviolet (UV) region [10]. This makes the detection of MCD arduous. In order to enhance the MCD signal, surface plasmon enhancing technique has been in practice [11]. In the near field interaction of chiral molecules and nanostructure, not only the MCD is enhanced by strong localized optical chiral field around the nanostructures [12, 13], the induced CD (ICD) signal also arises in nanostructure [11, 14–17]. Since ICD is few orders larger than the MCD [11, 18], it is considered has a potential method to detect single molecular chirality.

In past decades, many experimental and theoretical efforts have been carried out to enhance detection limit of molecular chirality by surface enhanced technique [14–16, 18–20]. On one hand, the enhanced local optical chiral field from nanostructure is considered for enhancing the molecular inherent MCD which is useful in chirality detection [11, 18, 21] and enantioselective septation of enantiomers [5, 6], while on the other hand, ICD by chiral molecules in achiral nanostructure extensively enhances the MCD signal [14, 15, 22–28]. Different shapes such as spheres, crosses, cubes and cylinders [14, 15, 22–27], and materials such as gold, silver and dielectric [25–28] have been put forward for enhancing the MCD. The enhancement factor of MCD, however, is still far from expectation. Another important aspect of MCD enhancement is the spectral overlapping of enhancement peak and molecular vibrational resonance which is more beneficial to detect the ICD, because the value of molecular chirality parameter decays exponentially with vibrational wavelength [10]. ICD enhancement in visible range (VR) or short-wavelength near-infrared (SW-NIR) region is, therefore, desirable.

In this paper, quadrilateral arranged nanoholes (QAN) are proposed to enhance MCD in VR and SW-NIR region. Two ICD peaks in VR and SW-NIR are observed with two orders enhancement of MCD. We explained the generation of ICD and insight into relation between ICD and surface plasmon electric dipole (ED) and magnetic dipole (MD) mode shapes. By analyzing ED and MD mode, we found that the ICD is larger when the ED and
MD overlap. Beside this, the origin of ICD enhancement is explained by analytical formula. Furthermore, we investigated the effect of thickness, length of holes and periods on ICD.

II. STRUCTURE AND COMPUTATIONAL METHOD

Figure 1(a) depicts the proposed chiral molecule–quadrilateral arranged nanoholes composed system. The material of structure is chosen to gold be and the refractive index is calculated by Brendel–Bormann model [29]. The structure is supposed to be prepared on glass substrate with thickness $t_s = 100 \text{ nm}$. Thickness and width of each nanohole are respectively $t = 30 \text{ nm}$ and $w = 20 \text{ nm}$ while length of each of the vertical nanoholes is $l_1 = 140 \text{ nm}$ and that of horizontal nanoholes is $l_2 = 240 \text{ nm}$ with periods fixed as $P_x = P_y = 400 \text{ nm}$. CD is defined as $CD = A_{RCP} - A_{LCP}$, where $A_{RCP}$ and $A_{LCP}$ are the absorption of right circularly polarized (RCP) light and left circularly polarized (LCP) light, respectively. Usually chiral molecules have vibrational absorption and chirality peak in UV region [1, 10]. The chiral molecules are, therefore, modeled with a complex refractive index that has absorption peak at 192 nm, as same as molecular chirality parameter.

![FIG. 1. (a) Schematic plot of QAN and chiral medium composed system, (b) The unit cell of QAN.](image)

We used finite element method (FEM) to perform the simulations, and modulated the simulation environment for chiral molecule by implementing chiral constitutive relations given by [30, 31]

\[
D = \varepsilon_0\varepsilon_c E - \frac{i\kappa}{c} H,
\]

\[
B = \mu_0\mu_c H + \frac{i\kappa}{c} E,
\]
where $\kappa$ is the molecular chirality parameter and $\varepsilon_c$ is the permittivity of the chiral molecule. In all calculations, relative permeability was set as $\mu = 1$. The molecular chirality parameter $\kappa$ and permittivity $\varepsilon_c$ are given by [10, 32]

$$
\varepsilon_c = \varepsilon_b + \frac{Nd\omega_0}{\omega_0^2 - \omega^2 + i\omega\Gamma},
\kappa = \frac{Nr\omega}{\omega_0^2 - \omega^2 + i\omega\Gamma},
$$

where $\varepsilon_b$ is relative permittivity of background solvent, $N$ is number density of molecules, $d$ is electric dipole strength, $r$ is rotatory strength, and $\omega_0$ is molecular absorption band frequency. The parameters were set as $\varepsilon_b = 1.77$, $Nd = 0.8 \times 10^{14}$ s$^{-1}$, $ Nr = 0.8 \times 10^{12}$ s$^{-1}$, $\Gamma = 3.77 \times 10^{14}$ s$^{-1}$, $\lambda_0 = 192$ nm and $\omega_0 = 2\pi c/\lambda_0$. Generally, the chirality parameter of a chiral molecule is written in the following tensor form [33–35]

$$
\bar{\kappa} = \begin{pmatrix}
\kappa_{xx} & \kappa_{xy} & 0 \\
\kappa_{yx} & \kappa_{yy} & 0 \\
0 & 0 & \kappa_{zz}
\end{pmatrix},
$$

For randomly oriented molecules, the parameters were set as $\kappa_{xx} = \kappa_{yy} = \kappa_{zz} = \kappa$, $\kappa_{xy} = \kappa_{yx} = 0$ [31, 33] whereas for oriented molecules the five elements of chirality tensor elements were set as $\kappa_{xx} = \kappa_{yy} = 0.25\kappa$, $\kappa_{zz} = 2.5\kappa$ and $\kappa_{xy} = \kappa_{yx} = 0.025\kappa$. Initially, the molecular orientation is defined as parallel to $z$-axis, and the unitary transformation $\kappa_f = R(\varphi)\kappa_i R^{-1}(\varphi)$ is used for changing of molecular orientation, where, $\kappa_i$ is the initial orientation and $\kappa_f$ is the final orientation, $R(\varphi)$ is unit rotation matrix for angle $\varphi$ which is different for rotations about $x$, $y$ and $z$-axis [36].

III. RESULTS AND DISCUSSION

The absorption and CD spectra of the chiral molecule-QAN system is illustrated in figure 2(a) where the absorption spectrum shows three SPR modes labelled as I, II and III at 830 nm, 1040 nm and 1370 nm respectively. Two peaks, coinciding with modes I and II of absorption spectrum, appear in CD spectrum. ED and MD resonance on QAN were analyzed through charge and induced current distributions which are displayed in figure 2(b). At mode I, ED resonance is composed of quadruple mode around longitudinal holes and dipole mode around transversal holes whereas MD resonance is a tripolar mode occurring
around longitudinal holes only. At mode II, ED resonance is the same as that at mode I, but MD resonance occurs around transversal holes only in form of dipole modes. At mode III, ED resonance occurs in coupled dipolar mode form around all holes whereas no MD resonance shows up. Modes I and II, have therefore ICD peak due to occurrence of both ED and MD resonance (overlapping of ED and MD). Since overlapping of MD and ED resonance is supposed mandatory for ICD generation [37, 38], mode III therefore does not show ICD peak because of absence of MD resonance.

FIG. 2. (a) Absorption and CD spectra of composed system (b) charge and current distribution on QAN.

CD of composed system originated from the molecular inherent MCD and induced ICD in nanostructure. MCD has three origins which are electric term $\text{CD}_E$, magnetic term $\text{CD}_M$ and chiral term $\text{CD}_C$ [32]

$$\text{MCD} = \text{CD}_E + \text{CD}_M \text{CD}_C,$$

$$\text{CD}_E = \frac{\varepsilon}{2} \int_{V_c} \text{Im}(\varepsilon_c) [|\mathbf{E}_+|^2 - |\mathbf{E}_-|^2] dV_c,$$  \hspace{1cm} (5)

$$\text{CD}_M = \frac{\varepsilon}{2} \int_{V_c} \text{Im}(\mu_c) [|\mathbf{H}_+|^2 - |\mathbf{H}_-|^2] dV_c,$$  \hspace{1cm} (6)

$$\text{CD}_C = \omega \int_{V_c} \text{Im}(\kappa) [\text{Im}(\mathbf{E}_+ \cdot \mathbf{H}_+^*) - \text{Im}(\mathbf{E}_- \cdot \mathbf{H}_-^*)] dV_c,$$  \hspace{1cm} (7)

where the subscripts +/- stand for the RCP and LCP illuminations. Figure 3(a) shows the spectra of $\text{CD}_E$, $\text{CD}_M$, $\text{CD}_C$ and total molecular MCD. $\text{CD}_M$ and $\text{CD}_E$ are two order larger than the total MCD, but they are opposite to each other such that their contribution to MCD is relatively small. MCD, ICD and the total CD of composed system is depicted in
figure 3(b) which reveals that ICD dominates the total CD. In the following discussion, only ICD will therefore be analyzed with no further consideration of MCD. In order to present the enhancement result, enhancement factor of the chiral molecule-QAN system is calculated by $f = \frac{CD}{MCD}$ and the spectrum for enhancement factor is presented in figure 3(b) where from one can clearly see 85 times enhancement in MCD at mode I and 94 times enhancement at mode II.

FIG. 3. (a) The spectra of CD, CD, CD and total molecular MCD, (b) the spectra of MCD, ICD, total CD and enhancement factor $f$.

ICD originates from symmetry breaking of electric field in QAN by electric field radiated from molecular dipole, and ICD is proportional to electric field in the nanostructure and magnetic field in molecular region (Eq. S12), that is [38, 39]

$$ICD \propto \omega \kappa E_{ns}^{s} \cdot B^{c},$$

where $E_{ns}^{s}$ is electric field strength in nanostructure, and $B^{c}$ is magnetic flux density in chiral medium. According to Eq (8), the ICD is proportional to electric field $E_{ns}^{s}$ and magnetic field $B^{c}$. Therefore, we analyzed the averaged electric field $E_{ns}^{s}$ and magnetic field $B^{c}$. The electric field is relatively strong at mode I and II, but small at mode III while the magnetic field is comparable all the three modes (figure 4(a)). Moreover, ICD is also proportional to angular frequency $\omega$ and molecular chirality $\kappa$, and the two parameters decay with increase of wavelength. ICD is thus larger at mode I whereas smaller at mode II. At mode III, only ED resonance is appear while maximize of $E_{ns}^{s} \cdot B^{c}$ is needed for overlapping of ED and MD resonance [37]. Thus, ICD peak is absent at mode III (figure 4(b)). Mode III therefore will not be analyzed further in the following discussion.
To further enhance the ICD, the structural parameters of QAN were changed. As a first attempt, thickness of the gold film was changed from 40 nm to 20 nm by step of 5 nm. Figure 5(a) depicts the enhancement factor spectra for different thickness. ICD is increased with decrease of thickness and the enhancement factor reached 170 for 20 nm thick QAN. We found that the increase of ICD originated from change of MD resonance. Figure 5(b) presents current distributions at mode I and mode II for different thickness. The MD resonance strengthened with decrease of thickness at both modes and the electric field $E^{ns}$ increased. CD, therefore, increased at both two modes.

For investigating the effect of coupling between the transversal and longitudinal holes on
the ICD, the length of longitudinal holes was changed from 120 nm to 240 nm by step of 30 nm. In figure 6(a) which displays the enhancement factor $f$ spectra for different values of length $l_1$, ICD can be spotted to increase with red-shift at mode I and to decrease with red-shift at mode II as a result of $l_1$ increase. This behavior originates from ED resonance at both modes (figure 6(b)). At mode I, ED resonance strengthens with increase in $l_1$ thus leading to an increase in ICD peak at this mode, whereas ED resonance at mode II weakens with $l_1$ increment thereby yielding a decrease in ICD peak at this mode.

![Enhancement factor spectra for different length $l_1$, current distribution for different length $l_1$ at mode I and mode II.](image)

**FIG. 6.** (a) Enhancement factor spectra for different length $l_1$, (b) current distribution for different length $l_1$ at mode I and mode II.

The impact of variation in length $l_2$ of transversal holes from 160 nm to 120 nm can be looked at in figure 7(a). At both modes, I and II, ICD shows an increase with $l_2$ decrease whereas blue-shift in ICD peak occurs at mode II only. Current distributions given in figure 7(b) show that tripolar MD resonance at mode I and mode II. Tripolar MD resonance is not affected by variation in $l_2$ but dipolar MD resonance arises around transversal nanoholes leading to a net increase in MD resonance hence in ICD peak at mode I. At mode II, shorter distance is favorable and MD resonance strengthens with decrease in $l_2$ which causes ICD peak enhancement.

Position of transversal holes also affects the coupling of holes, distance $d$ between transversal holes was therefore changed from 120 nm to 200 nm and the resulting spectra for enhancement factor $f$ are shown in figure 8(a). These spectra reveal a decrease in ICD from 120 nm to 160 nm distance and increase in ICD from 160 nm to 200 nm distance. Change
FIG. 7. (a) Enhancement factor spectra for different length $l_2$, (b) current distribution for different length $l_2$ at mode I and mode II.

FIG. 8. (a) Enhancement factor spectra for different distance $d$, (b) current distribution at mode I and charge distribution at mode II for different distance $d$.

in ICD at mode I originates from MD resonance whereas at mode II it originates from ED resonance. Figure 8(b) shows induced current distribution at mode I and charge distribution at mode II. Owing to the missing size-match of structure for generation of SPP resonance, MD resonance at mode I weakened with increase of $d$ and disappeared at 160 nm. As a result, ICD peak at mode I gradually decreased and disappeared at $d = 160$ nm. Upon fur-
increase in ICD peak. In a similar manner, quadruple ED resonance around longitudinal holes decreased up to \( d = 160 \text{ nm} \) leading to a decrease in ICD at mode II. With further increase in \( d \), ED resonance around longitudinal holes strengthened thereby letting ICD to increase at mode II.

![Graph](image)

**FIG. 9.** (a) Enhancement factor spectra for different periods, (b) current distribution for different periods at mode I and mode II.

The periods \( P \) affect the coupling strength of two neighbor structures. The electric field strength \( E^{ns} \) and magnetic field strength \( B^c \) can be modulated by changing the periods \( P \). Periods \( P_x \) and \( P_y \) were therefore changed from \( 300 \text{ nm} \) to \( 500 \text{ nm} \) by step of \( 50 \text{ nm} \). Figure 9(a) illustrates spectra for enhancement factor \( f \) whereas figure 9(b) illustrates current distribution for varying the periods \( P \) from \( 300 \text{ nm} \) to \( 500 \text{ nm} \) by \( 50 \text{ nm} \) step. At both modes ICD increased with decrease in period \( P \). This is caused by increase in magnetic resonance strength with coupling of two neighbor cells.

**IV. CONCLUSION**

In this paper, quadrilateral arranged nanoholes structure is proposed for enhancing the chiral molecules MCD in the visual and shortwave–infrared range. Two ICD peaks in the selected wavelength range are observed with two order enhancement. By analyzing the electric and magnetic dipole modes, we found that the ICD is larger when the ED and MD overlap, and the ICD peak is disappears when MD resonance is missing. Besides this, the
origin of ICD enhancement is analyzed by analytical formula. Furthermore, we investigated the effects of thickness, length of holes, distance between transversal holes, and periods on MCD enhancement. The value and wavelength positions of enhancement peaks are tunable by changing the parameters. It is worth noting that the proposed structure is planer which is easy to prepare, and the location for chiral molecules is easy to access. The maximum enhancement factor reached by the proposed system is 200 at 950 nm, this is beneficial to detect the MCD chirality.

ACKNOWLEDGMENT

This work was supported by Fundamental Research Funds for the Central Universities (Grant No. 2018TS066).

REFERENCE

[1] G. D. Fasman, Circular dichroism and the conformational analysis of biomolecules. (Springer, Boston, 1996).
[2] R. Tullius, A. S. Karimullah, M. Rodier at al., “Superchiral” spectroscopy: detection of protein higher order hierarchical structure with chiral plasmonic nanostructures, J. Am. Chem. Soc. 137(26), 8380(2015).
[3] A. Rodger and B. Norden, Circular dichroism and linear dichroism, (Oxford University Press: New York, 1997).
[4] S. M. A. Kelly, T. J. Jess and N. C.Price, How to study proteins by circular dichroism, Biochimica et Biophysica Acta 1751(2),119(2005).
[5] R. S. Ho, G. E. Aitzol, Y. Zhao, at al., Enhancing enantioselective absorption using dielectric nanospheres, ACS. Photonis 4(2), 197(2017).
[6] M. L. Solomon, J. Hu, M. Lawrence, at al., Enantiospecific optical enhancement of chiral sensing and separation with dielectric metasurfaces, ACS. Photonis 6(1), 43(2019).
[7] A. J. Hutt and S. C. Tan, Drug chirality and its clinical significance, Drugs 52, 1(2019).
[8] E. J.Ariens, Stereochemistry, a basis for sophisticated nonsense in pharmacokinetics and clinical-pharmacology, Eur. J. Clin. Pharmacol. 26, 663(1984).
[9] T. Eriksson, S. Jorkman and P. Hoglund, Clinical pharmacology of thalidomide, *Eur. J. Clin. Pharmacol*. 57, 365(2001).

[10] L. D. Barron, Molecular light scattering and optical activity, (Cambridge University Press, Cambridge, 2004).

[11] E. H. Khoo, E. S. P. Leong, S. J. Wu, et al., Effects of asymmetric nanostructures on the extinction difference properties of actin biomolecules and filaments, *Sci. Rep. 6*, 19658(2016).

[12] M. Schäferling, N. Engheta, H. Giessen and W. Thomas, Reducing the complexity: enantioselective chiral near-fields by diagonal slit and mirror configuration, *ACS. Photonics* 3(6), 1076(2016).

[13] L. Yang, K. Chak-Shing, L. Zhang, X. Li, et al., Chiral nanoparticle-induced enantioselective amplification of molecular optical activity, *Adv. Funct. Mater.* 29(8), 1807307(2018).

[14] J. M. Slocik, A. O. Govorov and R. R. Naik, Plasmonic circular dichroism of peptide-functionalized gold nanoparticles, *Nano Lett* 11(2), 701(2011).

[15] N. A. Abdulrahman, Z. Fan, T. Tonooka, et al., Induced chirality through electromagnetic coupling between chiral molecular layers and plasmonic nanostructures, *Nano Lett* 12(2), 977(2012).

[16] I. Dolamic, S. Knoppe and A. Dass, et al., First enantioseparation and circular dichroism spectra of Au$_{38}$ clusters protected by achiral ligands, *Nat. Comm* 3, 798 (2012).

[17] Z. N. Zhu, W.J. Liu, Z. T. Li, et al., Manipulation of collective optical activity in one-dimensional plasmonic assembly, *ACS. NANO* 6(3), 2326(2012).

[18] E. Hendry, T. Carpy, J. Johnston, et al., Ultrasensitive detection and characterization of biomolecules using superchiral fields, *Nat. Nanotechnol.* 5, 783(2010).

[19] A. O. Govorov, Z. Y. Fan, P. Hernandez, et al., Theory of circular dichroism of nanomaterials comprising chiral molecules and nanocrystals: plasmon enhancement, dipole interactions, and dielectric effects, *Nano Lett* 10(4), 137(2010).

[20] M. L. Nesterov, X. H. Yin, M. Schaferling, et al., The role of plasmon-generated near fields for enhanced circular dichroism spectroscopy, *Nano Lett* 3(4), 578(2016).

[21] Y. Zhao, N. A. Askarpour, L. Sun, et al., Chirality detection of enantiomers using twisted optical metamaterials, *Nat. Comm* 8, 514180(2017).

[22] D. Vestler, A. Ben-Moshe, G. Markovich, Enhancement of circular dichroism of a chiral material by dielectric nanospheres, *J. Phys. Chem. C* 123(8), 5017(2019).
[23] J. J. Wei, Y. Y. Jia, J. Z. Li, et al., Optically active ultrafine Au-Ag alloy nanoparticles used for colorimetric chiral recognition and circular dichroism sensing of enantiomers, Anal Chem. 89(18), 9781(2017).

[24] F. Lu, Y. Tian, M. Liu, et al., Discrete nanocubes as plasmonic reporters of molecular chirality, Nano Lett 12(2), 977(2012).

[25] M. C. Gregorio, A. Ben Moshe, E. Tiross, et al., Chiroptical study of plasmon-molecule interaction: the case of interaction of glutathione with silver nanocubes, J. Phys. Chem. C 119(30), 977(2015).

[26] B. M. Maoz, Y. Chaikin, A. B. Tesler, et al., Amplification of chiroptical activity of chiral biomolecules by surface plasmons, J. Phys. Chem. C 13(3), 1203(2013).

[27] J. Garcia-Guirado, M. Svedendahl, J. Puigdollers, et al., Enhanced chiral sensing with dielectric nanoresonators, Nano Lett. 20(1), 585(2020).

[28] G. Rui, H. F. Hu, M. Singer, et al., Circular dichroism enhancement: symmetric meta-absorber-induced superchirality, Adv. Optical Mater. 7(21), 1901038(2019).

[29] A. D. Rakic, A. B. Djurisic, J. M. Elazar, et al., Optical properties of metallic films for vertical-cavity optoelectronic devices, Appl. Opt. 37(22), 5271(1998).

[30] A. H. Sihvola and I. V. Lindell, BI-isotropic constitutive relations, Microwave Opt. technol. lett. 4(8), 295(1991).

[31] I. P. Theron, J. H. Cloete, The electric quadrupole contribution to the circular birefringence of nonmagnetic anisotropic chiral media: A circular waveguide experiment, IEEE Transactions on Microwave Theory and Techniques 44(8), 145(2002).

[32] S. Lee, S. Yoo, Q. Park, Microscopic origin of surface-enhanced circular dichroism, ACS Photonics, 2017, 4-2047-2052. ACS Photonics 4(8), 2047(2017).

[33] C. Kelly, R. Tullius and A. J. Lapthorn, et al., Chiral plasmonic fields probe structural order of biointerfaces, J. Am. Chem. Soc. 140(27), 2047(2018).

[34] Y. Liu, R. Wang and X. Zhang, et al., Giant circular dichroism enhancement and chiroptical illusion in hybrid molecule-plasmonic nanostructures, Optics Express 22(4), 4357(2014).

[35] T. Wu, J. Ren, and Y. Wang, et al., Competition of chiroptical effect caused by nanostructure and chiral molecules, J. Phys. Chem. C 118(35), 20529(2014).

[36] A. Abdukelimu, Y. Bai, Y. Qu, et al., The causality of circular dichroism inducement by isotropic and anisotropic chiral molecules, J. Phys. D: Appl. Phys. 52, 305306(2019).
[37] G. E. Aitzol and A. D. Jennifer, Surface-enhanced circular dichroism spectroscopy mediated by nonchiral nanoantennas, Phys. Rev. B 87(23), 235409(2013).

[38] A. Abudukelimu, I. Muhammd, T. Yebibulla, et al., Surface enhanced circular dichroism by electric and magnetic dipole resonance of cross shaped nanoholes, Arxive, 2011.09215v1(2019).

[39] A. Abudukelimu, Z. Y. Zhang, T. Yebibulla, et al., Quantitative study on circular dichroism induction from achiral nanostructure-chiral matter near field interactions, Arxive, 2011.05508v1(2019).
Supporting Informations for
Surface Enhanced Circular Dichroism by Quadrilateral Arranged Nanoholes

Abuduwilli. Abudukelimu,1 * Tursunay. Yibibulla,2 Muhammad. Ikram1 and Ziyan Zhang1

1. School of Physics and Information Technology, Shaanxi Normal University, Xi’an, 710119, China
2. School of Physics and Electronics, Central South University, Changsha, 410083, P. R. China

S1. OORIGIN OF INDUCED CD

Absorption of a nanostructure is generally given by [1]

\[ A_{\pm}^{ns} = \frac{\omega}{2} \int_{V_{ns}} \left[ \text{Im}(\varepsilon_{ns})(E_{\pm}^0 \cdot E_{\pm}^0) + \text{Im}(\mu_{ns})(H_{\pm}^0 \cdot H_{\pm}^0) \right] dV, \]  

where, \( \omega \) is angular frequency of CPL, \( \varepsilon_{ns} \) and \( \mu_{ns} \) are relative permittivity and permeability of nanostructure, \( E_{\pm}^0 \) and \( H_{\pm}^0 \) are electric and magnetic field strengths. The magnetic susceptibility of plasmonic nanostructure is very small, the magnetic loss can therefore be neglected. In presence of chiral molecule, \( E_{\pm}^0 \) will be affected by electric field radiated by chiral molecular dipole. Equation (S2) can then be written as [2]

\[ A_{\pm}^{ns} = \frac{\omega}{2} \text{Im}(\varepsilon_{ns}) \int_{V_{ns}} (E_{\pm}^0 + E_{\pm}^d)^* \cdot (E_{\pm}^0 + E_{\pm}^d) dV, \]

where, \( E_{\pm}^d \) is dipole radiated electric field. The dipole radiated electric field can be written in terms of Green’s function. For time harmonic electromagnetic fields, the Green functions are dyadic functions, because the source is vector. Thus, the dipole radiated electric field can be written in terms of Green dyadic integral form

\[ E^d(r) = \int_{V'} \left( \overline{G}_{ee}(r-r') \cdot \overline{G}_{em}(r-r') \right) \begin{pmatrix} J \\ M \end{pmatrix} \]   

where \( J \) and \( M \) electric and magnetic currents. The Green functions satisfy the Maxwell equations. Using chiral constitutive relation to solve the Maxwell equations we derive Green

* Email: Abduwelee@snmu.edu.cn
functions for chiral medium [3]

\[
\overline{G}_{ee}(r) = \overline{G}_{e+e}(r) + \overline{G}_{e-e}(r)
\]

\[
\overline{G}_{e+e}(r) = -\frac{i\eta}{2}[(k \pm G_\pm(r))\mathbb{I} \pm \mathbf{\nabla} G_\pm(r) \times \mathbb{I} + \mathbf{\nabla} \nabla \left( \frac{G_\pm(r)}{k_\pm} \right)], \quad (S5)
\]

\[
\overline{G}_{e+e}(r) = \overline{G}_{e+e} + \overline{G}_{e-e}(r)
\]

\[
\overline{G}_{e+e}(r) = -\frac{1}{2}[(k \pm G_\pm(r))\mathbb{I} + \mathbf{\nabla} G_\pm(r) \times \mathbb{I} + \mathbf{\nabla} \nabla \left( \frac{G_\pm(r)}{k_\pm} \right)]
\]

where \( G_\pm(r) = \frac{e^{-i kr}}{4\pi r} \), \( k_\pm = k(1 \pm \frac{\kappa}{n_c}) \) and \( n_c \) is refractive index of chiral medium. Thus, the dipole radiated electric field is

\[
E^d_\pm = i\omega \omega_{\text{mol}}^\alpha G \cdot E^c_\pm + \omega \omega_{\text{mol}} \frac{\kappa}{c} \mathbf{G} \cdot \mathbf{B}^c_\pm.
\]

(S6)

The induced CD in nanostructure is [4]

\[
\text{CD}_{\text{ind}} = \frac{\omega}{2} \text{Im}(\varepsilon_{\text{ns}}) \int_{V_{\text{ns}}} (E^0_+ + E^d_+)^* \cdot (E^0_+ + E^d_+) dV
\]

\[
- \frac{\omega}{2} \text{Im}(\varepsilon_{\text{ns}}) \int_{V_{\text{ns}}} (E^0_- + E^d_-)^* \cdot (E^0_- + E^d_-) dV
\]

\[
= \frac{\omega}{2} \text{Im}(\varepsilon_{\text{ns}}) \int_{V_{\text{ns}}} \left( (E^0_+ + E^d_+)^* \cdot (E^0_+ + E^d_+) - (E^0_- + E^d_-)^* \cdot (E^0_- + E^d_-) \right) dV.
\]

(S7)

The dipole radiated electric field \( E^d_\pm \) is much smaller than original near field in nanostructure. Then neglecting the second order term \( E^d_+ \cdot E^{d*}_- \) we derive

\[
\text{CD}_{\text{ind}} = \frac{\omega}{2} \text{Im}(\varepsilon_{\text{ns}}) \int_{V_{\text{ns}}} 2\text{Re} \left( E^0_+ \cdot E^{d*}_- - E^0_- \cdot E^d_+ \right) dV.
\]

(S8)

Replace \( E^d_+ \) to calculate \( E^0_+ \cdot E^{d*}_- \)

\[
\begin{align*}
(E^0_+ \cdot E^{d}_-) \\
= & E^0_+ \cdot \left\{ \frac{\omega \omega_{\text{mol}}^\alpha}{2r^2k} \left[ 3(G_+ + G_-)\hat{u}_r\hat{u}_r - (G_+ + G_-)\mathbb{I} \right] \cdot E^c_+ \\
& + \frac{-i\omega \omega_{\text{mol}} \kappa}{2r^2k} \cdot \left[ 3(G_+ + G_-)\hat{u}_r\hat{u}_r - (G_+ + G_-)\mathbb{I} \right] \cdot E^c_+ \right\} \\
= & \frac{3\omega \omega_{\text{mol}}^\alpha}{2r^2k} \left[ (G_+ + G_-) \frac{1}{r^2} \left( E^{0x}_{\pm}(x^2E^{cx}_{\pm} + xyE^{cy}_{\pm} + xzE^{cz}_{\pm}) \\
& + E^{0y*}(yxE^{cx}_{\pm} + y^2E^{cy}_{\pm} + yzE^{cz}_{\pm}) + E^{0z*}(zxE^{cx}_{\pm} + yzE^{cy}_{\pm} + z^2E^{cz}_{\pm}) \right) \\
& + \frac{\omega \omega_{\text{mol}} \kappa}{2r^2k} \left( (G_+ + G_-) \left( E^{0yx}_{\pm}E^{cx}_{\pm} + E^{0yx}_{\pm}E^{cy}_{\pm} + E^{0yx}_{\pm}E^{cz}_{\pm} \\
& + E^{0ys*}(yxB^{cx}_{\pm} + y^2B^{cy}_{\pm} + yzB^{cz}_{\pm}) + E^{0zs*}(zxB^{cx}_{\pm} + yzB^{cy}_{\pm} + z^2B^{cz}_{\pm}) \right) \\
& + \frac{-3\omega \omega_{\text{mol}} \kappa}{2r^2k} \left( (G_+ + G_-) \frac{1}{r^2} \left( E^{0x}_{\pm}(x^2B^{cx}_{\pm} + xyB^{cy}_{\pm} + xzB^{cz}_{\pm}) \\
& + E^{0y*}(yxB^{cx}_{\pm} + y^2B^{cy}_{\pm} + yzB^{cz}_{\pm}) + E^{0z*}(zxB^{cx}_{\pm} + yzB^{cy}_{\pm} + z^2B^{cz}_{\pm}) \right) \\
& - \frac{-i\omega \omega_{\text{mol}} \kappa}{2r^2k} \right\} \left( (G_+ + G_-)(E^{0x*}_{\pm}B^{cx}_{\pm} + E^{0yx*}_{\pm}B^{cy}_{\pm} + E^{0zx*}_{\pm}B^{cz}_{\pm}) \right)
\end{align*}
\]

(S9)
If we suppose that the incident light propagates along the $z$ direction and the achiral nanostructure is symmetric to the $y$ (or $x$, any achiral structure has symmetric axis) axis, the near field in the $xy$ plane has properties $E^x_+(x,y) = E^x_-(x,-y)$, $E^y_+(x,y) = E^y_-(x,-y)$, $B^x_+(x,y) = -B^x_-(x,-y)$, $B^y_+(x,y) = B^y_-(x,-y)$, $B^z_+(x,y) = -B^z_-(x,-y)$. Applying coordinate transformation $y \rightarrow -y$ (or $x \rightarrow -x$, depending on the symmetry axis) to the near field, we derive

$$\frac{1}{r^2}(x - x')^2E^{0x*y}_+(x', y')E^{cx}_{-+}(x, y),$$

Equation (S10) means the term $\frac{1}{r^2}(x - x')^2E^{0x*y}_+(x', y')E^{cx}_{-+}(x, y)$ is equal for RCP and LCP illumination. Using the same coordinate transformations to other terms, we finally derive

$$\frac{E^0_+ \cdot E^{ds}_- - E^0_- \cdot E^{ds}_+}{r^2k} = -\frac{3i\omega\eta\eta_0\kappa}{c}(G_+ + G_-) \frac{1}{r^2} \left( x^2E^{0x*y}_x B^{cx}_x + y^2E^{0y*y}_y B^{cy}_y + z^2E^{0z*y}_z B^{cz}_z \right)$$

(S11)

According to Eqs. S8 and S11, ICD is proportional to electric field in nanostructure and magnetic field in molecular region, that is

$$\text{ICD} \propto \omega \kappa E^{ns*y} \cdot B^c$$

(S12)

**S2. CALCULATION OF CHIRAL MEDIUM BY FEM**

We used COMSOL software for the simulation. For calculation of chiral medium we changed part of equations through implementing chiral constitutive relation[5]. To confirm our calculation results, we applied these modifications to solve for the transmission coefficients for a chiral slab and compared the simulation results of the co- and cross-components of the transmission coefficients at normal incidence from a slab with thickness $L$. The results are:

$$T_{co} = \frac{2\eta_0\cos(kL)\cos(\kappa kL)}{2\eta_0\cos(kL) + i(\eta^2_0 + \eta^2)\sin(kL)}$$

(S13)

$$T_{cr} = \frac{2\eta_0\cos(kL)\sin(\kappa kL)}{2\eta_0\cos(kL) + i(\eta^2_0 + \eta^2)\sin(kL)}$$

Figure S1 depicts infinite chiral slab in air and calculation result. The simulated and analytical results are in a good agreement.
FIG. S1. (a) Chiral slab (b) Analytical (dashed line) and simulated (solid line) co-component of transmission (c) Analytical (dashed line) and simulated (solid line) cross-component of transmission

For anisotropic chiral medium, the constitutive relations are expressed by tensorial chirality parameter. The unitary transformations are used for rotation of orientation, for example, for rotation about y axis the constitutive relations are modulated as

\[
\begin{pmatrix}
D_x \\
D_y \\
D_z
\end{pmatrix}
= \varepsilon_0 \varepsilon_c
\begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix}
\]

\[
- \frac{i}{c}
\begin{pmatrix}
cos(\alpha) & 0 & -\sin(\alpha) \\
0 & 1 & 0 \\
\sin(\alpha) & 0 & \cos(\alpha)
\end{pmatrix}
\begin{pmatrix}
\kappa_{xx} & \kappa_{xy} & 0 \\
\kappa_{yx} & \kappa_{yy} & 0 \\
0 & 0 & \kappa_{zz}
\end{pmatrix}
\begin{pmatrix}
cos(\alpha) & 0 & \sin(\alpha) \\
0 & 1 & 0 \\
-sin(\alpha) & 0 & \cos(\alpha)
\end{pmatrix}
\begin{pmatrix}
B_x \\
B_y \\
B_z
\end{pmatrix}
\]

\[
\begin{pmatrix}
B_x \\
B_y \\
B_z
\end{pmatrix}
= \mu_0 \mu_c
\begin{pmatrix}
H_x \\
H_y \\
H_z
\end{pmatrix}
\]

\[
+ \frac{i}{c}
\begin{pmatrix}
cos(\alpha) & 0 & -\sin(\alpha) \\
0 & 1 & 0 \\
\sin(\alpha) & 0 & \cos(\alpha)
\end{pmatrix}
\begin{pmatrix}
\kappa_{xx} & \kappa_{xy} & 0 \\
\kappa_{yx} & \kappa_{yy} & 0 \\
0 & 0 & \kappa_{zz}
\end{pmatrix}
\begin{pmatrix}
cos(\alpha) & 0 & \sin(\alpha) \\
0 & 1 & 0 \\
-sin(\alpha) & 0 & \cos(\alpha)
\end{pmatrix}
\begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix}
\]

(S14)

(S15)
REFERENCE

[1] A. O. Govorov and Z. Fan, Theory of chiral plasmonic nanostructures comprising metal nanocrystals and chiral molecular media, ChemPhysChem 13(10), 2551(2012).

[2] B. Han, Z. Zhu, Z. Li, et al., Conformation modulated optical activity enhancement in chiral cysteine and Au nanorod assemblies, J. Am. Chem. Soc. 36(46), 16104(2014).

[3] I. V. Lindell, A. J. Viitanen, S. A. Tretyakov, et al., Electromagnetic waves in chiral and bi-isotropic media, (Artech House, Boston, 1994).

[4] A. Abudukelimu, Z. Y. Zhang, T. Yebibulla, et al., Quantitative study on circular dichroism induction from achiral nanostructure-chiral matter near field interactions, Arxive, 2011.05508v1(2019).

[5] C. Kelly, R. Tullins and A. J. Lapthorn, et al., Chiral plasmonic fields probe structural order of biointerfaces, J. Am. Chem. Soc. 140(27), 2047(2018).