Two-Photon Absorption towards Pulse Modulation in Mechanically Exfoliated and CVD Monolayer Cascaded MoS₂ Structures

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Mechanically exfoliated (ME) and chemical vapor deposition (CVD) MoS₂ monolayers have been extensively studied, but the large differences of nonlinear optical performance between them have never been clarified. Here, we prepared MoS₂ monolayers using ME and CVD methods and investigated the two-photon absorption (TPA) response and its saturation. We found TPA coefficient of ME monolayer was about $(1.88 \pm 0.21) \times 10^3$ cm/GW, nearly two times of CVD one, $(1.04 \pm 0.15) \times 10^3$ cm/GW. Furthermore, we simulated and compared the TPA-induced optical pulse modulation in multilayer cascaded structures, which is instructive and meaningful for the design of optical devices such as beam shaper, optical limiter.

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The atomically thin semiconducting transition metal dichalcogenides (TMDs) exhibit remarkable nonlinear optical (NLO) properties including layer-dependent second/third harmonic generation [1], two/multi-photon absorption [2-4], ultrafast saturable absorption [5-9], *etc.*, which have been widely applied in two-dimensional (2D) photonics and optoelectronic devices [10-12]. Especially for 2D MoS₂, researchers have made great effort to prepare large area monolayer and few-layer films with distinct NLO properties using chemical vapor deposition (CVD), mechanical exfoliation (ME) and liquid phase exfoliation (LPE) methods. However, samples prepared by different methods show distinct optical performance. Taking the second harmonic generation (SHG) as an example, the ME monolayer MoS₂ ($\chi^{(2)} \approx 10^{-7}$ m/V) exhibits much stronger second-order nonlinear optical response than the CVD one ($\chi^{(2)} \approx 10^{-9}$ m/V) [13,14]. In terms of nonlinear absorption, the ME MoS₂ is greatly different from the CVD and LPE ones, which is reflected in practical mode-locking and Q-switching devices [15-17]. As a result, it is crucial for optical device applications to reveal the intrinsic optical properties of 2D TMDs prepared by different methods. As is well known, in the TMDs MX₂ ($M = \text{Mo}$ and W ; $X = \text{S}$, Se , and Te), various types of defects, e.g., X vacancy, X

interstitial, M vacancy, M interstitial, and MX and XX double vacancies, have been considered [18-20]. However, it still remains obscure how the defects affect the NLO properties of as-prepared MoS₂ nanosheets.

Here, we choose CVD and ME MoS₂ monolayers, typical TMDs with superior nonlinear optical properties, and make a comparative study of the two-photon absorption (TPA) using a modified micro-intensity scan system. We found that the TPA coefficients of the two samples differed by nearly two times, which is ascribed to the large difference of the defect concentration between them [18-21]. In view of the huge advantages of MoS₂ in applications of pulse shaping and optical limiting due to its giant TPA coefficient, we simulated and compared the TPA-induced pulse modulation between CVD and ME monolayer cascaded structures.

Monolayer MoS₂ nanosheets were prepared onto transparent quartz using mechanical exfoliation from natural crystal [22] and CVD method [23], respectively. All these samples were preliminarily identified by the optical microscope. As shown in Fig. 1(a) and (c), the side length of the samples was determined to be ~ 50 μm . The thickness and surface morphology were measured using the atomic force microscopy, as shown in Figs. 1(b) and (d). The thickness of the ME monolayer is ~ 1.1 nm, and is slightly larger than that

in general, which should be caused by the air gap between the sample and the substrate, while the thickness of CVD monolayer is ~ 0.7 nm.

Raman spectroscopy has been identified as a convincing tool to determine the crystal structure of 2D MoS₂ nanosheets [24,25]. In this work, Raman spectroscopy measurements were conducted by using a confocal microscopy system combining with a diode laser at 532 nm. The Raman peak interval between two active vibration modes, E_{2g}¹ and A_{1g}, is ~ 17.99 cm⁻¹ and ~ 19.87 cm⁻¹ for CVD and ME monolayers, respectively. **Figure 1(e) shows the broadening of two Raman peaks in CVD monolayer, indicating that defects have made an impact on the crystal structure [26,27].** In addition, the two Raman vibration modes give a strong proof that all the samples used in our work are 2H-MoS₂ [28].

Under the same excitation, we acquired the steady photoluminescence (PL) spectra of ME and CVD monolayer MoS₂. It is obvious that the ME monolayer exhibited much stronger PL intensity than CVD one, as shown in Fig. 1(f). The PL quenching in CVD monolayer indicates that the defect-assisted non-radiative transition plays an important role in it [29,30]. In addition, the PL lifetime was measured using a streak camera (*Optronis*). The samples were excited by the ultrafast laser with the pulse width of 120 fs at the wavelength of 600 nm and repetition rate of 80 MHz. **As Figs. 1(g) and (h) show, the CVD monolayer exhibited much faster and weaker excitonic emission than the ME one, which is exponentially fitted (SI, Fig. S1).** It can be ascribed to stronger defect-assisted Auger scattering, leading to fast exciton annihilation and non-radiative electron-hole recombination [31].

Fig. 1. (a)-(d) Optical microscope and AFM characterization of both CVD and ME MoS₂ monolayers. (e) Raman spectra imply that there are much more defects in CVD MoS₂ monolayer than that in ME one. (f) Steady photoluminescence spectra were measured, and strong PL

quenching was observed in CVD monolayer. (g), (h) The PL lifetime of A exciton in CVD and ME monolayer was measured using a streak camera.

In this work, TPA processes in monolayer MoS₂ were investigated at room temperature (~ 300 K) with a modified micro-intensity scan system as illustrated in Fig. 2 [3,32]. The 350 fs laser pulses at 1030 nm (~ 1.2 eV) were generated from a mode-locked fiber laser (1 kHz) and attenuated with an electrically tunable neutral density filter. The laser beam was finally focused with a waist radius ω_0 of ~ 5 μ m on the surface of MoS₂ using an f/35 mm lens. Herein, the excitation source with photon energy of 1.2 eV was chosen to generate good resonant interaction with monolayer MoS₂ through distinct two-photon process due to the existence of dark excitonic states [33-35].

Fig. 2. Schematic diagram about the setup of micro-intensity scan.

Here, absorption process can be analyzed using the propagation equation [32,36]:

$$\frac{dI(z)}{dz} = -\alpha I - \beta(I)I^2(z), \quad (1)$$

where z is the propagation distance in the sample. α is the coefficient of one-photon absorption, which is negligible owing to the smaller value of the photon energy of 1.2 eV than the optical bandgap. $\beta(I)$, the two-photon absorption coefficient, is dependent on the incident laser intensity. In our experiment, the excitation source was a series of Gaussian pulses in time and space, that is

$$I(r, t) = I_0 \cdot \exp(-2r^2/w_p^2) \cdot \exp(-t^2/\tau_0^2). \quad (2)$$

Here, w_p and τ_0 represent the radius of the pump beam waist and the half pulse width, respectively.

The effective TPA coefficient can be obtained quantitatively using a homogeneously broadened two-band theory [37-39]:

$$\beta_{\text{eff}}(I) = \frac{\beta_0}{1 + (I/I_{\text{sat}})^2}, \quad (3)$$

where $\beta_0 = \sigma_{\text{TPA}} \frac{g_2}{g_1} N_0$, N_0 is the concentration of absorber (*i.e.* MoS₂ molecular density, in units of cm⁻³). In an ideal monolayer MoS₂ crystalline, N_0 is estimated to be $\sim 1.8 \times 10^{22}$ cm⁻³. σ_{TPA} is the TPA cross

section, $g_2(g_1)$ is the electronic degeneracy of the upper (lower) state. The TPA-active excitons are sixfold degenerate, which corresponds to the three degenerate $2p$ states in a 2D hydrogen model, multiplied by the two valleys of K and K' points in the Brillouin zone, so that $\frac{g_2}{g_1}$ equals to 6 in Eq. (4) [40].

Fig. 3. (a) Schematic structures of monolayer MoS₂ and vacancies in it. SV: sulfur vacancy; MoV: molybdenum vacancy. (b) Energy levels in CVD and ME MoS₂, optical transition and defect-induced fast carrier capture processes (TPA: two-photon absorption; OPA: one-photon absorption. (c) Nonlinear transmittance versus incident pulse peak irradiance for MoS₂ monolayers. The solid lines are the fitting results obtained by numerically solving Eq. (1). (Inset: the values of TPA coefficient and corresponding saturation intensity)

Based on above theories, the TPA coefficient are acquired and shown in Fig. 3(c). The ME monolayer exhibits much larger TPA coefficient of $(1.88 \pm 0.21) \times 10^3$ cm/GW than the CVD one of $(1.04 \pm 0.15) \times 10^3$ cm/GW. The TPA process in MoS₂ during the pulse duration time ($\tau_p = 350$ fs) is illustrated in Fig. 3(b), where an electron transition from the energy level E_0 to E_2 via absorbing two degenerate photons instantaneously. According to the selection rule, E_2 represents the $2p$ dark excitonic state here. Then, the excited excitons relax to E_1 through an electron-electron scattering process in less than 60 fs [41,42]. The detailed carrier dynamics of TPA process are simulated in the SI, and schematically shown in Fig. S2. The mid-gap defect states will decrease the TPA coefficients as defect-induced one-photon absorption in CVD monolayer may play some role [21].

The saturation intensity I_{sat} obtained in the micro-intensity scan experiment based on Eqns. (1) and (3), as shown in the inset of Fig. 3(c), can be deduced theoretically. In the homogeneously broadened model, the saturation intensity can be expressed as [37,38]:

$$I_{\text{sat}} = \sqrt{\frac{2\hbar\omega}{\tau_p \sigma_{\text{TPA}} \left(1 + \frac{g_2}{g_1}\right)}}, \quad (4)$$

where τ_p is the full width at half maximum of the femtosecond laser pulse ($\tau_p = 350$ fs). Therefore, with the TPA cross section σ_{TPA} obtained from

$$\sigma_{\text{TPA}} = \frac{\beta_0}{N_0} \frac{g_1}{g_2},$$

the saturation intensity of ME monolayer

MoS₂ can be calculated as ~ 128 GW/cm², while the value of our experimental fitting result is ~ 146 GW/cm² according to Eqns. (1) and (3). Likewise, the calculated value for the I_{sat} of CVD-grown monolayer is ~ 172 GW/cm², which is comparable with the fitting value of ~ 217 GW/cm². The estimation of the saturation intensity is in the same order of magnitude with the experimental fitting results for both CVD and ME monolayers, implying that our fitting is reasonable. **The saturation intensity of TPA is larger than that of monolayer WS₂ (~ 26 GW/cm²) [2].** Our results indicate that it is more difficult for CVD monolayer MoS₂ to be saturated in the TPA process than ME one.

Fig. 4. (a, b) Differential intensity ($\Delta I/I_0$) distribution of the output pulse under the same excitation intensity of 300 GW/cm² in 1L, 50L and 100L CVD and ME MoS₂, respectively. (c) Optical limiting performance.

The TPA coefficient of monolayer MoS₂ is 3~4 orders of magnitude larger than many common semiconductors like ZnO, GaAs [43,44]. In view of this

giant advantage, it possesses great potential in optical pulse modulation and optical limiting applications. Therefore, it is necessary and interesting to examine the difference between CVD and ME MoS₂. In this part, we simulated the way how TPA saturation effect modulates the optical pulse in CVD and ME monolayer and made a comparison with a cascaded multilayer structure.

The spatial intensity distribution of femtosecond pulses we used is of Gaussian profile with a waist radius of $\omega_0 \approx 5 \mu\text{m}$, the same as the experiment. Considering that the value of β changes with pulse intensity according to the homogeneously broadened model, the TPA coefficient will not be a constant in the radial direction of a laser spot. This means that the differential transmission intensity $\Delta I/I_0$ at different radial positions in the spot will change. The differential intensity reflects the spatial modulation ability of the MoS₂ nanofilms. However, the ultrashort interaction length in the monolayer is detrimental to the modulator design. As a result, a simple solution to this problem is to put a series of MoS₂ monolayers cascading [45], and the simulated results are demonstrated in Fig. 4. Figure 4(a) depicts the resulting $\Delta I/I_0$ distribution when a pulse passes through the 1L, 50L and 100L CVD and ME MoS₂, respectively, under the same excitation of 300 GW/cm². We can see that in CVD-1L case, TPA saturation effect is not large enough and the central area shows an intensive absorption. But in ME-1L case, the TPA is remarkably saturated and the absorption decreases, which results in the darker spot in Fig. 4(a). In a cascaded structure, the transmitted intensity decreases layer by layer making the TPA saturation insignificant. Therefore, a more uniform absorption can be seen in the multi-layer systems and the largest pulse intensity differential will move from the margin of the spot to the center. From Fig. 4(b), it can be seen that the stronger TPA effect in ME cascaded structure results in greater pulse modulation amplitude with the increasing of layers. Furthermore, Figure 4(c) shows the optical limiting performance of both CVD and ME cascaded structures, which directly reveals the difference these two systems. In conclusion, according to the simulation results, due to larger TPA coefficient, the ME MoS₂ monolayer and the cascaded structure exhibit better optical pulse modulation and optical limiting performance compared to CVD ones.

In summary, monolayer MoS₂ nanosheets have been prepared by ME and CVD methods. We studied the difference of degenerate TPA effect between them. The TPA coefficient of the CVD monolayer is only about one half of that of the ME one, mainly due to the one-photon absorption induced by midgap defect states. Furthermore, we simulated and compared the pulse

modulation performance between CVD and ME cascaded monolayer structures. It can provide meaningful guides for the design of optical devices like beam shaper, optical limiters, *etc.*

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172x128mm (300 x 300 DPI)

Fig. 2. Schematic diagram about the setup of micro-intensity scan.

42x16mm (300 x 300 DPI)

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Fig. 4. (a, b) Differential intensity ($\Delta I/I_0$) distribution of the output pulse under the same excitation intensity of 300 GW/cm² in 1L, 50L and 100L CVD and ME MoS₂, respectively. (c) Optical limiting performance.

Supporting Information

The PL lifetime was measured using a streak camera (*Optronis*). The samples were excited by the ultrafast laser with the pulse width of 120 fs at the wavelength of 600 nm and repetition rate of 80 MHz. Figs. 1(g) and (h) show the time-resolved PL for CVD and ME monolayer MoS₂, respectively. It is obvious that the PL intensity is much lower with shorter lifetime for CVD monolayer. By comparison, we fitted the PL decay time at ~ 1.88 eV (A exciton position) with double exponential model, where the PL efficiency is strongest due to the resonant emission. As shown in Fig. S1, the fast decay for exciton emission in CVD-grown monolayer is ~ 14 ps, which is much shorter than that in ME one (~ 27 ps). The slow decay time scale is up to hundreds of picoseconds and agrees with pump probe measurements (refer to Ref. 40–42 in the main text). As discussed in previous study, the fast decay process in monolayer MoS₂ was ascribed to fast capture of electrons and holes by defects *via* Auger processes due to strong Coulomb interaction and large exciton binding energy in 2D TMDs. In addition, the PL intensity and decay time should make a difference at different excitation energies owing to the change of the EEA rate at different density of carriers. Therefore, the excitation energy remains the same for both CVD and ME monolayer MoS₂. Basically, the Auger process can be understood as that an electron (in the valence band) scatters off a hole (in the conduction band), and the electron is captured by a mid-gap defect level and the hole takes the energy released in the electron capture process, which greatly shortens the exciton radiation time and quenches the PL.

Fig. S1. Time-resolved PL signal at the position of A exciton (~ 1.88 eV) with double exponential fitting.

The TPA process in MoS₂ during the pulse duration time ($\tau_p = 350$ fs) is illustrated in Fig. 3(b), where an electron absorbs two degenerate photons instantaneously *via* transition from the energy level E_0 to E_2 . According to the transition selection rule, E_2 represents the $2p$ dark excitonic state here. Then, the excited excitons relax to E_1 through an electron-electron scattering process in less than $\tau_{21} \approx 60$ fs. Subsequently, as we observed in the ultrafast time-resolved PL measurements, photoexcited excitons in monolayer will decay in a fast defect assisted non-radiative Auger process with lifetime τ_{10} of 27 ps for ME and 14 ps for CVD. The slow decay time contributes little to the ultrafast TPA saturation and can be neglected. It is worth noting that the exciton-exciton annihilation (EEA) would dominate the relaxation channel at the carrier concentration larger than $10^9 \sim 10^{10}$ cm⁻² in TMD monolayers. In consequence, the above processes can be described by the equations:

Supporting Information

$$\begin{cases} \frac{dn_2(t)}{dt} = \frac{\sigma I(t)^2}{2h\omega} (n_0(t) - n_2(t)) - \frac{n_2(t)}{\tau_{21}} \\ \frac{dn_1(t)}{dt} = \frac{n_2(t)}{\tau_{21}} - \frac{n_1(t)}{\tau_{10}} - kn_1^2(t) \end{cases} \quad (S1),$$

where $n_0(t)$, $n_1(t)$, and $n_2(t)$ are the areal density (cm^{-2} in unit) of electrons in the E_0 state, 1s excitons in the E_1 state, and two-photon excited excitons in the E_2 state, respectively. σ is the TPA cross section that can be deduced from $\sigma = \beta d / N_0'$, where $N_0' = n_0 + n_1 + n_2$ represents the total population areal density in the three energy levels, and d is the layer thickness. In the simulation, we assume N_0' equals $1 \times 10^{15} \text{ cm}^{-2}$, which is derived from the bulk carrier density of 10^{22} cm^{-3} in our previous paper assuming the MoS_2 is a flawless crystal. k is the EEA rate with a value of $0.043 \text{ cm}^2/\text{s}$. Here, the contributions of defects stem from introducing the term $kn_1^2(t)$ and taking the difference of τ_{10} between CVD and ME monolayer into consideration. The pulse intensity distribution obeys a temporal Gaussian profile (Fig. S2, gray solid line), and I_0 is the incident pulse intensity. Using Eq. (S1), we simulated the variation of n_0 , n_1 , and n_2 versus decay time during the TPA process under three excitation pulse intensities of 20 GW/cm^2 ($< I_{\text{sat}}$), 125 GW/cm^2 ($\sim I_{\text{sat}}$ of ME), and 300 GW/cm^2 ($> I_{\text{sat}}$ of both CVD and ME) for monolayer MoS_2 . As depicted in Fig. S2(a) and (d), for ME monolayer, the depletion of the electron population (blue curve) in the ground state (E_0) is stronger than that of CVD one. Due to fast relaxation rate of excitons in the high energy level ($E_2 \rightarrow E_1$) and EEA, as well as slow recombination process of the 1s excitons ($E_1 \rightarrow \text{defect states} \rightarrow E_0$), the TPA saturation occurs first for ME monolayer when intensity gradually increases to 125 GW/cm^2 , indicated by the appearing of the flat bottom in Fig. S2(e). From the dynamic simulation, we can see that the CVD monolayer is harder to be saturated in the TPA process, which is consistent with its larger saturation intensity.

Fig. S2. Evolution of the population of electrons in the ground state (n_0), the photoexcited carriers in the E_2 state (n_2), and carriers in E_1 (n_1) with a time delay under excitation of 20, 125, and 300 GW/cm^2 , respectively. N_0' was set to $1 \times 10^{15} \text{ cm}^{-2}$. The gray line shows the Gaussian profile of the excitation pulse.