Electrical Control of Interband Resonant Nonlinear Optics in Monolayer MoS_2

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ABSTRACT: Monolayer transition metal dichalcogenides show strong optical nonlinearity with great potential for various emerging applications. Here, we demonstrate the gate-tunable interband resonant four-wave mixing and sum-frequency generation in monolayer MoS_2. Up to 80% modulation depth in four-wave mixing is achieved when the generated signal is resonant with A-exciton at room temperature, corresponding to an effective third-order optical nonlinearity $|\chi^{(3)}_{eff}|$ tuning from ~12.0 to 5.45 × 10^{-18} m^2/V^2. The tunability of the effective second-order optical nonlinearity $|\chi^{(2)}_{eff}|$ at 440 nm C-exciton resonance wavelength is also demonstrated from ~11.6 to 7.40 × 10^{-9} m/V with sum-frequency generation. Such large tunability in optical nonlinearities arises from the strong excitonic charging effect in monolayer transition metal dichalcogenides, which allows for electrical control of the interband excitonic transitions and thus nonlinear optical responses for future on-chip nonlinear optoelectronics.

KEYWORDS: nonlinear optics, four-wave mixing, sum-frequency generation, gate-tunability, exciton, MoS_2

Atomically thin transition metal dichalcogenides (TMDs) have stimulated great interest due to their favorable physical properties,[1, 2] such as extremely large exciton binding energy,[3] and valley pseudospin physics arising from a large spin-orbit interaction.[4] Particularly, TMD monolayers feature a direct bandgap in the visible spectral range,[2, 5] enabling diverse photonic applications including modulators,[6] photodetectors,[7] and light-emitting diodes.[8] Furthermore, TMD monolayers have recently attracted a surge of attention focusing on their fascinating optical nonlinearities[9] (*e.g.*, harmonic generation[10-12] and saturable absorption[13, 14]), promising

for various applications,[15] such as wavelength conversion[16, 17] and ultrafast pulse generation.[18-20]

In TMD monolayers, the strongly bound and tunable excitons[3, 21, 22] enable the enhanced light-matter interaction[23, 24] and tunable linear and nonlinear optical responses at the atomic thickness scale.[25, 26] For example, it has been demonstrated that the strong interband excitonic effect results in the significant enhancement of various harmonic generation processes[27, 28] in TMD monolayers. Additionally, it has been reported that second-harmonic generation in WSe_2 monolayer can be electrically tuned at A-exciton resonance.[26] The interband excitonic enhancement and tunability of nonlinear optical (NLO) responses are fascinating for numerous applications and will enable the versatility of future modern photonics, which is challenging with traditional NLO materials.[26, 29-31] However, the electrical control of the other NLO responses in TMDs still remains unexplored, although it is highly desired for future applications.

In this work, we report the interband excitonic effect of various nonlinear optical processes, including four-wave mixing (FWM) and sum-frequency generation (SFG), in monolayer MoS_2 at room temperature. We fabricate an ion-gel gated monolayer MoS_2 device for effective electron doping by applying positive gate voltages. We demonstrate the excitonic enhancement and the gate-tunable FWM of monolayer MoS_2. Similarly, for the SFG process, the enhancement and the nonlinear optical tunability at the interband excitonic resonance are also reported. Besides, the second- and third-order nonlinear coefficients are calculated as a function of doping carrier densities.

RESULTS AND DISCUSSION

Linear optical characterization in monolayer MoS_2. A schematic and an optical image of the MoS_2 device are shown in Figure 1a, b. The device consists of a chemical vapor

deposited (CVD) monolayer MoS_2 sheet on a SiO_2/Si substrate, with Ti/Au (5/50 nm) as the source and drain electrodes. The ion-gel top gate method[32] is used for electrostatic gating, which changes the doping level and therefore the optical responses of MoS_2. By examining Raman and photoluminescence spectra (Figure S1 in Supporting Information), the CVD MoS_2 film is identified as a monolayer. Here, the electrical property of the monolayer MoS_2 is measured with different gate voltages. The transport curve is characteristic of an *n*-type semiconductor, as shown in Figure 1b. Over a gate voltage range (-3V to 3V), the source-drain current increases with positive gating (*i.e.*, Vg > 0.4 V), indicating effectively electron-injection to MoS_2. The low off-current is due to the MoS_2-contact Schottky barrier.[33] Note that, in our experimental range (*i.e.*, the gate voltage range is between -3 and 3 V), we are not able to obtain effective hole doping. Therefore, in the following experiments, we mainly study the device at positive gating with effective electron doping.

In order to understand the excitonic effect on linear optical properties, the reflection spectra of the MoS_2 device are measured with electron doping at positive gating. The linear absorption spectrum of monolayer MoS_2 on a reference sapphire substrate shows pronounced absorption peaks attributed to A (~650 nm), B (~610 nm) and C (~440 nm) excitonic transitions with no electrostatic gating (grey curve in Figure 1c). However, at a large gate-voltage (*e.g.*, V_g = 3 V with doping carrier density of ~4×10^{13} /cm^2), the excitonic effect is strongly suppressed (Supporting Information Figure S2a). The carrier density is estimated using the capacitor model $N = C(V_g - V_{on})/e$, in which C is the ion-gel capacitance 2.45 μF/cm^2, e is the elementary charge, and V_{on} = 0.4 V is the turn-on voltage in the monolayer MoS_2 device[32]. Here, we plot the differential reflection spectra $\frac{R(V_g)-R(3V)}{R(3V)}$ in Figure 1c, where $R(V_g)$ represents the reflection of the monolayer MoS_2 film on the Si/SiO_2 substrate at V_g. The differential reflection spectra clearly show a gate-tunable linear optical response at A and B

excitons. This is mainly because the injected carriers (*e.g.*, electrons when V_g > 0.4 V) decrease the oscillator strength of interband excitonic transitions:[25] The higher the positive gate voltage is, the weaker the excitonic transitions induced linear absorption will be. And with high enough gate-voltage (*e.g.*, V_g = 3 V), the interband excitonic transitions could even be switched off, while a lower-energy resonance known as trion (*e.g.*, A-) emerges (Figure S2b in Supporting Information).[34] The trion (A-) resonance is quite weak, which is observable only by the derivative of the reflection spectra. Therefore, the influence of trion is insignificant in our experiments at room temperature. Note that negligible change is observed at C exciton, which is consistent with the result discussed in Ref. 25.

Gate-control of interband resonant FWM in MoS_2. A home-built femtosecond laser based microscopic system (Figure S3a in Supporting Information) is employed for the nonlinear optical measurements in monolayer MoS_2, as described in Methods. The monolayer MoS_2 film, excited by two pump frequencies at ω_1 and ω_2 ($\omega_1 > \omega_2$), typically generates various nonlinear optical signals, *e.g.*, second-harmonic signals ($2\omega_1$ and $2\omega_2$), SFG signal ($\omega_1 + \omega_2$), and FWM ($2\omega_1 \pm \omega_2$, $\omega_1 \pm 2\omega_2$), as shown in Supporting Information Figure S4.

Here, we mainly study the FWM generation (inset of Figure 2a): pump light ($\hbar\omega_1$) is fixed at ~1.55 eV (*i.e.*, λ_1 = ~800 nm) and idler light ($\hbar\omega_2$) is tunable in a near-infrared spectral range from ~1.1 to 1.33 eV (*i.e.*, λ_2 = ~930 – 1120 nm). As a result, wavelength-dependent FWM ($\omega_{FWM} = 2\omega_1 - \omega_2$) from ~1.77 to 2.00 eV (*i.e.*, λ_{FWM} = ~620 – 700 nm) is studied as shown in Figure 2a. The average power for both pump and idler input light beams in the experiment is ~1 μW (with a corresponding peak intensity of ~44 GW/cm^2). We find that the FWM is enhanced at around 650 nm, when the generated FWM photon energy (*i.e.*, $\hbar\omega_{FWM}$ = ~1.91 eV) matches the A-excitonic energy of monolayer MoS_2, suggesting the interband resonance at A-exciton (Figure 2b).

We further study the interband resonant FWM at A-exciton. Here, we use pump light ($\hbar\omega_1$) at ~1.55 eV (*i.e.*, λ_1 = ~800 nm) and idler light ($\hbar\omega_2$) at ~1.19 eV (*i.e.*, λ_2= ~1040 nm), and the generated FWM ($\omega_{FWM} = 2\omega_1 - \omega_2$) is at ~1.91 eV (*i.e.*, λ_{FWM}= ~650 nm). To examine the power dependence of the resonant FWM signal, the nonlinear optical spectra are measured when the power of pump (P_1) and idler (P_2) light beams is changed, respectively. The upper panel of Figure 2c shows the peak intensities of the FWM spectra with increasing P_1 while P_2 = 1 μW. The lower panel of Figure 2c shows the peak intensities of FWM spectra with increasing P_2 while P_1 = 1 μW. It roughly follows a square and linear power law behavior as a function of P_1 and P_2, respectively, which confirms the two-color FWM process ($\omega_{FWM} = 2\omega_1 - \omega_2$) involving the pump and idler light beams (details in Supporting Information). We also study the gate-tunable resonant FWM in monolayer MoS_2 with interband A-excitonic resonance, as shown in Figure 2d. The FWM intensities decrease significantly when V_g changes from 0 to 3 V. We attribute the gate tunable FWM to the modulation of oscillator strength of interband excitonic resonance by the gate injected electrons.[26] With increasing gate voltages, the oscillator strength at the excitonic resonance decreases with increased doping (as shown in Figure 1c), thus suppressing the exciton enhancement of nonlinear processes.[26] As a result, the FWM signals decrease with increasing gate voltage at the excitonic resonant wavelength. Note that the gate tunable FWM results are repeatable (Figure S5 in Supporting Information).

Similarly, with pump light ($\hbar\omega_1$) at ~1.55 eV (*i.e.,* λ_1 = ~800 nm) and idler light ($\hbar\omega_2$) at ~1.07 eV (*i.e.*, λ_2= ~1160 nm), the generated FWM ($\omega_{FWM} = 2\omega_1 - \omega_2$) at ~2.03 eV (*i.e.*, λ_{FWM}= ~610 nm) is resonant with B-excitonic state. Figure 2e shows gate-tunable resonant FWM spectra at B-exciton, where the FWM intensities also decrease with increased electrostatic doping due to the same operation principle.

The normalized gate-tunable FWM ($\frac{I_{\mathrm{FWM}}(V_{\mathrm{g}})}{I_{\mathrm{FWM}}(0\ \mathrm{V})}$) is plotted in Figure 2f, where $I_{\mathrm{FWM}}(V_{\mathrm{g}})$ is the peak intensity of FWM at V_{g}. Here, we achieve a nearly 80% (70%) modulation depth ($\frac{|I_{\mathrm{FWM}}(V_{\mathrm{g}})-I_{\mathrm{FWM}}(0\ \mathrm{V})|}{I_{\mathrm{FWM}}(0\ \mathrm{V})}$) when FWM is resonant at A(B)-excitonic states with V_{g} tuning from 0 to 3 V. As a comparison, for the FWM at 700 nm (*i.e.*, λ_1 at 800 nm and λ_2 at 920 nm), which is off excitonic resonance, gating does not change the FWM intensity (black dots in Figure 2f). This further demonstrates the dominance of the interband excitonic effect on the optical nonlinearity of monolayer TMDs. Note that the FWM remains constant when V_{g} < ~0.4 V, which is due to that the effective electron injection to MoS_2 has a turn-on threshold V_{on} at 0.4 V. This critical V_{on} is also indicated by the transport characteristics of monolayer MoS_2 (Figure 1b).

Gate-control of interband resonant SFG in MoS_2. We also use the home-built femtosecond laser based microscopic system to study SFG in monolayer MoS_2, as described in Methods. The SFG at the sum frequency ($\omega_{\mathrm{SFG}} = \omega_1 + \omega_2$) is generated with the two input light beams at ω_1 and ω_2. In our SFG experiment, pump1 ($\hbar\omega_1$) is fixed at ~1.55 eV (*i.e.*, λ_1 = ~800 nm) and pump2 ($\hbar\omega_2$) is tunable in the near-infrared spectral range from ~1.11 to 1.33 eV (*i.e.*, λ_2 = ~930 – 1120 nm). As a result, wavelength-dependent SFG is achieved from ~2.66 to 2.88 eV (*i.e.*, λ_{SFG} = ~430 – 465 nm) (Figure 3a). We find that SFG is enhanced at around 440 nm, when the generated SFG photon energy (*i.e.*, $\hbar\omega_{\mathrm{SFG}}$ = ~2.82 eV) matches the C-excitonic energy of monolayer MoS_2 (the inset of Figure 3a). The enhancement suggests that interband excitonic transition at C-exciton significantly contributes to the enhanced SFG process. The power dependent SFG signals are examined (Figure 3b). The peak intensities of the SFG spectra scale linearly with pump1 power P_1

(while pump2 power P_2 = ~1 μW) and P_2 (while P_1 = ~1 μW), respectively, following the linear power law behavior of SFG.

We also study the gate-tunable SFG of MoS_2 with interband C-excitonic resonance. The peak intensities of the resonant SFG at 440 nm decrease with increased electrostatic doping (Figure 3c), showing a nearly 60% modulation depth ($\frac{|I_{SFG}(V_g)-I_{SFG}(0\ V)|}{I_{SFG}(0\ V)}$) at V_g = 3 V, where $I_{SFG}(V_g)$ is the peak intensity of SFG at V_g. This demonstrates gate-tunability of the SFG process in monolayer MoS_2.

Gate-tunable nonlinear optical coefficients. We have realized the tunability of nonlinear optical signals, which arises from the strong excitonic charging effects in monolayer MoS_2, allowing for exceptional control over the oscillator strengths at the excitonic resonances. Based on the measured tunable FWM and SFG intensities, we can estimate the tunability of nonlinear coefficients of MoS_2. The second- and third-order nonlinear coefficients $\chi^{(2)}$ and $\chi^{(3)}$ are calculated from the measured average powers of the incident light and the generated nonlinear optical signals as follows,[35]

$$\left|\chi^{(2)}\right| = \frac{8n_s c}{\alpha_S \omega_S}\sqrt{\frac{\varphi f \tau_1 \tau_2 {D_1}^2 {D_2}^2 n_1 n_2 \varepsilon_0 c P_S}{\tau_S {D_S}^2 n_S P_1 P_2}}, \quad (1)$$

$$\left|\chi^{(3)}\right| = \frac{8n_F c}{\alpha_F \omega_F}\frac{\varphi f \tau_1 {D_1}^2 n_1 \varepsilon_0 c}{P_1}\sqrt{\frac{\tau_2 {D_2}^2 n_2 P_F}{\tau_F {D_F}^2 n_F P_2}}, \quad (2)$$

where $P_{(1,2,S,F)}$ are the average powers of the two incident pump beams and generated SFG/FWM signals, and f = 2 kHz is the repetition rate, and $\tau_{(1,2,S,F)}$ = ~230 fs is the estimated pulse duration of pump light beams and SFG/FWM signals, and $D_{(1,2,S,F)}$ = ~2.5 μm is the diameter of the Gaussian spatial profile on the sample, and $n_{(1,2,S,F)}$ = ~4.2 is refractive index of the material at the pump light frequencies and SFG/FWM frequencies[25], and α_S = 2 for two-color SFG process, α_F = 3 for two-color FWM process, and $\varphi = (\pi/\ln 2)^{3/2}/8$. Therefore, the effective bulk-like second- and third-order nonlinear coefficients of monolayer MoS_2

($\chi^{(2)}_{eff}$, $\chi^{(3)}_{eff}$) can be obtained, $\chi^{(2)}_{eff} = \chi^{(2)}/t$ and $\chi^{(3)}_{eff} = \chi^{(3)}/t$, where t = ~0.7 nm is the thickness of monolayer MoS_2. The detailed calibration and calculation method are discussed in Supporting Information. The typical average power of two pump light beams is ~1 μW for each light beam. When the gate voltage varies from 0 to 3 V, corresponding to carrier density change from 0 to ~4×10^{13} /cm^2, the SFG signal at C-exciton is changing from ~2.5 to 1.0 pW, and the FWM signal is changing from ~0.14 to 0.029 pW at A-exciton, and from ~0.093 to 0.028 pW at B-exciton. Therefore, we obtain the gate-tunable $|\chi^{(2)}_{eff}|$ and $|\chi^{(3)}_{eff}|$ of monolayer MoS_2, as shown in Figure 4. The tunability of $|\chi^{(3)}_{eff}|$ changes from ~12.0 – 5.45 × 10^{-18} m^2/V^2 at interband A-excitonic resonance (~9.16 – 5.03 × 10^{-18} m^2/V^2 at interband B-excitonic resonance) as a function of doping carrier density (Figure 4a). Similarly, the tunability of $|\chi^{(2)}_{eff}|$ with interband C-exciton resonance at 440 nm changes from ~11.6 – 7.40 × 10^{-9} m/V with varying the doping carrier density (Figure 4b).

The calculated second and third-order nonlinear coefficients $|\chi^{(2)}_{eff}|$ and $|\chi^{(3)}_{eff}|$ are of the order of 10^{-9} m/V and 10^{-18} m^2/V^2, which are in the same range of previously reported work (*e.g.*, $|\chi^{(2)}_{eff}|$ = ~5×10^{-9} m/V in Ref. 36; $|\chi^{(3)}_{eff}|$ = ~10^{-17}–10^{-19} m^2/V^2 in Ref. 12). Besides the electrical tunability, different approaches have been developed to tune nonlinear optical responses of TMDs. For example, strain[37, 38] and plasmonic antenna[39] induced tunability of nonlinear optical response has been studied in TMDs (fully discussed in Supporting Information). For further improvement, integrating monolayer MoS_2 with waveguides,[40] optical fibers,[41] or optical cavities[31] will enhance light-matter interactions for higher light conversion efficiency. Besides, gate-tunable optical nonlinearity at low temperature offers the possibility for higher tunability and better understanding of the underlying physics.[26]

CONCLUSIONS

To conclude, the interband excitonic resonance of FWM and SFG is investigated in ion-gel gated monolayer MoS_2 at room temperature. The gate-tunable interband excitonic FWM and SFG are demonstrated by electrostatic doping, which originates from the modulation of oscillator strength of interband excitonic resonances. For interband resonant FWM, $|\chi^{(3)}_{eff}|$ of monolayer MoS_2 changes from ~12.0 – 5.45 × 10^{-18} m^2/V^2 at A-exciton (650 nm), and from ~9.16 – 5.03 × 10^{-18} m^2/V^2 at B-exciton (610 nm). Similarly, the tunability of $|\chi^{(2)}_{eff}|$ with interband C-exciton resonance at 440 nm is tuned from ~11.6 – 7.40 × 10^{-9} m/V with gate voltage varying from 0 to 3 V. Note that the similar nonlinear optical tunability is anticipated to other TMDs (*e.g.*, WS_2). Therefore, our study is promising for electrically-controlled NLO devices based on two-dimensional layered materials (*e.g.*, tunable saturable absorbers,[42] on-chip nonlinear optics[43]), extending the versatility of modern photonic systems.

METHODS

MoS_2 device fabrication. The monolayer MoS_2 is grown on a SiO_2/Si substrate by CVD method.[44] The source, drain and gate electrodes were first patterned using electron-beam lithography (Vistec) and then deposited with Ti/Au (5/50 nm) using electron-beam evaporation. All the electrodes were wire-bonded to a chip for electrical control. Ion-gel was spin-coated uniformly on the MoS_2 device. The ion-gel solution was prepared by dissolving 22 mg of poly(styrene)-*b*-poly(ethylene oxide)-*b*-poly(styrene) (PS-PEO-PS) and 0.56 g of ion liquid ([EMIM][TFSI]) in 20 ml of anhydrous dichloromethane.[32] The ion liquid and dry dichloromethane were purchased from Sigma Aldrich, and PS-PEO-PS was purchased from Polymer Source.

Nonlinear optical spectra measurement. A home-built femtosecond laser based microscopic system is employed for the nonlinear optical sexperiments. The schematic of this system is shown in Figure S3a in Supporting Information. Two incident light beams, with

different frequencies, are linearly polarized with polarization directions parallel with each other. Their typical spectra are shown in Supporting Information Figure S3b. The pulse duration of the incident pulses is ~230 fs, which is estimated by the cross-correlation measurement (Figure S3c in Supporting Information). The pulses of the two pump light beams are spatially and temporally overlapped, focused collinearly on the sample and generate the nonlinear optical signals in the monolayer MoS_2 film. The spectra of nonlinear optical signals are detected by a spectrometer (Andor, Hamamatsu) in the reflection configuration. The nonlinear optical signals of the monolayer MoS_2 were measured under different gate voltages. Note that when different source-drain voltages were applied, no change was observed in nonlinear optical signals. Therefore, to fully exclude electric current-induced nonlinear optical effects (*e.g.*, current-induced second-order nonlinearity[45]), we only apply gate voltage and ground source and drain electrodes (*i.e.*, no source-drain current) in our experiments.

ASSOCIATED CONTENT

Supporting Information. MoS_2 film characterization, gate-tunable electrical and linear optical properties of monolayer MoS_2, FWM and SFG experiment setup and spectra of pump light, nonlinear optical spectra in monolayer MoS_2, the repeatable gate-tunable FWM, gate-tunable SFG spectra with excitonic resonance and off-resonance, calculation of nonlinear coefficients for SFG and FWM signals in MoS_2, and wavelength-dependent third-order nonlinear coefficients of monolayer MoS_2, comparison among different tuning approaches

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Y.D. and Z.S. conceived the idea. Y. D. performed the measurements with assistance from Y. W., S. D., H. X., X. B., and E. H. on the device preparation and gate-tunable optical measurements. G. Z., X. Y., and Q. D. provided the CVD-grown MoS_2 sample. Y. D. analysed 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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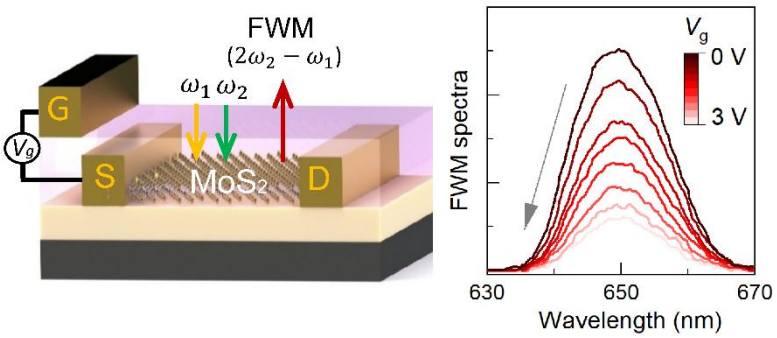
SYNOPSIS TOC



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