Spectral properties of chiral electromagnetic near fields created by chiral plasmonic nanostructures

S. Hashiyada1*, K. Endo2, T. Narushima1,3, Y. Togawa2,4 and H. Okamoto1,3*

1 Center for Mesoscopic Sciences, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan
2 Department of Physics and Electronics, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
3 School of Physical Sciences, Department of Structural Molecular Sciences, The Graduate University for Advanced Studies (Sokendai), Okazaki, Aichi 444-8585, Japan
4 Chirality Research Center (CResCent), Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan

*E-mail: shun_hashiyada@anet.soken.ac.jp, aho@ims.ac.jp

Abstract. The surface-enhanced chiral-optical spectroscopy is based on the interaction of chiral molecules with chiral electromagnetic near field localized on a chiral plasmonic nanostructure. It is of fundamental importance to reveal the spectral characteristics of chiral near fields for maximizing the chiral interaction. Here we investigate relations between near field and far field polarization characteristics of the chiral plasmonic nanostructures, using electromagnetic simulations. We found that spectral features of chiral near fields created by the nanostructures intercorrelate with those of far field optical rotation. This finding may provide us a method to characterize and design the chiral near field.

1. Introduction

The advent of artificially engineered nanomaterials has allowed light to be manipulated in ways previously unseen in nature. One of the most intriguing phenomena arising from this is the creation of electromagnetic (EM) near fields around chiral plasmonic nanostructures which display greater chiral asymmetry than circularly polarized light in free space (referred to as superchiral fields) [1,2]. Spectroscopic applications of superchiral near fields, named “superchiral spectroscopy”, affords new opportunities for the ultrasensitive characterization of chiral molecules [1,3]. In superchiral spectroscopy, asymmetric spectral shifts induced by chiral molecules are measured; they arise from asymmetry of effective refractive indices for left- and right-handed superchiral near fields. This spectroscopy is based on the same principle as that for surface plasmon resonance sensor [4], that is, dependence of spectral positions of plasmon resonances on dielectric environments at the surfaces of nanostructures. The asymmetry of chirality-induced spectral peak shift should be maximized when the chiral asymmetry of EM near field is maximized. However, the spectral characteristics of superchiral near fields remain unclear.

In this study, we investigate the spectral properties of chiral asymmetry of EM near field created by chiral plasmonic nanostructures, using rigorous EM field simulation based on the finite-difference time-domain (FDTD) method. We evaluate the chiral near field with the ellipticity angle (that corresponds to circular dichroism, CD), which is experimentally obtained by near field polarimetry measurements [5].
Our simulation results show that spectral features of the ellipticity angle of near field created by the nanostructures intercorrelate with those of far field optical rotation (OR). We also show that this relation obtained with the numerical simulation on the chiral plasmonic nanostructure can be explained by a qualitative model where the excited plasmon on the nanostructure is represented as an oscillating chiral electric-magnetic dipole [6]. These results suggest that spectral features of chiral near fields (more specifically, ellipticity) can be evaluated approximately from those of far field OR. Our finding may provide a method to characterize and design the chiral near field.

2. Finite-difference time-domain (FDTD) simulation

We simulated the EM fields for two-dimensional square lattice gold nano-gammadion arrays on a glass substrate (Fig. 1a) [1,7]. We used commercial FDTD simulation software (Poynting for Optics, Fujitsu Ltd., Japan) for this purpose. Drude-Lorentz model parameter was used for the dielectric function ($\varepsilon_{\text{gold}}$) of gold. For the glass, $\varepsilon_{\text{glass}} = 2.25$ (wavelength independent). The computational domain was defined with periodic boundary condition in x,y to mimic the arrays, and with perfectly matched layer condition in z. A plane wave of linearly polarized EM field was irradiated from the substrate side of the nanostructure (+z direction), and the polarization characteristics (the ellipticity angle $\eta$ and the azimuth angle $\theta$) of the electric field in an x-y-plane above the gold surface (“PFF” and “PNF” in Fig. 1a) were evaluated. We can calculate $\eta = \tan^{-1}(S_3/S_0)/2$ and $\theta = \sin^{-1}(S_2/S_1)/2$ using the Stokes parameters, $S_0 = |\tilde{E}_x|^2 + |\tilde{E}_y|^2$, $S_1 = |\tilde{E}_x|^2 - |\tilde{E}_y|^2$, $S_2 = 2\text{Re}(\tilde{E}_x\tilde{E}_y^*)$, and $S_3 = 2\text{Im}(\tilde{E}_x\tilde{E}_y^*)$. Quantities with tildes are complex.

![Figure 1](image_url)

**Figure 1.** (a) The model of the FDTD simulation. The near field and far field polarization characteristics of two-dimensional square lattice gold nano gammadion arrays on a glass substrate were evaluated at the plane “PNF” and at the position “PFF”, respectively. (b,c) Far field extinction (b), circular dichroism $\eta_{\text{FF}}$ (blue) and optical rotation $\theta_{\text{FF}}$ (red) (c) spectra of the nanostructures. (d,e) Maps of near field ellipticity angle $\eta_{\text{NF}}$ of the electric field generated near the nanostructure using linearly polarized light (polarization direction indicated by arrows) for the wavelength of 645 nm (d) and 720 nm (e). (f) Spectrum of the areal averaged value of near field ellipticity angle $\langle \eta_{\text{NF}} \rangle$ calculated from the $\eta_{\text{NF}}$ maps (Figs. 1d,e for instance).
We first investigated the far field polarization characteristics of the gammadions at the position “$P_{ff}$”. As shown in Fig. 1b, gammadions showed plasmon resonances with peaks at ~670 nm and at ~720 nm. At around these wavelengths, gammadions exhibited OR (given by $\theta_{fy}$) and CD (given by $\eta_{ff}$) in the far-field regime (shown in Fig. 1c). The spectral features of the far field CD and OR were not changed, even if the direction of the light incidence was reversed (i.e., $-z$ direction). This result indicates that the observed polarization effect from gammadions on a glass substrate is reciprocal [7], and similar to that observed for three-dimensional chiral materials such as chiral molecules and chiral crystals.

We, then, probed the near field polarization characteristics of the gammadions in the evaluation area $A$ at the plane “$P_{NF}$”. Figures 1d,e show maps of the ellipticity angle ($\eta_{NF}$) of the electric near field generated by the gammadions with linearly polarized light at around the plasmon resonance wavelengths. The $\eta_{NF}$ signal from the central region of the gammadion always showed a prominent signal, and its sign (handedness of chirality) was governed by the handedness of the structural chirality of the nanostructure. In practical applications of chiral near fields, where the fields interact with molecules that are uniformly distributed on the nanostructured substrate, the areal averaged value rather than the local value of $\eta_{NF}$ should be important. We here calculated the areal averaged value of $\eta_{NF}$, $\langle \eta_{NF} \rangle = \int \eta_{NF}(\mathbf{r}) dA/A$, from the $\eta_{NF}$ maps, where $A$ is the area of the unit cell whose size is 570×570 nm$^2$. As shown in Figure 1f, the $\langle \eta_{NF} \rangle$ spectrum showed two negative peaks at ~645 and ~720 nm. Interestingly, peak wavelengths of the $\langle \eta_{NF} \rangle$ spectrum were consistent with those of the far field OR spectrum, while the signs of the $\langle \eta_{NF} \rangle$ peaks were opposite to those of the far field OR peaks. We thus found that the spectral features of chiral near fields (ellipticity) created by chiral plasmonic nanostructures intercorrelate with those of far field OR.

3. Chiral dipole model

To discuss the intercorrelation between near and far field polarization characteristics, we simulated $\langle \eta_{NF} \rangle$ based on a simple model where the excited plasmon on the chiral nanostructure is represented as an oscillating chiral electric-magnetic dipole [6]. A chiral dipole induced by a monochromatic EM field can be described by an electric $\mathbf{p}$ and magnetic $\mathbf{m}$ dipole moments:

$$\begin{align*}
\mathbf{p} &= \varepsilon_0 \tilde{\mathbf{a}}_e \mathbf{E} + i(\tilde{\mathbf{a}}_c/c) \mathbf{H} \\
\mathbf{m} &= \mu_0 \tilde{\mathbf{a}}_m \mathbf{H} - i(\tilde{\mathbf{a}}_c/c) \mathbf{E},
\end{align*}$$

where $\tilde{\mathbf{a}}_e$, $\tilde{\mathbf{a}}_m$, and $\tilde{\mathbf{a}}_c$ are the isotropic electric, magnetic, and electric-magnetic polarizability, respectively. $\mathbf{E}$ and $\mathbf{H}$ are the local electric and magnetic fields at the position of the dipole. It should be noted that the real and the imaginary parts of the complex electric-magnetic polarizability $\tilde{\mathbf{a}}_c$ determine spectral features of the far field OR ($\theta_{ff}$) and CD ($\eta_{ff}$), respectively.

Figure 2 shows the model we considered. Suppose that the chiral dipole is induced by the linearly polarized plane wave electric field propagating in $+z$ direction, $\mathbf{E}_0 = (E_0, 0, 0)e^{i(kz - \omega t)}$, where $\omega$ and $k$ represent the angular frequency and the wavenumber, respectively. The electric near fields ($kr << 1$) induced by electric and magnetic dipoles can be described approximately by [8]

$$\begin{align*}
\mathbf{E}_p(r) &= \frac{3[r(r\mathbf{p}) - r^2\mathbf{p}]}{(4\pi\varepsilon_0 r^3)} \\
\mathbf{E}_m(r) &= -i k c (r \times \mathbf{m})/(4\pi r^2).
\end{align*}$$

The total electric fields in $xy$-plane near the dipole are then expressed as

$$\begin{align*}
\mathbf{E}_{\text{total}}(r) &= \mathbf{E}_{\text{in}} + \mathbf{E}_p(r) + \mathbf{E}_m(r) \\
&\approx E_0 e^{-i\omega t} \left( 1 + \tilde{\mathbf{a}}_e f'_{\omega}(\mathbf{r}) + i\tilde{\mathbf{a}}_c g(\mathbf{r}) + \tilde{\mathbf{a}}_m h(\mathbf{r}) \right),
\end{align*}$$

Figure 2. The model for the polarization analysis of the electric field around an oscillating chiral electric-magnetic dipole. The evaluation area $A' (= \pi d^2)$ is located at a plane $d$ away from the dipole.
where \( f_\ell(r) = (3x^2-r^2)/(4\pi r^2) \), \( f_1(r) = (3y^2-r^2)/(4\pi r^2) \), \( g(r) = 3x y/(4\pi r^2) \), and \( h(r) = kz/(4\pi r^2) \). Using equation (3), we obtained the ellipticity angle (\( \eta_{ NF}(r) \)) of the electric field near the chiral dipole

\[
\eta_{ NF}(r) \propto \text{Im} \left( \tilde{\alpha}_c f_\ell(r) + \tilde{\alpha}_c g(r) - \tilde{\alpha}_c h(r) \right) = \text{Re}(\tilde{\alpha}_c) f_\ell(r) + \text{Im}(\tilde{\alpha}_c) g(r) - \text{Im}(\tilde{\alpha}_c) h(r). \tag{4}
\]

For deriving equation (4), we used three approximations: (i) \( \eta_{ NF}(r) \approx (S_3(r)/S_0(r))/2 \) because \( \eta_{ NF} \) should be small near the dipole (\( |\eta_{ NF}| \ll 0.5 \text{ rad} \approx 28.6^\circ \)), (ii) the properties of local \( \eta_{ NF}(r) \) can be determined by \( S_0(r) \) because \( S_0(r) \) (the intensity of the total electric field) does not vary rapidly in the evaluation area \( A' \) shown in Fig. 2, and (iii) the quadratic terms of polarizabilities can be neglected because these terms vanish rapidly with the distance \( d \). Here, \( A' \) is the area of the circle with a radius \( l \), located at a plane \( d \) away from the dipole. Finally, we obtained the area averaged value of \( \eta_{ NF} \) in the near field region (\( kr = k(l^2 + d^2)^{1/2} \approx 0.1 \))

\[
\langle \eta_{ NF} \rangle \propto \text{Re}(\tilde{\alpha}_c) \int f_\ell(r) \, dA' + \text{Im}(\tilde{\alpha}_c) \int g(r) \, dA' - \text{Im}(\tilde{\alpha}_c) \int h(r) \, dA' = -[\sin \Phi \sin 2\Phi \text{Re}(\tilde{\alpha}_c) + 4kd(1 - \cos \Phi)\text{Im}(\tilde{\alpha}_c)]/(8d) \approx -\sin \Phi \sin 2\Phi \text{Re}(\tilde{\alpha}_c)/(8d) \propto -\text{Re}(\tilde{\alpha}_c), \tag{5}
\]

where \( \Phi = \tan^{-1}(l/d) \). Equation (5) indicates that \( \langle \eta_{ NF} \rangle \) is correlated approximately with the far field OR (given by \( \text{Re}(\tilde{\alpha}_c) \)) with opposite sign. This result suggests that the spectral features of near field ellipticity can be evaluated from those of far field OR. This result is consistent with that obtained with the FDTD simulation.

4. Conclusion

In the present study, we have qualitatively discussed relations between near and far field polarization characteristics of chiral plasmonic nanostructures. Our theoretical considerations revealed that spectral features of chiral near fields (ellipticity) intercorrelate with those of far field OR. This result may provide a method to characterize chiral near fields based on far field observables. This also suggests a way to design chiral near fields, as the far field OR spectrum of chiral nanostructures can be designed by the geometric design of the nanostructure [9].

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