Searching the Theoretical Ultimate Limits of Probing Surface-Enhanced Raman Optical Activity

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Supporting Information

ABSTRACT: The single-molecule Raman detection has been realized for a long time because of the enhancement effect of surface plasmons. However, the small cross section of Raman optical activity (ROA) makes it so hard to detect the ROA of even a few molecules; and a normal surface-enhanced ROA (SE-ROA) is also very time consumable even with strong laser power. Detecting ROA in an economic way is an important issue. In this paper, we discuss the ultimate limit of the SE-ROA and provide the enhancement factor formula for SE-ROA. Following the formula, we proposed a structure with both huge Raman enhancement and ROA enhancement, which is helpful for single-molecule ROA detection.

INTRODUCTION

The term chirality is used to describe the object whose mirror image cannot be made to coincide with itself by simple rotations or translations. One of the most important consequences of the structural property is optical activity, which is the phenomenon that the optical constant characterizing the material is different for left-handed and right-handed circularly polarized light (LCP and RCP, respectively). Most of the biomolecules, such as amino acids, many proteins, and nucleic acids, exhibit optical activity because of their chiral structures.1,2 With the development of technology, many spectroscopic techniques have been proposed for the determination of the molecular chirality, such as circular dichroism (CD), optical rotatory dispersion, and Raman optical activity (ROA) spectroscopy.3,4 Because the ROA is sensitive to the configuration of molecules, it has been used to assign the configuration of molecules, study the dynamics of biomolecules, and so on. However, the ROA of most biomolecules or other natural chiral media is inherently weak-effected and difficult to detect because their signal intensities are always 3−5 orders of magnitude smaller than their parent Raman intensities, which greatly hampers their wide applications. In recent years, a lot of attention has been focused on the surface-enhanced Raman optical activity (SE-ROA) based on the surface plasmon enhancement. It is expected that the ROA signal of chiral molecules can be dramatically enhanced owing to the SERS (surface-enhanced Raman scattering)-type enhancement of the overall scattering and chiral field enhancements, resulting from large electric field gradients at the metal surface.5−9

The enhancement of ROA signals from plasmon response was first proposed in the literature by Efima, which shows that the enhancements caused by a large evanescent electric field at the metal surface and the electric field gradient plays a key role in amplifying the ROA signal.10,11 Recently, Chulhai and Jensen showed that the field gradient causes significant changes in the SE-ROA spectrum for the chiral molecules with fixed orientations with respect to the surface of the nanoparticles.12 Wu et al. demonstrated that the SE-ROA signal can be strongly enhanced by magnetic response of nanoparticles;5 however, it is still difficult in experiments. In the meantime, a large number of current research studies have been devoted to the optimization of plasmonic nanostructures for high SERS enhancement and chiral field enhancement, for example, nanodimers or multi-particle−film configurations13−16 and shell-isolated nanospheres17,18 three-dimensional (3D) helical nanostructures19−21 or multilayers artificial chiral structures22,23 and two-dimensional or planar nanostructures24−26 to name just a few. Maximizing the SE-ROA enhancement is a continuous effort focused on the design of corresponding nanostructures both theoretically and experimentally. When designing the structures, we should consider both SERS enhancement and chiral field enhancement. In ref 14, the SERS is greatly enhanced because of the coupling effect between nanoparticles and film. At the same time, many works indicated that nanostructures with 2D planar or 3D geometrical chirality show a high
enhancement of optical chirality, but many of their designs led to both left- and right-handed near-fields that cancel each other on average, which makes them not good candidates for chirality enhancement. Recently, the Schäfering group proposed a geometrically achiral configuration to generate chiral near-field with linearly polarized light at normal incidence, and then, they theoretically demonstrated that the near-field with high optical chirality over an extended region could be generated with a helical structure. In 2015, Tian et al. theoretically predicted that simple Au block dimer structures can provide very uniform chiral fields with optical chirality in the gaps under linearly polarized light illumination with polarization off the dimer axis, but the averaged optical chirality is limited.

Therefore, in this work, drawing on insights from the SERS enhancement factor, we proposed a definition of the SE-ROA enhancement factor and theoretically investigated that its maximum value stemmed from the local electromagnetic (EM) field and chiral field. Accordingly, to demonstrate the accuracy of this definition, we designed a film–particle system to achieve a high SERS enhancement and a chiral enhancement factor due to the strong coupling between the surface charge on the nanoparticle surface and the induced image charge on the film and then to achieve huge SE-ROA. Furthermore, the distribution of electric field and surface charge in the film–particle systems is suggested to explain qualitatively the enhancement of SE-ROA. Also, the influences from the size of the gold film and block dimer on SE-ROA are investigated.

## RESULTS AND DISCUSSION

### Enhancement Factor for Surface-Enhanced ROA.

As we all know, the main mechanisms of SERS enhancement are due to local field enhancement (excitation) and radiation enhancement (re-emission), and the SERS enhancement factor is approximately proportional to the $|E|^4$, that is

$$E_{\text{Raman}} = \left| \frac{E_{\text{local,excit}}}{E_0} \right|^4 \approx \left| \frac{E_{\text{local,excit}}}{E_0} \right|^4$$

where $E_0$ is the electric field intensity of the incident light. Analogously, the local field enhancement and radiation enhancement are the main causes that result in the chiral field enhancement. Therefore, we seek a simple expression to describe the relationship between the SE-ROA enhancement factor and the EM field. For a chiral material,

$$\text{CD} \propto G^* \cdot C$$

where $G^*$ is the imaginary part of the mixed electric–magnetic dipole polarizability ($G = G' + iG^*$), which is fixed or has chemical enhancement it ROA similar to the chemical enhancement in SERS. Also, thanks to Lipkin and Tang, we have a quantitative parameter $C = \frac{-1}{2} \text{Im}(E^* \cdot B)$ to express the chirality of the EM field. For circularly polarized light (CPL), $C_{\text{CPL}} = \pm \frac{-1}{2} E_0 \cdot B_0$, and for linearly polarized light, $C_{\text{linear}} = 0$. However, with the help of the field chirality $C_0$ once the molecule is in a chiral field, no matter whether the chiral field is excited by linearly or circularly polarized light, it exhibits optical activity.

$$C_{\text{local,excit}} = \text{Im}(E_{\text{local,excit}}^* \cdot B_{\text{local}}) \approx \text{Im}(E_{\text{local}}^* \cdot B_0)$$

where $B_0$ is the magnetic field intensity of the incident light. Therefore, for the chiral near field the enhancement factor is

$$E_{\text{ROA,excit}} \propto \left| \frac{E_{\text{local,excit}}}{E_0} \right|^4 \times \left| \frac{B_{\text{local,excit}}}{B_0} \right|^4$$

Similar to the Raman scattering process, the power emitted by the chiral molecules dipole $p$ is

$$I_{\text{emit}} \propto |p|^2 = |\alpha E - iG^* B|^2 = \alpha^2 E^2 - G^* B^2 - 2i\alpha G^* \times E_{\text{local}}^* B_{\text{local}}$$

which gives the circular dichroism

$$\Delta I_{\text{emit}} \approx -4i\alpha G^* \times E_{\text{local}}^* B_{\text{local}}$$

For Raman shift, the wavelength is not far from the excitation wavelength, so the enhancement factor for emission is

$$E_{\text{ROA,emit}} \propto \left| \frac{E_{\text{local,emit}}}{E_0} \right|^4 \times \left| \frac{B_{\text{local,emit}}}{B_0} \right|^4$$

The total enhancement factor for ROA is

$$E_{\text{ROA}} = E_{\text{ROA,excit}} \times E_{\text{ROA,emit}}$$

$$E_{\text{ROA}} \propto \left| \frac{E_{\text{local,excit}}}{E_0} \right|^4 \times \left| \frac{B_{\text{local,excit}}}{B_0} \right|^4 \approx \left| \frac{E_{\text{local}}}{E_0} \right|^4$$

Therefore, if someone wants to get SE-ROA, one should have both enhanced electric field $E$ and chiral near field $C$ (Figure 1). For an enhanced local field $E/E_0 = 10^3$, $E_{\text{Raman}} \approx 10^3$, and $E_{\text{ROA}} \approx 10^6$. With this enhancement factor, one can get single-molecule Raman scattering with $I_{\text{Raman}} \propto E_{\text{Raman}} \times \sigma_{\text{Raman}} \approx 10^{12} \times 10^{-28} \text{ cm}^2 = 10^{-17} \text{ cm}^2$. However, for CDROA $\propto E_{\text{ROA}} \times \sigma_{\text{Raman}} \approx 10^{10} \times 10^{-28} \text{ cm}^2 = 10^{-23} \text{ cm}^2$. Therefore, basically, one needs $10^6$ times molecules to get a signal similar to the phase ratio with the same experimental parameters. With 1000 times laser intensity, like 10 mW, and 100 times integration time, like 3000 s, one can get a resolvable ROA spectrum of 10 molecules in ideal condition. In reality, one

![Figure 1: (a) Scheme of a chiral molecule in the hot spot gap of a plasmonic dimer. (b) Scheme of a chiral molecule in the hot spot gap of a plasmonic dimer with chiral near field.](Image)
need to consider if the Raman scattering is excited resonantly, the ROA cross section of molecules will increase a lot, which will be good for the measurement. Also, the most important thing is that all of the discussion above is based on the assumption of the local field when the molecules are located in a maximum chiral field, that is

$$C = \text{Im}[\max\{E_{\text{local}}^*B\}]$$

(10)

However, in most of the conditions, the dot product of \(E\) and \(B\) are decided by the structures and excitation. However, usually it is also quite easy to calculate \(C_{\text{local}}\) in numerical simulations. Thus, the enhancement factor can be written as

$$E_{\text{ROA}} = \frac{C}{C_{\text{CPL}}} = \langle \hat{C}\rangle^2$$

(11)

Also, because the local chiral field varies, the formula above is only usable for single small molecules. If the molecule is very large, it is usable when the molecule is located in homogeneous chiral field \(C\). In addition, if the large molecule overlaps with both positive and negative chiral field \(C\), it is out of our discussion. Therefore, we usually need uniform strong enhanced chiral near field and strong enhanced EM field. In the reported \(l(\hat{C})\) in the literature is usually at orders of ten, and in some conditions, if one does not consider about the average value, but just focus on the maximum value of \(|\hat{C}|\), it can reach 85. However, in this situation, the available hot site area for SERS of adsorbing molecules is really small and the SERS enhancement factor is not very large. Therefore, we usually need uniform strong enhanced chiral near field and strong enhanced EM field. In the reported \(l(\hat{C})\) \(\approx 80\) condition, the \(E_{\text{ROA}} \approx 10^4\), so \(10^8\) molecules needed for getting efficient ROA with the same experimental parameters of single-molecule SERS. However, in a 1000 times laser intensity and 1000 times integrating time measurement, one still needs around 100 molecules in case the measurement did not damage any molecules. That is why one needs high concentrations of molecules, intensive laser, and long time to get surface-enhanced ROA.

Here, in the discussion, we use \(<\hat{C}\>) but not the asymmetry factor \(j\) because we still need to measure SERS with enhancement factor \(E_{\text{Raman}} = \int \frac{E_{\text{local}}}{E_0} \cdot dV\) for many molecules adsorbed in a volume, and the strongest of \(\hat{C}\) is not always the strongest \(E_{\text{local}}/E_0\).

As we discussed above, there are now two missions to get the strongest enhancement factor for Raman and ROA: first, find a structure that the strongest enhancement spots of electric field \(E\) and chiral near field \(C\) are overlapped and, second, find a structure that has the as stronger averaged chiral near field \(C\) as we can. Because the chiral near field is characterized by the dot product of \(E\) and \(B\) \((C \approx \text{Im}(E^*B))\), we expect such structures where the part of the structure has strong response to incident electric field \(E\) and part of the structure has strong response to incident magnetic field \(H\) (shown in Figure 2a). However, there is no such material that has a rapid magnetic response in light frequency \((\mu = 1\) in light frequency\), so now the popular way is to use a plasmonic material to yield circular current in light frequency to get enhanced magnetic field (Figure 2b). If one wants to use the incident magnetic field to excite the structure, the plasmonic material should have an equivalent current loop surface in the direction of \(H\) (Figure 2c). However, in this way, as well as in Figure 2b, the electric field \(E\) and magnetic field \(H\) are perpendicular to each other, which makes the dot product \(C\) almost zero. This is also the reason that in a lot of dimer structures, the chiral near field is almost zero at the hot spots. A solution is to make the current response loop surface in the direction of electric field \(E\) (Figure 2d). This kind of structure has been realized in spring structures. However, the drawbacks of such structures are also obvious: low electric enhanced field and too complex fabrication.

**Plasmonic Chiral Enhancement of the Particle–Film System.** As we all known, metal nanoparticle aggregates on a gold (or silver) film substrate can confine more energy in the particle–particle gaps or the particle–film gaps and make the electric field enhancement induced by the plasmonic coupling between the nanoparticle aggregates and the film. However, there is very little knowledge about the influences of the gold (or silver) film substrate on the optical chirality. Some time ago, a block dimer structure was proposed with the linear polarization excitation to obtain chiral near field for enhancing as shown in Figure 3a. In the configuration, the enhanced electric field has nonperpendicular direction with the incident magnetic field, which yields the chiral near field. The advantage of the structure is that it can yield strong uniform chiral near...
Figure 3. (a) Schematic illustration of the near chiral field yielded in a plasmonic structure that excited with a linearly polarized light. The induced electric field in the gap is always perpendicular to the structure surface and has nonzero dot product with the incident magnetic field \( \mathbf{C} \approx \text{Im}(\mathbf{E}^\perp \cdot \mathbf{B}) \). (b(i)) Schematic illustration of two plasmonic blocks on top of a gold film excited by the linearly polarized light. The induced polarization of the two blocks is shown as the thick red arrows. Because of the metal film, there are imaginary opposite charge distributions on the film surface shown as the dashed red arrows. The two sets of arrows forming two circular current loops, which are equivalent to magnetons. The electric field in the gap is always perpendicular to the boundaries. (ii) Schematic illustration of the effect behaved in (i): the two magnetons will yield magnetic field between the gap, and the magnetic response can follow the light frequency because of the plasmonic material. The incident magnetic component \( H_0 \) can also interact with the structure because of the gap between the blocks and the film. The magnetic field in the gap is enhanced as well and has nonzero dot product with the induced electric field \( \mathbf{C} \approx \text{Im}(\mathbf{E}^\perp \cdot \mathbf{B}) \).

field with a simple structure and is usable under both CPL and linearly polarized light excitation, and under linear excitation, the near field is even stronger. Now, if we put the block dimer structure on a plasmonic metal film with very narrow gap, the block polarization will induce imaging dipoles on the film as shown in Figure 3b(i) (larger red solid and dashed arrows). The block dipole and the imaging dipole will form a current circular loop (see Figure 4c inset as well), which is equivalent to a magneton shown as the blue arrow. It is very important to notice that the current loop will respond to the incident magnetic field as well because of the gap. The two magnetons which respond in the light frequency range will yield magnetic field between them as shown in Figure 3b(ii). The yielded magnetic field is much stronger than the incident magnetic field and can superpose with the incident field. Also, the angle between the electric field and the magnetic field is small which makes the dot product even larger \( \mathbf{C} \approx \text{Im}(\mathbf{E}^\perp \cdot \mathbf{B}) \). However, because the substrate attracts most of the electric field close to the film, the enhanced magnetic field is also concentrated close to the film. Thus, the enhancement for both electric field \( E \) and chiral near field \( C \) are not uniform anymore.

To further demonstrate the theoretical analysis above, we designed an Au block dimer—film system and analyzed with a numerical method, as shown in Figure 4a,b. The simulations were performed with the system using the finite element method (FEM, COMSOL Multiphysics 5.0). A Au block dimer on Au film was located in the \( x-y \) plane, the incident light propagated along the \( z \) axis, and the linearly polarized light with the polarization was off the \( x \) axis (and \( y \) axis) 45°. The length and width of the blocks were set as the same value \( w \), the thickness of the block and film were set as \( h_1 \) and \( h_2 \), respectively, the gap between the two nanoparticles was set as \( g \) and its volume was represented as \( V_0 \) and the gap between the dimer and the film was set as \( d \), each of which was marked in Figure 4a,b. All calculations were done by assuming that the structure is in air, and the permittivity of materials was adopted according to Johnson and Christy’s work.\(^{35}\) As shown in Figure 4c, when excited by linearly polarized light as shown in Figure 4b, there is a strong resonance peak in the near-infrared region and two weaker resonance peaks in the visible region. From the surface charge density distributions (inset of Figure 4c), we can see that there is a strong coupling between the two particles and between the particles and the film in the near-infrared region, and the imaging charges on the film and the charges on the blocks form current loops, which behaves exactly as we discussed in Figure 3. For the higher order resonances, the EM and optical chirality enhancements are inconspicuous. Therefore, the optical chirality for dipole resonance was usable for SE-ROA and focused on the following studies. Correspondingly, in the resonance peak, the maximum of the electric field enhancement and chirality enhancement can reach 113 and 2500 at 1 nm above the film in the center of the gap.
Compared with the SE-ROA experiment performed before, it is possible to get SE-ROA of a few or even single molecules in the same condition to get ROA signals (10 mW and 3000 s). If the measured molecule is in resonance (surface-enhanced resonant Raman scattering), it is possible that we use less laser intensity and less time to get ROA of the single molecule. However, if we have many molecules between the gap, we can get the Raman and ROA signal with averaged enhancement factors. In the calculations, if a few molecules adsorbed randomly on the blocks, because of the huge enhancement, we only approximately need to consider the volume of the gap between the two blocks. Meanwhile, the averaged optical chirality enhancement in the gap of the dimer is larger than that of in the gap between the dimer and the film, thanks to the uniform chiral fields (Supporting Information, Figure S1a), and chiral fields with opposite handedness can be obtained simply by changing the polarization to the other side of the dimer axis (Supporting Information, Figure S1b). The averaged electric field enhancement and averaged optical chirality enhancement in the configuration can reach 80 and 492 in the gap ($V_0$) of the dimer, which means that we have $E_{\text{Raman,ave}} \approx 4 \times 10^5$, $E_{\text{ROA,ave}} \approx 2.4 \times 10^5$, as shown in Figure 4e. The averaged chiral field is 1 order of magnitude stronger than the dimer in air because of the coupling effect from the film (Supporting Information, Figure S1c). If there are tens of molecules in the gap, with the averaged enhancement value, we need almost the same condition to get ROA signals (10 mW and 3000 s). Therefore, if we do perform the experiment in such a structure, it is possible to get SE-ROA of a few or even single molecules. Compared with the SE-ROA experiment performed before with high concentration,10 mW and 3000 s is not a strict situation with the concentration of 0.1 nM in experiment (to get only a few molecules adsorbed). In the discussion above, we of course assumed that the two blocks are perfect. However, in real experiments, the blocks are not so regular (no matter whether top-down fabricated or bottom-up synthesized). In such case, if the irregular protrusion is symmetric related to the axis of the two blocks, it will not affect the result a lot. However, if it is asymmetric, then both the electric field and chiral field intensity will be different for the two linearly polarized light directions. Thus, there are two effects for the spectrum: the first is that the two spectra will have a little bit different base line, for which one just need to align the spectrum base line with one peak without CD in the experiment for calculating ROA; the second is that for the peaks with CD information, the intensity difference is related to the original value, which does not affect the results very seriously if one does not want the absolute intensity information of ROA. However, if the molecules are many, the effect is not a problem anymore because the small field difference will be averaged. In such experiment, even though there is no CPL shining on the sample, one can still calculate the enhancement factor. We get the ROA cross section of molecules from the traditional method with CPL excitation pure molecules. Then, when calculating the SE-ROA cross section, one just uses the intensity of the linearly polarized light as a CPL intensity. The other steps are the same.

It is widely acknowledged that the plasmonic resonance depends on the geometry of nanoparticles, and to compare the effect from the shape of nanostructures, we utilized the sphere dimer instead of the block dimer, as shown in Figure S1d (Supporting Information), and investigated that the optical chirality enhancement declines extremely, which is due to a weaker coupling between the sphere dimer and the film. Thus, the block dimer on the film is focused on the following section as the optical chirality enhancement system.

**Analysis of the Electric Field Enhancement and Optical Chirality for the Block-Dimer–Film System.** To obtain a direct picture of the optical chirality enhancement and electric field enhancement in the block dimer–film system proposed above, the electric field and the optical chirality enhancement distributions of the system were investigated, as shown in Figure 5. Figure 5a–c shows the chiral field (the top panel) and electric field (the bottom panel) distributions of different cut planes of the dimer–film system. The $x$–$z$ slices are cut from the middle position of the gap between the dimer. The $y$–$z$ slices are cut along the axis of the dimer. The $x$–$y$ slices (c) are cut from the middle position of the gap between the dimer and film and (d) are cut with different depths from the upper surface of the dimer (0, 5, 10, 15, 20, 25, and 30 nm).

![Figure 5: Chiral field and electric field distributions of different cut planes at the dipole resonant wavelength.](image-url) Corresponding optical chiral near-field distributions in the $x$–$z$ plane (a), $y$–$z$ plane (b) and $x$–$y$ plane (c,d). The $x$–$z$ slices are cut from the middle position of the gap between the dimer. The $y$–$z$ slices are cut along the axis of the dimer. The $x$–$y$ slices (c) are cut from the middle position of the gap between the dimer and film and (d) are cut with different depths from the upper surface of the dimer (0, 5, 10, 15, 20, 25, and 30 nm).
ment with the distance from the film, Figure 5d shows the optical chirality and electric field enhancement with different depths from the upper surface of the dimer. At the same time, we calculated the electric field and optical chirality enhancement for a series of points in the middle of gap between the dimer every 5 nm, as shown in Figure S2a,b (Supporting Information). It can be seen that the maximal optical chirality can reach $10^5$ in the bottom, which further demonstrates the feasibility of $E_{R OA,max}$.

Influences of the Parameters of the Block-Dimer—Film Structure on Optical Chirality. As shown in formula 11, for larger molecules, the SE-ROA enhancement factor is proportional to the $I(C)^3$. We all know that the structure factors play a great role in the surface plasmon in metal nanostructures, and thus, their influences on optical chirality were investigated, as shown in Figure 6. Block dimers with heights of 20, 30, and 40 nm are studied, with other parameters remaining unchanged as shown in Figure 4. From Figure 6a, we can see that the volume averaged optical chirality in $V_0$ is the largest with the height of 30 nm. When the height increases from 20 to 30 nm, the induced current and dipole moment become stronger, which induces the enhancement of the optical chirality. However, when the thickness increases further, the induced electric field in the higher position becomes weaker because of the screening effect of the metal, and the coupled electric field between the film and the dimer becomes weaker because of the delay effect, especially in the upper section of the dimer, and therefore, the optical chirality in the upper section of the gap becomes weaker and the averaged optical chirality becomes smaller (Figure S3a in Supporting Information).

Meanwhile, we studied the optical chirality in $V_0$ changed with the thickness of the film varying from 60 to 100 nm, as shown in Figure 6b. From Figure 6b, it can be seen that the volume averaged optical chirality increases with the increasing of the thickness. However, when the thickness increases from 80 to 100 nm, the increasing of the optical chirality is very limited, because when the film is thin, there is still coupling effect between two surfaces; when the film is thicker, it is almost the same as the bulk material (Figure S3b in Supporting Information). Meanwhile, the separation distance between the two blocks and the film is a very important factor for plasmonic resonance. As shown in Figure 6c, when the distance $g$ between two blocks increases from 4 to 7 nm, the averaged optical chirality increases initially and then decreases. Because when the $g$ is smaller, the strong coupling between two blocks will tend to align the electric dipole in one line, which makes the magnetic field lines have larger angles with the electric field lines. However, when the $g$ is bigger, the coupling effect between the two blocks becomes weaker, and thus, the averaged optical chirality reaches maximum when $g$ is 5 nm. The influence from the distance between the dimer and the film is similar; as shown in Figure 6d, when the dimer comes in contact with the film, the averaged optical chirality is smaller, because there is no imaging dipole in the film, which could not form a current circular loop between the dimer and the film as a magneton. However, when the gap increases further, the averaged optical chirality also becomes smaller because of the weaker coupling effect.

Comparison with CPL Excitation. The mechanism discussed in Figure 3 is adaptable for CPL excitation as well, and like the blocks without film in ref 29, here the enhancement of chiral field $C$ is smaller when excited with CPL; Figure 7 shows the results. We can see that for CPL, the electric field enhancement is not as large as linear excitation because, in some period, the $E_0$ direction is perpendicular to the gap. Also, the $C$ enhancement is also smaller. Therefore, linear polarization excitation is still an option if we want to reach the ultimate limit of $EF_{R OA,max}$.

### CONCLUSIONS

In summary, we discussed the enhancement factor for SE-ROA just as the enhancement factor in SERS. The direct result shows that the enhancement factor for SE-ROA is proportional to the enhancement of chiral near field. Depending on single or many molecules, maximum and averaged values should be considered. Meanwhile, because the aim is searching for an ultimate limit of ROA signals for single or a few molecules, electric field enhancement should be considered as well. A nanostructure consisting of plasmonic block dimers on Au films was proposed to evaluate the enhancement and measurement consumption in experiments because of the huge enhancement factors for both
Raman and ROA. The maximum $EF_{\text{SERS}}$ is around $1 \times 10^8 \text{V}^2 / \text{m}^4$, and the maximum chiral enhancement $\tilde{C}$ arrives 2500 which makes the maximum $EF_{\text{SEROA}}$ $6 \times 10^6$. For the measurement of many molecules, the averaged $(EF_{\text{SERS}})$ is about $4 \times 10^7 \text{V}^2 / \text{m}^4$, and $(EF_{\text{SEROA}})$ is about $2.4 \times 10^5$. With the enhancement factors of SERS and SE-ROA, we find that it is possible to obtain ROA signals of a single molecule. The results proposed in this paper are helpful for SE-ROA research at a few-molecule level.

## METHODS

**FEM Simulation.** All full wave numerical simulations were done by using the FEM (commercial software package, COMSOL Multiphysics 5.0). The three-dimensional (3D) nanostructures were put on the substrate. Nonuniform meshes were used for formatting the object. The largest mesh was set less than $\lambda / 6$. The perfectly matched layer was used to minimize the scattering from the outer boundary. The incident light was set to 1 V/m and propagated along the z axis. The absorption cross sections were obtained by integrating the Ohmic heating within the nanostructure. The super chiral field was plotted with $\tilde{C} = C/C_{\text{CPL}}$, where $C$ is defined as $C = -\frac{\epsilon_{\omega}^*}{2} \text{Im}(E^* \cdot B)$ and $C_{\text{CPL}} = \pm \frac{\epsilon_{\omega}^*}{2} \frac{E_0^2}{V}$. The volume-averaged chiral spectra were obtained using $\langle \tilde{C} \rangle = \frac{1}{V} \int \tilde{C} \, dV$.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b02098.

Volume averaged optical chirality in different gaps, electric field and optical chirality versus wavelength plots, and chiral near field distributions at the dipole resonance wavelength for different size parameters (PDF)

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**Author Contributions**

Y.F. conceived the idea and supervised the project. L.H. and F.X. did the FEM simulations. L.H., L.Q., and Y.F. analyzed the data. L.H. and Y.F. wrote the paper.

**Notes**

The authors declare no competing financial interest.

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