Chiral Second-Harmonic Generation from Monolayer WS₂/Aluminum Plasmonic Vortex Metalens

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ABSTRACT: Two-dimensional spiral plasmonic structures have emerged as a versatile approach to generate near-field vortex fields with tunable topological charges. We demonstrate here a far-field approach to observe the chiral second-harmonic generation (SHG) at designated visible wavelengths from a single plasmonic vortex metalens. This metalens comprises an Archimedean spiral slit fabricated on atomically flat aluminum epitaxial film, which allows for precise tuning of plasmonic resonances and subsequent transfer of two-dimensional materials on top of the spiral slit. The nonlinear optical measurements show a giant SHG circular dichroism. Furthermore, we have achieved an enhanced chiral SHG conversion efficiency (about an order of magnitude greater than the bare aluminum lens) from monolayer tungsten disulfide (WS₂)/aluminum metalens, which is designed at the C-exciton resonance of WS₂. Since the C-exciton is not a valley exciton, the enhanced chiral SHG in this hybrid system originates from the plasmonic vortex field-enhanced SHG under the optical spin–orbit interaction.

KEYWORDS: Surface plasmonic vortex metalens, optical spin–orbit interaction, chiral nonlinearity, second-harmonic generation, aluminum epitaxial film, monolayer tungsten disulfide

Besides spin angular momentum (SAM) associated with circular polarization, a light beam can carry orbital angular momentum (OAM) in free space, which corresponds to an optical vortex beam along the propagation axis with a helical phase front.1–2 It is well-known that the value of SAM per photon is limited to ±ℏ (ℏ is the reduced Planck constant, ℏ = ℏ/2π), depending on right- or left-handed circular polarization (RCP or LCP). In contrast to SAM, the azimuthal phase (φ) dependence in the optical vortex beam is exp(ılφ), where l is the topological charge per photon (positive or negative integer) and the value of OAM per photon is ℏl. In anisotropic and inhomogeneous optical media, these two momenta can interact with each other, changing both the polarization and phase of the beam.3 This interaction can be controlled by the polarization of incident beam and the geometry of media resulting from their inhomogeneity. In the past two decades, optical vortex beams have found numerous applications such as optical manipulation of microparticles,4,5 super-resolution focusing, nonlinear vortex optics,6 optical communication,7 quantum information processing,8–10 topological photonics using the geometric phases,11–13 and optical vortex beam microemitters.14–17

Optical vortex beams are typically generated in free space by diffraction-limited optical approaches.1–4 In the past decade or so, surface plasmonic vortices generated by plasmonic nanostructures, such as Archimedean spiral nanoslits or nanogrooves fabricated on noble metal films,18–25 have attracted much interest because of the capability of plasmonic nanostructures to confine, manipulate, and enhance electromagnetic fields into subwavelength mode volumes.26–29 Therefore, plasmonic vortices formed through excitation of surface plasmon polaritons (SPPs) at the metal–dielectric interfaces by circularly polarized excitation beams can open a new pathway to dramatically shrink the vortex sizes,24,25 which could be exploited for integrated nanophotonic applications. However, to date, surface plasmonic vortices are mostly limited by investigations using near-field techniques, such as scanning near-field optical microscopy (SNOM),19–23 photoemission electron microscopy (PEEM),24,25 and scanning electron-beam-based cathodoluminescence (CL).30 Therefore, it is highly desirable to generate far-field orbital angular momenta
from near-field optical chirality both for fundamental studies and applications.11

In this work, we combine plasmon-enhanced second-harmonic generation (SHG)32−35 with circular dichroism (CD) for probing the chirality of a plasmonic vortex metalens (PVML) consisting of an aluminum Archimedean spiral nanoslit and a semiconducting transition metal dichalcogenide (TMDC) monolayer. The advantage of SHG for probing near-field chirality is that the absorption cross section is not constrained by reciprocity,36 and it can exhibit CD in planar chiral geometries and metasurfaces.37,38 As an optical medium, monolayer TMDC belongs to a class of layered materials, most notably the indirect-to-direct bandgap transition in the monolayer limit. Furthermore, the broken inversion symmetry in monolayer TMDCs can lead to strong nonlinear optical responses, such as SHG,40−42 and valley-selective circular dichroism in the emerging field of valleytronics.43 Additional advantage for the hybrid-metallic materials applications is that monolayer TMDCs can be easily integrated with dissimilar materials (semiconductors, dielectrics, and metals) via vdW bonding without the constraint of lattice matching condition in conventional semiconductor and metal heteroepitaxy.

The plasmonic spiral structures used here were fabricated on aluminum epitaxial films, which exhibit dual resonance bands (442 and 600 nm), where the 442 nm resonance is specifically designed to match with the C-exciton resonance in monolayer tungsten disulfide (WS2) originating from “band nesting”.44 Unlike the valley excitons, that is, A and B excitons associated with the interband transitions at the degenerate but inequivalent K and K′ (i.e., K and −K) valleys of the Brillouin zone, the C-exciton resonance does not exhibit the intrinsic chiroptical properties of valley excitons.43 Therefore, it is suitable for the demonstration of artificially engineered chirality using the plasmonic enhancement effects of PVML under the optical spin−orbit interaction. Furthermore, we can significantly enhance the SHG intensity, in comparison to the bare aluminum lens, by incorporating a monolayer of WS2 onto the lens.

In our PVML design, SPPs are excited at the Archimedean spiral slit edge at designated wavelengths (i.e., plasmonic gap modes) and propagate radially at the top (air/metal) and bottom (metal/substrate) interfaces (Figures S1 and S2). Moreover, a large-area exfoliated monolayer WS2 is transferred to the Archimedean spiral slit by using a gold-mediated technique.45 In Figure 1a, we show the actual Archimedean spiral slit fabricated by focused-ion beam (FIB) milling on an atomically flat aluminum (Al) film epitaxially grown on sapphire (root-mean-square roughness: ∼0.5 nm over a 5 × 5 μm2 area).46,47 The advantages of Al are that it is an excellent plasmonic material at both visible and ultraviolet (UV) wavelengths (alternative to silver (Ag) in the visible and better than Ag in the UV) and Al is chemically stable due to the formation a uniform native aluminum oxide layer with a self-passivating capability. Moreover, Al epitaxial films are compatible with the complementary metal-oxide semiconductor (CMOS) fabrication processes.48−50 It is also important for this study that Al is an appropriate plasmonic material for optical nonlinear processes, as demonstrated by earlier works.51−53

The simple formula \( r(\varphi) = r_0 + \varphi \cdot p/2\pi \) in the polar coordinate system, as shown in Figure 1b, is used to design the Archimedean spiral with the starting radius \( r_0 = 200 \text{ nm} \), the pitch \( p = 370 \text{ nm} \), and the cycle number \( n = 8 \). By using a single-crystalline and atomically smooth Al film, we can precisely engineer plasmonic gap modes by controlling the film thickness (90 nm) and the slit width (\( w = 140 \text{ nm} \)). Indeed, the optical microscopy images measured under LCP and RCP illumination at normal incidence clearly show chiroptical behavior of resonant absorption bands (Figure 1c,d). By performing reflectance spectromicroscopy (Figure 1e, optical measurements setup is shown in Figure S3) and finite-difference time-domain (FDTD) simulations (Figure S2), we show that this aluminum spiral has dual resonances at 442 and 600 nm (free-space wavelength).
According to the FDTD simulations, the 442 nm gap mode locates at the top (air/Al) interface, while the 600 nm gap mode is more complicated, involving both top and bottom (air/Al and Al/sapphire) interfaces. Therefore, in the following, we will focus more on the 442-mode because it is included in the Supporting Information (Figures S2 and S4). In a simple modeling, the electric field of linear surface plasmonic vortex along the z-direction can be expressed by the following equation in the cylindrical coordinate set \((r, \phi, z)\)

\[
E_{z,\ell}(\omega, r, \phi) = E_0(\omega)\exp\left[i\kappa_{z,\ell}(\omega)z\right]\exp\left[i\left(\omega t - c\frac{z}{\sqrt{\varepsilon_r \mu_r}}\right)\right]SPP(\omega)\]  

where \(E_0(\omega)\) is the amplitude of the incident electric field, \(\kappa_{z,\ell}(\omega) = \sqrt{k_0^2 - \omega^2\varepsilon_r\mu_r}\) (for the case of a thick metal film), \(k_0\) is the wavevector in vacuum, \(\varepsilon_r\) and \(\mu_r\) are the relative permittivity and permeability of the material, respectively. \(SPP(\omega)\) is the SPP field amplitude, which is determined by the FDTD technique to simulate the field distribution near the spiral surface. The wavenumber perpendicular to the surface \(k_{SPP}\) is given by \(k_{SPP}^2 = k_0^2 - \varepsilon_{SPP}\omega^2\) for an evanescent field, and \(k_{SPP}\) is the radius of the SPP circle.

In the case of monolayer WS\(_2\), the SPP dispersion relation derived from the dielectric function is not directly applicable due to the strong near-field coupling between top- and bottom-interface plasmonic modes, and we have to apply the FDTD technique to simulate the field distribution near the spiral interface, as shown in Figure 2b,c and e,f for the 442 nm incident light with RCP and LCP polarization, respectively. It is numerically confirmed for this specific Archimedean spiral that \(\lambda_{SPP} = 370\) nm (i.e., spiral pitch = SPP wavelength) at the top interface when the incident wavelength is at 442 nm (Figure 2e,f).

The topological charge of frequency-dependent plasmonic vortex, that is, \(l(\omega)\), comes from the contributions from both geometrical phase (\(\Phi_g\)) and dynamic phase (\(\Phi_d\)). Among them, one full cycle of spiral leads to a \(2\pi\) dynamic phase and the geometrical phase is \(2\pi\lambda_{SPP}\), where the geometrical topological charge \(m\) is defined by \(m = \frac{p}{\lambda_{SPP}}\). The resonant plasmonic vortex condition is that the total phase \(\Phi_{total} = \Phi_g + \Phi_d = 2\pi\lambda_{SPP}\) for an \(m\)-cycle spiral must be an even number of \(\pi\). Here, the spin quantum number (handedness) of the incident photon is defined with respect to the propagation direction of the incident beam and we denote \(\sigma_\ell\) for the SAM of RCP (\(\sigma_\ell = +1\)) and LCP (\(\sigma_\ell = -1\)) incident beam, respectively. The same convention is used here.

The topological charge \(l(\omega)\) of plasmonic vortex is then the sum of the spin angular momentum (\(\sigma_\ell\)) and the incident-frequency-dependent geometrical topological charge \(m(\omega)\), that is

\[
l_\ell(\omega) = \sigma_\ell + m(\omega)\]

For the top-interface plasmonic vortex mode at 442 nm, \(m = -1\) and then we have the following relation: \(l_\ell(\omega) = \sigma_\ell = -1\). As a result, the SPP field distribution at the center of the spiral strongly depends on the handedness of the circular polarization state of incoming light. For the present (counterclockwise) spiral structure, it can focus the RCP illumination into a bright spot (\(l = 0\)) at the center of lens. On the other hand, under the LCP illumination a doughnut-shaped intensity distribution with a hollow center appears at the center (\(l = -2\)).

Therefore, this spiral structure can function as a spin-number (i.e., chirality)-dependent plasmonic vortex lens. These theoretical predictions are experimentally confirmed by PEEM measurements and FDTD simulations (Figure 2a,d) and FDTD simulations (Figure 2b,c and e,f). In order to verify the chirality effects of the plasmonic vortex lens, circular-polarization-dependent PEEM measurements were performed by a commercial PEEM system (ELMITEC GmbH), which is capable of a 4 nm spatial resolution, and the experimental results are shown in Figure 2a.d. To perform the PEEM measurements, the circular-polarized excitation source is from circularly polarized light.
a near-resonance (λ = 430 nm) laser beam produced by a mode-locked femtosecond Ti:sapphire laser (pulse duration: 100 fs; repetition rate: 77 MHz), frequency doubling with a beta barium borate (BBO) nonlinear crystal and passing through a quarter wave plate. In Figure 2b,c and e,f, the simulated electric-field distributions are in good agreement with the laser PEEM experimental results. The circular-polarization-dependent near-field linear responses illustrate that under the RCP excitation, a bright point appears at the center of spiral (Figure 2a); while under the LCP excitation, a dark circular region forms at the center of spiral (Figure 2d), indicating that a plasmonic vortex has been built up. As an experimental verification, the chiroptical reflection image obtained with the LCP illumination (Figure 1c) is also consistent with the expected field intensity from the azimuthal phase variation of the $l = −2$ mode at 442 nm. On the basis of these results, we clearly demonstrate that chirality effects can be observed using our vortex lens design.

Now, we turn our attention to the discussion of the main results: chirality-dependent SHG from a PVML at room temperature. Figure 3 shows the chiral SHG spectra from the bare aluminum plasmonic vortex lens (note that we could not collect any SHG signal from a flat aluminum film). Two distinct chiral SHG peaks ($\lambda_1 = 885$ and $\lambda_2 = 1200$ nm) with strong dependence on the incident circular polarization states can be found while scanning the fundamental wavelength of excitation laser in the range of 820−1260 nm (more precisely, 820−980 nm and 1160−1260 nm). These results are in good agreement with the observed plasmonic resonance bands at 442 and 600 nm, as shown in Figure 1e. The chiral SHG response also exhibits a very sensitive dependence on the incident wavelength (Figure 3b), which can be expected from the superlinear dependence of SHG intensity, denoted as $I_{RCP/LCP}(2\omega)$, on the circularly polarized laser excitation power density. At $\lambda_1 = 885$ nm, the chirality-dependent SHG measurements indicates that the SHG intensity is stronger than that at $\lambda_2 = 1200$ nm and $SHG_{RCP} > SHG_{LCP}$ by a factor of about 4. Moreover, the SHG intensity shows a quadratic dependence (slope $\sim 2$ in the log-log scale). (e) The measured SHG-CD, that is, $I_{RCP}(2\omega) - I_{LCP}(2\omega))/(I_{RCP}(2\omega) + I_{LCP}(2\omega))/2$, is as high as $\pm 1.2$ (±120%) for two chiral SPP bands.
from the top interface (air/Al) and the observation of $\text{SHG}_{\text{RCP}} > \text{SHG}_{\text{LCP}}$ can be attributed to the effects of plasmonic vortex lens (Figure 2). On the other hand, for the 1200 nm excitation the SHG signals from RCP and LCP incident light occur at both top (air/Al) and bottom (Al/sapphire) interfaces, and the SHG signal is stronger at the bottom interface and $\text{SHG}_{\text{RCP}} < \text{SHG}_{\text{LCP}}$ at the top interface. These simulation results are in good agreement with the experimental observation.

If we define that the SHG circular dichroism (SHG-CD) is equal to $I_{\text{RCP}}(2\omega) - I_{\text{LCP}}(2\omega)/I_{\text{RCP}}(2\omega) + I_{\text{LCP}}(2\omega))$, we can quantitatively evaluate the plasmonic vortex lens performance for both RCP- and LCP-excitation to be as high as $\pm 1.2$ (i.e., 120%, see Figure 3e), which is much higher than the reported values for 2D chiral plasmonic nanostructures (Table S1) in the literature. The nonlinear power density dependence of the chiral SHG emission (C-exciton resonance at 442 nm) from monolayer WS$_2$ coupled to the aluminum plasmonic vortex, we show that the chiral SHG at the C-exciton resonance is another important figure of merit for SHG. For our metalens structure, under an average power density of $\sim 26 \text{ kW/cm}^2$ at $\lambda = 885$ nm, we obtain CEs of 6.7 $\times$ 10$^{-8}$ and 1.8 $\times$ 10$^{-8}$ at RCP and LCP excitation, respectively, which are comparable to the SHG-CES obtained for a gold Archimedean spiral lens.

To further enhance the SHG-CE, we incorporate a WS$_2$ monolayer onto the aluminum spiral lens because the broken inversion symmetry in monolayer TMDC can lead to a strong SHG response. For monolayer TMDCs, the conduction band minimum and the valence band maximum are both located at the K/K' corners of the hexagonal Brillouin zone. The A and B excitons associated with K/K' valley show a unique exciton-enhanced SHG process, following two-photon optical selection rules. It has been reported that two RCP photons at the fundamental frequency can generate a single LCP photon at the second-harmonic frequency with near-unity polarization, and vice versa. Therefore, we adopt the C-exciton absorption at $\sim 442$ nm (Figure S5) for the demonstration of artificially engineered chirality effect because the C-exciton does not have intrinsic chiral properties, such as the A and B valley excitons.

In Figure 4, a large-area monolayer WS$_2$ is transferred to the sample surface, covering both the region aluminum plasmonic vortex lens (region I) and bare aluminum film (region II). The plasmonic vortex lens show an enhancement of SHG about 2.5 (RCP) and 1.5 (LCP) times stronger, compared to the monolayer WS$_2$ region on the base aluminum film (Figure S6). More importantly, we have demonstrated that the C-exciton in WS$_2$ can exhibit an artificially engineered SHG chirality at room temperature on the plasmonic vortex lens (Figure 4b) and the SHG-CD is $\sim 0.40$ ($I_{\text{RCP}}/I_{\text{LCP}} \approx 1.5$). In comparison with the bare aluminum spiral, the SHG-CES have been enhanced to $4.26 \times 10^{-8}$ (6.4 times larger) and $2.74 \times 10^{-8}$ (15.2 times larger) for RCP and LCP laser excitation, respectively (the detailed CE values are listed in Table S2).

In summary, we have developed a CMOS-compatible epitaxial plasmonic system (aluminum on sapphire), which is used for large-scale fabrication and integration of planar chiral plasmonic structures and 2D van der Waals materials. Specifically, we have achieved an enhanced chiral SHG conversion efficiency from a monolayer WS$_2$/aluminum vortex meta-lens (about an order of magnitude greater than that of a bare aluminum vortex lens), where the plasmonic vortex field is at the achiral C-exciton resonance ($2\omega$). We have experimentally confirmed that using circularly polarized (RCP and LCP) laser excitation ($\omega$), the chiral SHG from the bare aluminum vortex lens at the C-exciton resonance shows a strong circular dichroism due to the incident-light chirality effects of the plasmonic vortex, such that the observed chiral ratio ($I_{\text{RCP}}/I_{\text{LCP}}$) $\approx 4$ and SHG-CD $\approx 120\%$. In the case of an exfoliated monolayer WS$_2$ resonantly coupled to the plasmonic vortex, we show that the chiral SHG at the C-exciton resonance can exhibit an artificially engineered chiral ratio $I_{\text{RCP}}/I_{\text{LCP}} \approx 1.5$ and SHG-CD $\approx 40\%$.

The hybrid material approach reported here, 2D materials in combination with chiral plasmonic structures on epitaxial aluminum films, has the potential to controllably integrate individual chiral hybrid-material systems into large-scale quantum architectures. These chiral quantum architectures can find important applications in chiral quantum optics, as well as chiral coupling of excitons and light through plasmon–exciton coupling and optical spin–orbit interactions.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c00645.

Experimental methods; details about the sample structure (Figure S1) and the plasmonic gap modes (additional FDTD simulations, Figures S2 and S4); linear and nonlinear optical measurement setups (Figure S3); SHG from an exfoliated monolayer WS$_2$ on SiO$_2$/Si.
at around the C-exciton resonance (Figure S5); circular polarization-dependent SHG enhancement factors from an exfoliated monolayer WS₂ (Figure S6); literature results of linear and nonlinear circular dichroism effects from 2D metal nanostructures (Table S1); circular polarization-dependent SHG-CD and conversion efficiencies of monolayer WS₂ with and without the plasmonic vortex lens (Table S2) (PDF)

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**Notes**

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