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Broadband Plasmon-Enhanced Four-Wave Mixing in Monolayer MoS$_2$

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ABSTRACT: Two-dimensional transition-metal dichalcogenide monolayers have remarkably large optical nonlinearity. However, the nonlinear optical conversion efficiency in monolayer transition-metal dichalcogenides is typically low due to small light–matter interaction length at the atomic thickness, which significantly obstructs their applications. Here, for the first time, we report broadband (up to ∼150 nm) enhancement of optical nonlinearity in monolayer MoS$_2$ with plasmonic structures. Substantial enhancement of four-wave mixing is demonstrated with the enhancement factor up to three orders of magnitude for broadband frequency conversion, covering the major visible spectral region. The equivalent third-order nonlinearity of the hybrid MoS$_2$-plasmonic structure is in the order of 10$^{-17}$ m$^2$/V$^2$, far superior (∼10–100-times larger) to the widely used conventional bulk materials (e.g., LiNbO$_3$, BBO) and nanomaterials (e.g., gold nanofilms). Such a considerable and broadband enhancement arises from the strongly confined electric field in the plasmonic structure, promising for numerous nonlinear photonic applications of two-dimensional materials.

KEYWORDS: Two-dimensional materials, nonlinear optics, four-wave mixing, plasmonic enhancement, MoS$_2$
induced significant and broadband FWM enhancement in 2D materials is promising for numerous applications in the future nonlinear photonics.

**Results and Discussion.** MoS$_2$-Plasmonic Nanostructures. A schematic layout and an optical image of the hybrid MoS$_2$-plasmonic structure are shown in Figure 1a and b. Monolayer MoS$_2$ flakes grown on a SiO$_2$/Si substrate by the chemical vapor deposition (CVD) method $^{39}$ are of the triangular shape and appear lighter colored compared to the substrate. By examining Raman and photoluminescence spectra (Figure S1, Supporting Information), the CVD MoS$_2$ flakes are identified as monolayers. The 50 nm-thick gold nanostructures are then patterned on top of the MoS$_2$ flakes (fabrication details in the Supporting Information). The scanning electron microscopy (SEM) image of a typical Au bowtie array is shown in Figure 1c. The size of each equilateral triangle ($s$) is $\sim$160 nm, and the gap ($g$) is $\sim$30 nm, with the unit cell pitch $P_x = P_y = \sim 600$ nm.

**Plasmon Enhanced FWM in Monolayer MoS$_2$.** An illustration of the FWM process in the hybrid MoS$_2$-plasmonic structure is shown in Figure 2a. The MoS$_2$ sample, excited by pump and idler beams with frequencies at $\omega_1$ and $\omega_2$ ($\omega_1 > \omega_2$), generates FWM signals at $\omega_{\text{FWM}} = 2\omega_1 - \omega_2$, following the law of conservation of energy. The lower panel in Figure 2a shows the energy level diagram of the FWM process. To measure the FWM signals, a home-built femtosecond laser based microscopic setup (Figure 2b) is employed. The input pump and idler laser beams are linearly polarized with polarizations parallel along the $x$-axis. For other polarizations (e.g., the pump and idler beams are cross-polarized), they are fully discussed in Figure S3 of the Supporting Information. The pump and idler beams are spatially merged using a dichroic mirror and are temporally synchronized by a delay line. The combined beams are focused on the sample through an objective lens. The generated nonlinear optical signals in the MoS$_2$ sample are measured in a reflection configuration by a spectrometer.

Here, we use a pump photon energy ($\hbar \omega_1$) at $\sim$1.55 eV ($\lambda_1 = \sim$800 nm) and an idler photon energy ($\hbar \omega_2$) at $\sim$1.19 eV ($\lambda_2 = \sim$1040 nm). Then the generated FWM photon energy ($\omega_{\text{FWM}} = 2\omega_1 - \omega_2$) is at $\sim$1.91 eV ($\lambda_{\text{FWM}} = \sim$650 nm). In the experiment, the average powers for both pump and idler input light are fixed as $\sim$1 $\mu$W (with a corresponding peak intensity of $\sim$44 GW/cm$^2$) unless otherwise specified. The plasmonic structures are fabricated on one portion of a few MoS$_2$ monolayer flakes (Figure 1b), which allows for a self-consistent comparison of FWM from the same MoS$_2$ flake with and without plasmonic structures. As shown in Figure 2c, the FWM peak intensity measured from the MoS$_2$-plasmonic structures is

![Figure 1. Hybrid MoS$_2$-plasmonic nanostructures. (a) Schematic illustration and (b) optical image of the MoS$_2$-plasmonic structure (Au bowtie) on a Si/SiO$_2$ substrate. In the optical image, the white dashed lines outline the edges of the MoS$_2$ flakes, and the red dashed line outlines the boundary of the plasmonic nanostructures and the bare SiO$_2$/Si substrate. (c) SEM image of the Au bowtie nanostructures. Scale bar: 500 nm. Inset: zoomed image of Au bowtie nanostructures. Structure parameters are also labeled.](image1)

![Figure 2. Plasmon-enhanced FWM in monolayer MoS$_2$. (a) Illustration of FWM from the hybrid MoS$_2$-plasmonic structures (upper panel) and the energy level diagram of FWM process (lower panel). (b) Schematic of the experimental setup for nonlinear optical measurements. (c) FWM spectra measured from hybrid MoS$_2$-plasmonic structures (red curve), bare MoS$_2$ monolayer without plasmonic structure (black curve), and the plasmonic structure only (gray dashed curve). (d) Generated FWM signals from the hybrid MoS$_2$-plasmonic structures (red) and the bare MoS$_2$ monolayer (black) through a polarization analyzer are plotted as a function of angle $\theta$ between the polarization analyzer axis and the $x$-axis. The experiment data (dots) can be well fitted by a $\cos^2 \theta$ curve. (e) Dependence of experimental FWM peak intensities on the average power of the pump ($P_1$) and probe light ($P_2$), with a fit to a power law $P$. Upper panel: Dependence of FWM on $P_1$ with a fit ($m \approx 1.89$). Lower panel: Dependence of FWM on $P_2$ with a fit ($m \approx 0.93$).](image2)
one order of magnitude (∼11-fold) higher than that from the bare MoS$_2$ region (i.e., without the plasmonic structure) and the pristine bowtie plasmonic structure. The results fully demonstrate the significant plasmonic enhancement of the third-order optical nonlinearity in 2D materials. Apart from FWM, there also exist multiple nonlinear optical processes in the hybrid MoS$_2$-plasmonic nanostructures. Figure S4 in the Supporting Information presents the spectra of the multiple nonlinear processes (e.g., SHG, Sum frequency generation, and FWM) on bare MoS$_2$ and hybrid MoS$_2$-plasmonic nanostructures.

The polarization of the generated FWM signal is also measured. Here, both the pump and idler beams are linearly polarized along the $x$-axis, and a polarization analyzer for the generated FWM signal is set at an angle $\theta$ with respect to the $x$-axis. Figure 2d presents the FWM versus field at 800 nm at different input polarizations (upper, the longitudinal mode; lower, the transverse mode). Here, both the pump and idler beams are linearly polarized along the $x$-axis, and a polarization analyzer for the generated FWM signal is set at an angle $\theta$ with respect to the $x$-axis. The polarization dependence of the hybrid MoS$_2$-plasmonic structure is calculated from the results shown in Figure 2c. The observed FWM signals from both the bare MoS$_2$ and the hybrid MoS$_2$-plasmonic structures, respectively. The estimated maximum $EF_{\text{ex}}$ at the plasmonic hot spot is calculated to be ∼4400 for the incident beam polarized along the $x$-axis shown in Figure 2. In addition, we also estimate the theoretical enhancement factor ($EF_{\text{th}}$) of ∼5250 (details in the Supporting Information), which agrees with our experimental results. Therefore, the plasmonic resonance strongly enhances the light–matter interactions in 2D materials, and the enhancement factor up to three orders of magnitude is achieved.

**FWM Enhancement with Different Polarizations.** The bowtie nanostructures typically support different plasmonic modes along with $x$ and $y$ directions. When the incident light is linearly polarized along the $x$-axis, the longitudinal plasmonic modes are excited. While the incident light is linearly polarized along the $y$-axis, the transverse plasmonic modes are excited. Here, we study the polarization dependence of the hybrid MoS$_2$-plasmonic structure. The experimental reflection spectra of the hybrid MoS$_2$-plasmonic structure on the SiO$_2$/Si substrate are measured with $x$ and $y$ polarizations, agreeing well with the simulated reflection spectra, as shown in Figure 3a. The relative reflection spectra ($R = R_{\text{MoS$_2$-bowtie}}/R_{\text{sub}}$) feature broad peaks for both polarizations, where $R_{\text{MoS$_2$-bowtie}}$ is the reflection from the hybrid MoS$_2$-plasmonic structures and $R_{\text{sub}}$ is the reflection from a bare SiO$_2$/Si substrate. Note that the small peaks at around 620 and 660 nm are the B- and A-excitonic states of MoS$_2$, clearly observed both in the experimental and simulated spectra. The significant peaks in the reflection spectra are attributed to the longitudinal and transverse plasmonic resonances, as confirmed by simulated electric field enhancement in the bowtie nanostructures at the wavelength of 800 nm (Figure 3b). The detailed simulations are introduced in Figure S5 in the Supporting Information. The longitudinal plasmonic resonance ($\omega_{p,L}$) is at ∼1.55 eV ($\lambda_{p,L} = ∼800$ nm), while the transverse plasmonic resonance is at a slightly higher energy ($\omega_{p,T}$) = 1.63 eV ($\lambda_{p,T} = ∼760$ nm).

$$EF_{\text{ex}} = \frac{I_{\text{MoS$_2$-bowtie}}}{I_{\text{MoS$_2$}} - A_{\text{gap}}/A_0}$$

where $I_{\text{MoS$_2$-bowtie}}$ and $I_{\text{MoS$_2$}}$ are the measured FWM intensities from MoS$_2$ with and without the bowtie plasmonic structure, $A_0$ represents the area of the unit cell in this array, and $A_{\text{gap}}$ represents the hot spot area of the plasmonic structure (i.e., the gap of the bowtie nanostructure). Accounting for the small hot spot area fraction ($A_{\text{gap}}/A_0 = ∼0.25\%$) and ∼11-fold FWM enhancement ($I_{\text{MoS$_2$-bowtie}}/I_{\text{MoS$_2$}}$) from the hybrid MoS$_2$-plasmonic structures, the estimated maximum $EF_{\text{ex}}$ at the plasmonic hot spot is calculated to be ∼4400 for the incident beam polarized along the $x$-axis shown in Figure 2. In addition, we also estimate the theoretical enhancement factor ($EF_{\text{th}}$) of ∼5250 (details in the Supporting Information), which agrees with our experimental results. Therefore, the plasmonic resonance strongly enhances the light–matter interactions in 2D materials, and the enhancement factor up to three orders of magnitude is achieved.

**FWM Enhancement with Different Polarizations.** The bowtie nanostructures typically support different plasmonic modes along with $x$ and $y$ directions. When the incident light is linearly polarized along the $x$-axis, the longitudinal plasmonic modes are excited. While the incident light is linearly polarized along the $y$-axis, the transverse plasmonic modes are excited. Here, we study the polarization dependence of the hybrid MoS$_2$-plasmonic structure. The experimental reflection spectra of the hybrid MoS$_2$-plasmonic structure on the SiO$_2$/Si substrate are measured with $x$ and $y$ polarizations, agreeing well with the simulated reflection spectra, as shown in Figure 3a. The relative reflection spectra ($R = R_{\text{MoS$_2$-bowtie}}/R_{\text{sub}}$) feature broad peaks for both polarizations, where $R_{\text{MoS$_2$-bowtie}}$ is the reflection from the hybrid MoS$_2$-plasmonic structures and $R_{\text{sub}}$ is the reflection from a bare SiO$_2$/Si substrate. Note that the small peaks at around 620 and 660 nm are the B- and A-excitonic states of MoS$_2$, clearly observed both in the experimental and simulated spectra. The significant peaks in the reflection spectra are attributed to the longitudinal and transverse plasmonic resonances, as confirmed by simulated electric field enhancement in the bowtie nanostructures at the wavelength of 800 nm (Figure 3b). The detailed simulations are introduced in Figure S5 in the Supporting Information. The longitudinal plasmonic resonance ($\omega_{p,L}$) is at ∼1.55 eV ($\lambda_{p,L} = ∼800$ nm), while the transverse plasmonic resonance is at a slightly higher energy ($\omega_{p,T}$) = 1.63 eV ($\lambda_{p,T} = ∼760$ nm).
For transverse mode, no interaction between the two neighboring triangular nanostructures is observed (the lower panel in Figure 3b), which corresponds to the dark spot in the gap. In contrast, for the longitudinal mode, the plasmonic modes supported by two neighboring triangular structures within one bowtie structure are strongly coupled, leading to the relative redshift of the longitudinal plasmonic mode. The hot spot inside the gap of the bowtie structure as illustrated in the upper panel of Figure 3b is an evidence for this strong interaction. We observe that the electric field enhancement with the longitudinal mode within the plasmonic structure (i.e., the gap of the bowtie) is much stronger than that of the transverse mode where the electric filed is only enhanced along the two sides of the bowtie.

The longitudinal and transverse plasmonic modes have totally different resonances (e.g., resonant wavelengths, electric fields), resulting in different enhancement behaviors in the nonlinear optical process. Here, we study the angular dependence of the FWM enhancement in the hybrid MoS2-plasmonic structure. Figure 3c shows the experimental FWM peak intensity measured from monolayer MoS2 with and without the plasmonic structure as a function of the polarization angle $\alpha$ between the incident beams and the $x$-axis. Note that the pump and idler beams are linearly polarized along the crystal $x$-axis. As a result, the generated FWM is totally dipolar with polarization parallel with each other. The details of the measurement setup are shown in Figure S6a in the Supporting Information. In contrast to the isotropic FWM from bare MoS2, the FWM intensity from the hybrid MoS2-plasmonic structure varies with $\alpha$. When the pump laser is polarized along the $x$-axis ($\alpha = 0^\circ$), it is resonant with the longitudinal plasmonic mode at the wavelength of 800 nm, the FWM enhancement reaches the maximum ($\sim$11-fold), higher than that from the transverse mode ($\sim$4-fold) with the $y$-axis polarized excitation ($\alpha = 90^\circ$). The spectra of the enhanced FWM signals at $\alpha = 0^\circ$ and $90^\circ$ are shown in Figure S6b in the Supporting Information. Between the two critical angles where is a superposition of two plasmonic modes, the enhancement of the nonlinear optical process varies between the maximum and the minimum. Therefore, tuning the polarization of the pump laser enables the modulation of the plasmons in the nanostructures, thus tuning the FWM intensity of the hybrid MoS2-plasmonic structure.

**FWM Enhancement with Different Plasmonic Structure Dimensions.** To further understand the plasmon-enhanced FWM process, we fabricate Au bowtie nanostructures with different dimensions on top of monolayer MoS2. The SEM images of the patterned Au bowties are shown in the left panel of Figure 4a, with structure size $s$ varying from 160 to 120 nm, while the gap ($g = 30$ nm) and the pitch ($P_x = P_y = 600$ nm) are fixed. The simulated electric field for the longitudinal polarization at 800 nm is presented in the right panel of Figure 4a. Figure 4b presents the experimental relative reflection spectra ($R = R_{MoS2-bowtie}/R_{sub}$) measured from the Au nanostructure arrays on monolayer MoS2 with the longitudinal polarization, agreeing well with the simulated reflection spectra. Details of the simulated reflection spectra are shown in Figure S5 in the Supporting Information. The plasmon resonance shows the redshift from 740 to 800 nm with the increment of the structure size $s$. The strengths of the plasmonic resonance, shown as the amplitude of the reflection peaks, are stronger with the increasing structure size, which fits well with the simulation results of the electric field in Figure 4a.

We further experimentally investigate the effect of the structure dimensions on the FWM enhancement in monolayer MoS2. The corresponding FWM spectra are measured from the hybrid MoS2-plasmonic structures with different nanostructure sizes (Figure 4c). Thus, the experimental ($EF_{ex}$) and theoretical ($EF_{th}$) enhancement factors can be calculated, respectively, as shown in Figure 4d. When nanostructure size $s$ changes from 120 to 160 nm, both the experimental and theoretical enhancement factors increase and show a similar tendency ($EF_{ex}$ from 1500 to 4400, and $EF_{th}$ from 1750 to 5250). We note that the nanostructure with $s = 160$ nm gives the highest $EF_{ex}$ with on-resonance excitation at 800 nm, while the FWM intensity drops with decreased nanostructure sizes, as expected from the simulation results (Figure 4a). Note that if the size of the nanostructure further increases (i.e., $s > 160$ nm), the plasmonic resonance is expected to redshift to a longer wavelength (i.e., $>800$ nm), and thus, the pump laser at 800 nm does not match the plasmonic resonance, leading to the suppression of the FWM enhancement.

**Broadband FWM Enhancement.** The schematic of broadband FWM enhancement is shown in Figure 5a. In our experiments, we fix the pump frequency and change the idler frequency to generate the tunable FWM enhancement in a broad wavelength range. In our case, since the fixed pump frequency matches the plasmonic resonance (i.e., $\omega_1 = \omega_{p_L}^{\text{MoS}_2}$), the FWM process is always kept on resonance. Hence, regardless of the tunable idler frequency, the FWM signal will be enhanced over a wide spectral range. To demonstrate the broadband FWM enhancement concept, our pump ($\hbar\omega_1$) is fixed at $\sim$1.55 eV (i.e., $\lambda_1 = \sim800$ nm) on resonance with the plasmonic resonance ($\omega_1 = \omega_{p_L}^{\text{MoS}_2}$), and the idler ($\hbar\omega_2$) changes from $\sim$0.98 to 1.41 eV (i.e., $\lambda_2 = \sim1260$ nm $\sim880$ nm), limited by the laser operation range. Both the pump and idler beams are linearly polarized along the $x$-axis. As a result, the generated FWM ($\omega_{FWM} = 2\omega_1 - \omega_2$) is tunable from $\sim$2.12 to 1.69 eV.
To summarize, we have demonstrated the broadband enhanced nonlinear light–matter interaction in MoS$_2$ with plasmonic structures. The enhancement factor of FWM up to three orders of magnitude is achieved. The enhancement is attributed to the localized electric field of the pump beam in the hot spot of the plasmonic nanostructures. With the longitudinal plasmonic mode, the plasmonic resonance with the extremely enhanced electric field at the hot spot results in the larger FWM enhancement compared to that of the transverse plasmonic mode. Moreover, a broadband FWM enhancement is realized over 150 nm in the visible spectral range. Our results show that the plasmonic structures can drastically improve the broadband nonlinear light–matter interactions in hybrid MoS$_2$-plasmonic structures, boosting the applications of 2D materials for future nonlinear optical devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c02381.

Device fabrication and the characterization of monolayer MoS$_2$, nonlinear optical measurement, polarization dependence of FWM, full spectra of different nonlinear optical processes, numerical simulation method, polarization dependence of FWM enhancement, theoretical calculation of enhancement factors, calculation of nonlinear coefficients for FWM signals in MoS$_2$, typical third-order nonlinear coefficients reported on 2D layered materials, enhancement factors for nonlinear coefficients of two-dimensional materials in hybrid structures (PDF)

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Author Contributions
Y.D. and Z.S. conceived the idea. Y.D. performed the experiments with assistance from Y.W. and S.D. H.X. and A.M. helped the nanostructure fabrication and characterization. S.L. provided the CVD-grown MoS2 sample. Y.D. analyzed the experimental data. Y.D. and Z.S. wrote the manuscript with contributions from all authors.

Notes
The authors declare no competing financial interest.

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