Circular Dichroism Control of Tungsten Diselenide (WSe$_2$) Atomic Layers with Plasmonic Metamolecules

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Supporting Information

ABSTRACT: Controlling circularly polarized (CP) states of light is critical to the development of functional devices for key and emerging applications such as display technology and quantum communication, and the compact circular polarization-tunable photon source is one critical element to realize the applications in the chip-scale integrated system. The atomic layers of transition metal dichalcogenides (TMDCs) exhibit intrinsic CP emissions and are potential chiroptical materials for ultrathin CP photon sources. In this work, we demonstrated CP photon sources of TMDCs with device thicknesses approximately 50 nm. CP photoluminescence from the atomic layers of tungsten diselenide (WSe$_2$) was precisely controlled with chiral metamolecules (MMs), and the optical chirality of WSe$_2$ was enhanced more than 4 times by integrating with the MMs. Both the enhanced and reversed circular dichroisms had been achieved. Through integrations of the novel gain material and plasmonic structure which are both low-dimensional, a compact device capable of efficiently manipulating emissions of CP photon was realized. These ultrathin devices are suitable for important applications such as the optical information technology and chip-scale biosensing.

KEYWORDS: two-dimensional materials, transition metal dichalcogenides (TMDCs), WSe$_2$, surface plasmon, metasurface, chirality, circular dichroism

INTRODUCTION

Controlling circularly polarized (CP) states of light is critical to their usages in various areas including display technology,1,2 quantum-based optical information processing, and communication.3−5 The distinct behaviors in the emission and absorption of two CP lights are known as the circular dichroism (CD). The phenomena take place as the light transmits through specific media which respond differently to the field components in two circular polarization states, namely, left-hand CP (LCP) and right-hand CP (RCP) states. In fact, the occurrences of such events usually indicate the optical chirality of media. Because many biological molecules and organic compounds exhibit CD, the CP radiation plays an increasingly important role not only in optics but also in the fields of chemistry, biomedicine, and elementary particle physics.6−11

Recently, it has been observed that the atomic layers of transition metal dichalcogenides (TMDCs)12−41 exhibit unusual absorption and emission of CP lights.12,13 TMDCs are layered semiconductors formed by transition metal atoms (M) and halogen atoms (X) with a typical chemical formula of MX$_2$. The thickness of each layer in TMDCs is less than 1 nm. In monolayer TMDCs, the M and X atoms are separately arranged in the respective hexagonal lattice structures. Their band gaps around the Fermi level are direct and range in 1−2 eV.14−18 The direct band gaps are located at the degenerate but inequivalent K points (also known as K valleys) in the Brillouin zone. Because their crystal structure comprises two types of atoms, the inversion symmetry is broken in monolayer TMDCs, and this makes the electron−hole pairs (excitons) in the two K valleys (denoted as K$_1$ and K$_2$) present in different states of electric polarizations ($\sigma_+$ and $\sigma_-$). As the CP light excites the monolayer TMDCs, the RCP and LCP fields couple only to the $\sigma_+$ and $\sigma_-$ state transitions in bands at the K$_1$ and K$_2$.
The phenomena of CD indicate that TMDCs are promising optical materials with a controllable optical chirality and may enable the generation of CP photons. However, the operation temperature and excitation photon energy need to be carefully controlled to induce observable CD in monolayer TMDCs. It had been shown that the CD of PL in monolayer MoS$_2$ quickly diminished at a temperature more than 90 K because of the elevated intervalley scattering of carriers at the higher temperatures. Moreover, even in the presence of the selective coupling between CP photons and electron–hole pairs near K points, as the excitation photon energy increases and gets much higher than the direct band gap, the degree of circular polarization of the emitted radiation would drop rapidly or simply vanish. Such trends had been observed in MoS$_2$ MoSe$_2$, and WSe$_2$. To counteract these behaviors, several researchers have proposed various approaches to maintain the CD of PL in TMDCs. Such methods include the applications of an in-plane electric field, an out-of-plane magnetic field, and a localized magnetic field.

One means of controlling CP light is to apply a chiral plasmonic metasurface. Owing to the confinement of localized surface plasmon resonance (LSPR) modes in metallic nanostructures, plasmonic metasurfaces with chiral building blocks exhibit a strong optical chirality. The optical chirality has been achieved in various plasmonic metasurfaces including helical structures, coupled achiral or chiral plasmonic elements, Tamm plasmonic structure, and pseudo-chirality effects. In this way, a plasmonic chiral metasurface with at least one dimension in the nanoscale can be utilized to manipulate the degree of circular polarization of the luminescence. Combining TMDCs with plasmonic metasurfaces is beneficial for several reasons. First, as the plasmonic metasurface is directly fabricated on a monolayer TMDC, tightly confined LSPR modes of the metasurface strongly interact with the carriers within the thin sheet material. Second, the geometry-dependent LSPR modes of plasmonic nanostructures in metasurfaces provide the wavelength tunability for emission windows of different materials. Third, the ultrathin atomic layer of TMDCs (<1 nm) and nanoscale plasmonic metasurface (several tens of nanometers) facilitate compact functional photonic devices. Therefore, chiral plasmonic metasurfaces would be suitable candidates for manipulating the CP PL of TMDCs. In this study, we demonstrated an ultrathin photon source by utilizing a chiral metamolecule (MM) nanostructure to precisely control the CD of the emission from TMDC WSe$_2$. The monolayer WSe$_2$ was selected because it has the high quantum yield, superior tolerance of excitation level, and an induced optical chirality potentially comparable to the more commonly used monolayer MoS$_2$, indicating that it is an appropriate candidate of active chiral materials. The chiral MMs are composed of a plasmonic shifted dimer nanorod, which is a simple structure of two parallel nanorods, which has been reported to successfully function as a chiral-emitting device integrated with nonchiral dyes. Here, we briefly introduce the manufacturing processes and fabrication procedures of the MM array integrated with monolayer WSe$_2$. Through simulations and transmittance measurements, the optical chirality of the MM would be analyzed. Finally, we examine the CD of PL from the WSe$_2$ monolayer integrated beneath the chiral metasurface under the CP excitations. 

**RESULTS AND DISCUSSION**

Figure 1a illustrates the schematic diagram of chiral metasurfaces fabricated on the stack of a monolayer WSe$_2$ and the substrate of silicon dioxide (SiO$_2$). As mentioned earlier, the chiral metasurfaces consisted of two nearby gold nanorods that were identical and arranged in parallel. In each MM, one of the nanorods was laterally shifted along its direction of the long axis. Accordingly, the MMs were divided into the achiral type D$_0$ and two chiral counterparts D$_+$ and D$_-$, as shown in Figure 1b–d. 

This nanorod-based design provides the resonance along the long axis of each single rod, and the pair arrangement in the MM array enables the resonant coupling as long as the two rods are sufficiently close. In addition, if the two nanorods are aligned with a finite lateral shift (D$_+$ and D$_-$ types), the resonant coupling occurs in different phases and produces a variable coupling strength along the long axis. Figure 2a,c shows the top view of mode profiles (electric field) on resonance, which are calculated with the three-dimensional finite-element method (3D FEM). The counterparts of the cross-sectional view on the vertical plane are illustrated in Figure 2b,d. The asymmetric coupling deforms the electric field and induces the coupled resonant modes with the characteristics of near-field optical chirality. Furthermore, the directions of electric fields indicate opposite optical chiralities in D$_+$ and D$_-$ MMs, which is expected as they are mirror images of each other.

The resonant modes are mainly confined near the bottom edges of MMs because the plasmon resonance tends to occur at the interface between gold and SiO$_2$, which has the higher refractive index than that of the surrounding air. This could lead to a strong field–matter interaction because MMs are directly fabricated on WSe$_2$. Additionally, by tuning the geometry, we
can easily match the spectral response of LSPRs in the corresponding MMs to the PL of monolayer WSe₂.

In this study, we fabricated the plasmonic MMs using standard electron-beam lithography on a SiO₂ substrate with a transferred monolayer of WSe₂, followed by the evaporation of 50 nm of gold through electron beams and the lift-off process. The fabricated individual nanorods were 150 nm long, 80 nm wide, and 50 nm thick. The two neighboring nanorods were separated by 50 nm and also laterally shifted about half the rod length in opposite directions for both the D+ and D− MMs.

Before examining the CD of emissions from these WSe₂-MM hybrid devices, we first characterized the intrinsic optical properties of MMs through transmittance measurements. FEM simulations discussed earlier indicated that chiral resonant modes could be excited in the D+ and D− MMs. Hereafter, we define the RCP/LCP unit vectors as those which rotate counterclockwise/clockwise with respect to the normal axis pointing from the substrate to the free space. For the far-field transmittance measurement, the optical chirality should be reflected on the CD spectra, indicating that the radiation passing through the MMs would contain unequal amounts of LCP and RCP components.

White light from a tungsten lamp was subsequently focused with a 20× objective lens on the back side of devices at the normal incidence. The transmitted light was then collected by a 10× objective lens before passing through the combination of a quarter-wavelength plate and a linear polarizer. Finally, the output beam was directed to a spectrometer for the examination of CD spectra.

Figure 2. Top and cross-sectional views of the field profiles calculated with 3D FEM. The magnitudes and directions of the electric fields for (a,b) chiral D+ MM and (c,d) chiral D− MM, respectively.

Figure 3a shows the RCP extinction spectrum EXT_R and LCP counterpart EXT_L of the D+ and D− MMs, respectively. As photons with specific wavelengths coupled to the MMs, the LSPR was induced, and the significant intensity extinction appeared as a peak in the spectrum. The peak height reflected the coupling strength to the structure, and the polarized component that matched the polarization of resonant modes better would trigger the more prominent extinction peak. Because the D− MM (D+ MM) interacted more with the RCP (LCP) component of the incident beam, the RCP (LCP) extinction would exhibit the more substantial peak in the related spectrum of D+ (D−) MM.

To quantify the degree of circular polarization, we look into the CD of extinction defined as

\[ CD_{\text{EXT}} = \frac{\text{EXT}_R - \text{EXT}_L}{\text{EXT}_R + \text{EXT}_L} \times 100\% \] (1)

where EXT_R and EXT_L are the RCP and LCP spectra, respectively, and EXT'_R and EXT'_L are the corresponding peak values. For the D− MM, the RCP extinction is relatively significant, and its CD_{EXT} is positive. In contrast, for the D+ MM, the CD_{EXT} is negative. The extrema of CD_{EXT} are +1 and −1, representing the much more significant extinction of the RCP and LCP components than their counterparts, respectively. All other values of CD_{EXT} ranged within +1 to −1, and for achiral structures such as the D0 MM, the CD_{EXT} is close to 0.

We convert the polarized extinction spectra into the spectra of CD_{EXT} for each device. Figure 3b shows the spectra of CD_{EXT} for the three types of MMs. The CD_{EXT} of the D− MM remained small at any wavelengths, indicating nearly identical absorbances of the RCP and LCP components and hence no preference of circular polarizations. On the other hand, one peak and dip occurred in the spectra of CD_{EXT} for the D+ and D− MMs, respectively, featuring nonvanishing optical chiralities of the corresponding resonant modes. The positive peak reflects the RCP coupling of the D+ MM, and the negative one marks the LCP counterpart of the D− MM. The extinction bandwidth of the MMs is wider than the PL spectral width of the WSe₂ monolayer, which is beneficial to simultaneously manipulate the optical emissions from different TMDCs on the same device platform.

The effects of chiral metasurfaces on the manipulation of CP-PL from the monolayer WSe₂ were subsequently investigated. In this study, we focused on the emission chirality because of the neutral exciton in the monolayer WSe₂. The CP-PL spectra were taken under the continuous-wave excitation at 532 nm and 77 K. The CP extinction of the two chiral MMs at 532 nm was very weak, and the chirality of metasurfaces should have no impacts on the valley-selective generation of carriers. Figure 4a,b shows the CP-PL spectra of the bare monolayer WSe₂ under the RCP and LCP excitations, respectively. In the presence of the RCP (LCP) excitation, the CP-PL (LCP-PL) would be slightly stronger than the LCP (RCP) counterpart. This correlation in the luminescence is typical of TMDCs. The emission of photons in the same CP state as that of the excitation is favored because of the selection rules at K₁ and K₂ points. The optical chirality of CP-PL can be quantified through the CD_{PL} in each luminescence measurement.
where \( I_R \) and \( I_L \) are resolved PL intensities in the RCP and LCP states, respectively. The CDPL is positive (negative) if the RCP-PL (LCP-PL) intensity is higher than the other. The larger magnitude \( |\text{CDPL}| \) indicates the more prominent role of optical chirality in the luminescence.

The CDPL of the bare WSe\(_2\) monolayer under the RCP (LCP) excitation was positive (negative). In both conditions, the magnitudes \( |\text{CDPL}| \) were approximately 6%. These numbers are not as high as those reported in previous studies because (1) the excitation photon energy was far above the band gap of the monolayer WSe\(_2\) and (2) the sample temperature in the present study was relatively high. Both conditions would depolarize the dipole moments associated with the excitons generated after the valley-selective excitation. However, even in such experimental conditions, we will see later that the magnitude \( |\text{CDPL}| \) of CP-PL could be significantly boosted up in the presence of chiral metasurfaces.

The polarization characteristics of the PL from the monolayer WSe\(_2\) remain unchanged when it is integrated with the achiral metasurface (D\(_0\) type). Figure 4c shows the CP-PL spectra of the monolayer WSe\(_2\) integrated with D\(_0\) MMs under LCP excitation. The CDPL is around \(-6\%\), similar to that of the bare sample in the same excitation condition. Once the metasurface of chiral MMs was introduced above the monolayer WSe\(_2\), the CP-PL spectra were very distinct from those of the bare sample. Figure 4d shows the CP-PL spectrum of the monolayer WSe\(_2\) integrated with the D\(_+\) MM under the LCP excitation. Notably, the LCP-PL became much stronger than the RCP-PL, which not only kept the CDPL negative but...
also increased the magnitude |CDPL| up to more than 26% (26.2%). Because the D- MM favored the coupling of photons in the LCP state, and the monolayer WSe2 emitted more LCP photons under the LCP excitation, the combination of the two mechanisms made CDPL more negative with an enhanced magnitude |CDPL|. On the other hand, for the monolayer WSe2 beneath the achiral D0 MM, the CDPL was similar to that of the bare WSe2. This confirms that the increase in |CDPL| in the presence of the D- MM and LCP excitation originated from their overall effects because both of them favor LCP photon emissions.

To determine which of the chiral metasurface and natural CP-PL of the monolayer WSe2 plays the key role in the CDPL, we next excited the same device under the RCP excitation (Figure 5a). Under such circumstances, the LCP-PL was still stronger than the RCP-PL, and the CDPL remained negative. The magnitude |CDPL| decreased to approximately 20% (19.7%) but still much higher than that of the bare WSe2 in the same excitation condition. Because the bare WSe2 under the RCP excitation exhibited a CDPL of about +5.8%, the negative counterpart in this case indicates that the optical chirality of the LCP-favored D- MM was sufficiently robust to reverse the intrinsic CDPL of bare WSe2. Similarly, for the monolayer WSe2 integrated with D- MMs under LCP excitation (Figure 5b), the CDPL is positive, and the magnitude |CDPL| is also around 20% (19.3%).

To understand the details of circular polarization states in PL, we propose a generic model of linear responses to describe the overall effect of the monolayer WSe2 integrated with the chiral metasurface. Let us consider the monolayer WSe2. The dipole moment can be decomposed into

\[ \delta_n \]

where the matrix elements \( M_{\alpha\alpha}^{(\rho)}(\rho^{(\alpha)}) \) correspond to a certain exciton at position \( \rho^{(\alpha)} \) in the presence of \( \alpha \) MM. The radiation fields \( E_n^{(\alpha)} \) far above the samples, we need to model the far-field response of dipoles in the presence of MMs. The radiation fields \( E_n^{(\alpha)} \) and \( E_n^{(\alpha')} \) are connected to the counterparts \( p_n^{(\alpha)} \) and \( p_n^{(\alpha')} \) of dipole \( n \) through a 2-by-2 matrix

\[
\begin{bmatrix}
E_R^{(\alpha)} \\
E_L^{(\alpha)}
\end{bmatrix} = \begin{bmatrix}
M_{RR}^{(\rho)}(\rho^{(\alpha)}) & M_{RL}^{(\rho)}(\rho^{(\alpha)}) \\
M_{LR}^{(\rho)}(\rho^{(\alpha)}) & M_{LL}^{(\rho)}(\rho^{(\alpha)})
\end{bmatrix}
\begin{bmatrix}
p_R^{(\alpha)} \\
p_L^{(\alpha)}
\end{bmatrix}
\]  

(4)

where the matrix elements \( M_{\alpha\alpha}^{(\rho)}(\rho^{(\alpha)}) \) (\( \alpha, \alpha' = R, L \)) at position \( \rho^{(\alpha)} \) in the presence of MM arrays can be evaluated by the far-field calculations of the Maxwell equations. The near-field effect of MMs on the far-field polarization states of dipoles is built into the matrix elements \( M_{\alpha\alpha}^{(\rho)}(\rho^{(\alpha)}) \). The total RCP and LCP field components \( E_R^{(\alpha)} \) and \( E_L^{(\alpha)} \) far above the MMs are the summations of respective constituents \( E_R^{(\alpha)} \) and \( E_L^{(\alpha)} \). With the independent dipole approximation in eq 3, the ensemble averages of the RCP and LCP intensities \( I_R^{(\alpha)} \) and \( I_L^{(\alpha)} \) in the presence of the MM can then be expressed as a weighted sum of the local counterpart CDPL \( |\rho^{(\alpha)}|/|\rho^{(\alpha)}| \) of matrices \( \alpha \), \( \alpha' \) of the matrix elements characterize the polarization effect of chiral MMs. In this way, the CD PL of the CP-PL in the presence of the MM can then be expressed as a weighted sum of local CDPL

\[
I_{\alpha}^{(\alpha')} = \sum_n I_n^{(\alpha)} = \sum_n \langle |E_n^{(\alpha)}|^2 \rangle,
\]  

\[
\alpha = R, L, \quad \langle |E_n^{(\alpha)}|^2 \rangle = |p_n^{(\alpha)}|^2 |M_{\alpha\alpha}^{(\rho)}(\rho^{(\alpha)})|^2 f_R^{(\alpha)} + |M_{\alpha\alpha}^{(\rho)}(\rho^{(\alpha)})|^2 f_L^{(\alpha)}
\]  

(5)

where \( I_n^{(\alpha)} \) are the RCP and LCP intensities from dipole \( n \). In eq 5, the roles played by fractions \( f_R^{(\alpha)} \) and \( f_L^{(\alpha)} \) in the CP state \( \alpha \) appear as the information of valleys, while square moduli \( |M_{\alpha\alpha}^{(\rho)}(\rho^{(\alpha)})|^2 \) of the matrix elements characterize the polarization effect of chiral MMs. In this way, the CD PL of the CP-PL in the presence of the MM can then be expressed as a weighted sum of local CDPL

\[
CD_{\text{PL}}^{(\alpha)} = \sum_n \left( \frac{I_n^{(\alpha)} + I_n^{(\alpha')}}{I_R^{(\alpha)} + I_L^{(\alpha)}} \right) CD_{\text{PL}}^{(\rho^{(\alpha)}, f_R^{(\alpha)}, f_L^{(\alpha)})}
\]  

(6)

In Figure 6a,b, we show CD PL of \( \rho, f_R, f_L \) in a unit cell of the D+ and D- MM arrays, respectively, assuming equal probabilities in the two K valleys (\( f_R = f_L = 1/2 \)). The wavelength is set to 721 nm, at which the peak CD occurs. To make the chirality of nanostructures clear, only the positive (negative) part of the local CD is shown in (a) [(b)].
the sign and magnitude of $\text{CD}^\text{PL}$ depend on the spatial profiles of K-point probabilities $f^{(i)}_\alpha \rightarrow f^{(i)}_\beta (\alpha = R, L)$ and how dipole emitters are distributed around MMs.

Before proceeding to the estimation of $\text{CD}^\text{PL}$, we may use rate equations to understand what may influence the probability $f^{(i)}_\alpha (\alpha = R, L)$ in the two valleys from a macroscopic point of views. Let us denote the exciton (dipole) densities in K1 and K2 valleys as $n_1$ and $n_2$, respectively. Their rate equations can be written as

$$\frac{\partial n_1}{\partial t} = -\gamma_{tot} n_1 - \gamma_\alpha (n_1 - n_2) + A \frac{I_p}{E_p},$$
$$\frac{\partial n_2}{\partial t} = -\gamma_{tot} n_2 - \gamma_\alpha (n_2 - n_1) + A \frac{I_p}{E_p}$$

(7)

where $\gamma_{tot} = \gamma_w + \gamma_p$ is the total recombination rate which is composed of the nonradiative one $\gamma_w$ and the spontaneous (SP) emission counterpart $\gamma_p$; $\gamma_\alpha$ is the intervalley scattering rate; $A$ is the absorbance of the pump photon; $I_\alpha$ and $I_p$ are the average RCP and LCP intensities in the near field of the pump in the monolayer WSe2, respectively; and $E_p$ is the photon energy of the pump. We note that there are no differences between SP emission rates $\gamma_p (\alpha = R, L)$ of excitons in K1 and K2 valleys because the system is reciprocal despite being chiral.\textsuperscript{59} By setting the time derivatives to zero, we can derive the steady-state densities $n_1^{(s)}$ and $n_2^{(s)}$ and obtain the expressions of macroscopic fractions $f^{(s)}_R$ and $f^{(s)}_L$ for RCP and LCP dipoles (averages of $f^{(i)}_R (\alpha)$ and $f^{(i)}_L (\alpha)$ in the real and phase spaces) and their difference $f^{(s)}_R - f^{(s)}_L$ as follows

$$f^{(s)}_R = \frac{n^{(s)}_1}{n^{(s)}_1 + n^{(s)}_2} = \frac{1}{2} \left[ 1 \pm \frac{\gamma_{tot}}{2 \gamma_\alpha} \left( \frac{I_\alpha - I_L}{I_\alpha + I_L} \right) \right],$$
$$f^{(s)}_L = \frac{n^{(s)}_2}{n^{(s)}_1 + n^{(s)}_2} = \frac{1}{2} \left[ 1 \mp \frac{\gamma_{tot}}{2 \gamma_\alpha} \left( \frac{I_\alpha - I_L}{I_\alpha + I_L} \right) \right],$$

$$f^{(s)}_R - f^{(s)}_L = \frac{1}{2 \gamma_\alpha} \left( \frac{I_\alpha - I_L}{I_\alpha + I_L} \right)$$

(8)

From eq 8, the magnitude $|f^{(s)}_R - f^{(s)}_L|$ of fractional difference increases with the recombination rates $\gamma_w$ and $\gamma_p$ (enhanced by the presence of MMs) and degree of circular polarization $I_\alpha = I_L/I_\alpha + I_L$ in the near field of the pump, but it decreases with the intervalley scattering rate $\gamma_\alpha$. In this way, the introduction of plasmonic MMs seems to enhance the fractional difference of dipoles in the two valleys because of the Purcell effect.\textsuperscript{59} However, the plasmonic MMs may also increase the intervalley-scattering rate $\gamma_\alpha$ but reduce the degree of circular polarization for the near field of the pump. Hence, the fractional difference $f^{(s)}_R - f^{(s)}_L$ is not necessarily boosted up by the plasmonic MMs. In fact, under the LCP pump, the experimental CDs of PLs from WSe2 monolayers seem to increase because of the Purcell effect.\textsuperscript{59} However, the plasmonic MMs may also increase the intervalley-scattering rate $\gamma_\alpha$ but reduce the degree of circular polarization for the near field of the pump. Hence, the fractional difference $f^{(s)}_R - f^{(s)}_L$ is not necessarily boosted up by the plasmonic MMs. In fact, under the LCP pump, the experimental CDs of PLs from the mirror structures of D1 and D2, MMs (to be shown later) simply change signs with close magnitudes, indicating that the fractional differences $f^{(s)}_R - f^{(s)}_L$ in these chiral structures may be small, and their effect on the observed CDs is minor. In other words, the observed CDs might mainly reflect the chiral response of the plasmonic MMs to the radiation of nearly unpolarized dipoles (an incomplete CP polarizer) rather than the imbalance of dipole populations in the two valleys.

For the estimation of $\text{CD}^\text{PL}$ and comparison with experimental $\text{CD}^\text{PL}$, we assume that most dipole emitters are resident inside a region with inner and outer boundaries of about 10 and 30 nm away from the rod surfaces, as indicated by the union of white curves in Figure 6a,b, respectively. The density profile $n(\rho)$ of electron–hole pairs in this region is set according to the intensity pattern of excitation at 532 nm. The areas within the 10 nm are excluded because of the prominent quenching from metal surfaces and significant nonradiative recombination because of defects introduced in fabrications. The outer boundary of 30 nm is adopted because numerical calculations show that the external excitation at 532 nm which generated carriers resulted in a surface field only within 25–35 nm away from the nanorods. One can see that the selected area encloses the central region with a significantly negative local CD of PL. Because of the uncertainties of probabilities $f^{(s)}_\alpha (\rho)$ by plasmonic MMs, we further assume that in the presence of CP...
excitations, the K-point probabilities \( f_r(\rho) \) are constant in the integration region and can be approximated as

\[
\bar{f}_{RL}(\rho) \rightarrow f_{RL} \approx \frac{1}{2} \left[ 1 \pm \text{CD}_{\text{bare}}^{\text{bare}} \right] 
\]

where \( \text{CD}_{\text{bare}}^{\text{bare}} \) now stands for the CD of PL from bare WSe\(_2\) in the presence of CP excitation. Under these settings, we can rewrite \( f_{\alpha}^{(MM)}(\alpha = \text{R}, \text{L}) \) as

\[
\begin{bmatrix}
    f_{\text{R}}^{(MM)} \\
    f_{\text{L}}^{(MM)}
\end{bmatrix} \propto \begin{bmatrix}
    |M_{\text{RR}}^{\text{R}}|^2 & |M_{\text{RL}}^{\text{R}}|^2 \\
    |M_{\text{LR}}^{\text{L}}|^2 & |M_{\text{LL}}^{\text{L}}|^2
\end{bmatrix} \begin{bmatrix}
    f_{\text{R}} \\
    f_{\text{L}}
\end{bmatrix}
\]

where \( |M_{\alpha\alpha}(\rho)|^2 = \int_{\Omega} d\rho(\rho)\int_{\Omega} d\rho(\rho) \) is the averaged square magnitude of \( M_{\alpha\alpha}(\rho) \) and \( \Omega \) is the integration region.

We utilize the 3D FEM to evaluate square magnitudes of matrix elements and obtain their relative magnitudes as \( |M_{\text{RR}}^{\text{R}}|^2, |M_{\text{RL}}^{\text{R}}|^2, |M_{\text{LR}}^{\text{L}}|^2, |M_{\text{LL}}^{\text{L}}|^2 \propto [0.160, 0.191, 0.337, 0.312] \), which are sufficient to characterize the far-field polarization state at 721 nm. Using these matrix elements, we recalculate the model-predicted \( \text{CD}_{\text{RCP}}^{\text{MM}}(\text{D}_\alpha \text{MMs from the RCP and LCP CD}) \text{and eqs 6, 9, and 10}. \) The model provides a \( \text{CD}_{\text{RCP}}^{\text{MM}} \) of \(-29.53\%\) under LCP excitation for WSe\(_2\) integrated with the D\_ MM and a close number under the RCP excitation. It correctly reproduces the sign and order of magnitudes for the experimentally CD of PL under the LCP and RCP excitations but somewhat overestimates their magnitudes (around 26 and 19.7% experimentally). This is probably due to the lack of knowledge on how electron-hole pairs were really distributed in the experiment. In addition, the close \( \text{CD}_{\text{RCP}}^{\text{MM}} \) under the LCP and RCP excitations in our estimations may arise from the presumption of identical spatial dipole distributions in both cases (the same density \( n(\rho) \) and integration region \( \Omega \)), which was probably not the case in the experiment. In fact, the two similar CD\( ^{\text{MM}} \) in our model result from the significant and comparable off-diagonal terms \( |M_{\text{RL}}^{\text{R}}|^2 \) and \( |M_{\text{LR}}^{\text{L}}|^2 \), which efficiently couple CP dipoles to the counter-polarized intensities and therefore weaken the roles of \( f_{\text{R}} \) and \( f_{\text{L}} \). Despite this discrepancy, the model does reflect a remarkable turnover of the experimental CD of PL under the RCP excitation in the presence/absence of D\_ MM.

On the basis of the experimental data, the CD of PL from the monolayer WSe\(_2\) can be manipulated with the coupling between the chiral MMs and intrinsic CP photon emissions. Figure 7 shows the CD of PL of the monolayer WSe\(_2\), integrated with various MMs (different lateral shifts) as a function of the CD\( ^{\text{EXT}} \) at 77 K. The data were collected under the LCP excitation at the PL peak around 721 nm. Because the D\_ MM monolayer WSe\(_2\) and D\_ MM metasurfaces exhibit non-CP, RCP, and LCP excitations in our estimations, we might also reverse the CD\( ^{\text{PL}} \) of WSe\(_2\) under LCP excitation with the RCP-favored D\_ MM. In this situation, the output CD\( ^{\text{PL}} \) turned positive, varying from +11.1 to +19.7%. Comparing these three cases, the intrinsic, enhanced, and reversed CD\( ^{\text{PL}} \) from the monolayer WSe\(_2\) were all achieved, and both positive and negative CD\( ^{\text{PL}} \) from -26 to +20% (more precisely, -26.2 to +19.7%) can be reached without switching the CP state of excitation. Figure 7c shows the circular polarization degrees of optical emissions from the bare WSe\(_2\) monolayer, the D\_ MM, and the integrated device under LCP excitation. With the TMDC-MM hybrid platform, the CD state of the optical emission was enhanced from -6 to -26%, which is more than 4 times the enhancement in optical CD. Therefore, the ultrathin hybrid platform which integrates the monolayer WSe\(_2\) with chiral MM metasurfaces for the manipulation of the CD of PL is feasible and efficient. Although, in this study, we only focus on the control and enhance circular polarization of the WSe\(_2\) emission, it is worth to note that the higher degree of circular polarization from the TMDC atomic layers could be observed by optimizing the excitation wavelength and under lower temperature.

## CONCLUSIONS

In summary, the ultrathin circular polarized light source was demonstrated by integrating the monolayer WSe\(_2\) with the plasmonic chiral metasurface. The polarization states of photons emitted from the monolayer WSe\(_2\) were controlled through the coupling between those photons and chiral MMs. The observed degree of circular polarization indicates that the optical chirality of WSe\(_2\) could be manipulated by integrating it with the MMs. Both the enhanced and reversed chiralities were feasible. The CD\( ^{\text{PL}} \) could be further fine-tuned from -26 to +20% (-26.2 to +19.7%). The optical circular polarization degree of the WSe\(_2\) atomic layer was also enhanced more than 4 times. This work could be a platform to realize the ultrathin TMDC devices in practical applications such as optical information technologies and chip-scale biosensing.

## METHOD

### Preparation of the WSe\(_2\) Atomic Layer.

The chemical vapor deposition method adopted for the growth of the monolayer WSe\(_2\) is based on the hydrogen reaction in the growth chamber to activate the selenization of WO\(_3\). In this way, large-size flakes of the monolayer WSe\(_2\) can be successfully grown on the sapphire substrate. To realize the device for this study, we transferred the monolayer WSe\(_2\) to the double-side polished silica substrate by the polymethyl methacrylate (PMMA)-based method. The WSe\(_2\) growth substrate was first spin-coated a PMMA film followed by baking at 100 gr for 1 h. Then the PMMA-capped WSe\(_2\)/sapphire was immersed into the buffer oxide etcher solution and shifted into deionized (DI) water to dilute the BOE residue. The etching process creates gaps between WSe\(_2\) and the substrates; meanwhile, the PMMA film holds WSe\(_2\). In DI water, we can easily lift the PMMA film with WSe\(_2\) and transfer this film to the target fused silica substrate. Finally, the PMMA film was removed by acetone, isopropanol alcohol, and DI water, and the monolayer WSe\(_2\) would stick on the silica substrate because of van der Waals force. The details had been reported by Huang et al.\(^{14}\)
**Device Fabrication.** The MM patterns were defined by the electron-beam lithography on a SiO$_2$ substrate with a transferred monolayer of WSe$_2$, followed by the electron-beam evaporation of 50 nm gold and lift-off process. The individual nanorod was 150 nm long, 80 nm wide, and 50 nm thick. The two nanorods were separated by 50 nm in an MM array and laterally shifted approximately half the rod length in opposite directions for the D$_+_1$ and D$_-1$. MMs.

**REFERENCES**


