Ultrafast Exciton Dynamics in Scalable Monolayer MoS₂ Synthesized by Metal Sulfurization

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ABSTRACT: Excitons in monolayer transition metal dichalcogenides (TMDs) have exceptionally large binding energies and dominate the optical properties of materials. Exploring the relaxation behavior of excitons is crucial for understanding the fundamental physics as well as the performance of TMD-based optoelectronic devices. However, ultrafast carrier dynamics is sensitive to the structural defects and surface conditions of TMDs, depending on the growth or transfer process. Here, we utilized pump-probe transient absorption (TA) spectroscopy with a white-light probe to investigate the dynamics of excitons in monolayer MoS₂ synthesized by the metal sulfurization method. The sulfurization method was used for the fabrication of large-scale, continuous, and uniform thin films with a controllable number of layers. The excitation dynamics of the wafer-size monolayer MoS₂ is found to be comparable to that of monolayer MoS₂ flakes grown by chemical vapor deposition (CVD). The dominant processes of carrier relaxation in the monolayer MoS₂ are exciton−exciton annihilation (hundreds of femtoseconds), the trapping of the excitons by surface states (a few picoseconds), and interband carrier-phonon scattering (tens of picoseconds). Moreover, the induced absorption due to mid-gap defects, which is often observed for samples fabricated by growth methods, such as CVD, is not observed for our continuous and uniform monolayer films. Understanding the charge carrier dynamics of the exciton in the scalable and uniform monolayer MoS₂ can provide physical insights that are valuable in the design and development of complex 2D devices.

INTRODUCTION

Transition metal dichalcogenides (TMDs) are layered structures constructed by stacking monolayers via interlayer van der Waals forces. It has recently been reported that semiconducting TMDs possess bandgap transition from indirect to direct as the monolayer was formed. The photoexcited electron−hole pairs bound by electrostatic Coulomb forces, so-called excitons, are confined to monolayer TMDs and dominate the optical properties of materials. In particular, the exciton binding energy of monolayer TMDs (0.3−0.7 eV) is exceptionally large, meaning that the excitons in monolayer TMDs are more stable at room temperature than those in conventional bulk semiconductors. Besides, the exciton fine structure in monolayer TMDs is attributed to strong spin-orbit coupling, broken inversion symmetry, and quantum confinement effects. As a result, there have been extensive studies on the exciton dynamics in MoS₂, pioneering a new family of 2D materials beyond graphene. Photoexcited carriers in monolayer MoS₂ are distributed nonthermally in the electronic bands and then undergo thermalization and cooling processes before the formation of excitons. Hence, a fundamental understanding of the exciton dynamics in TMDs is important. The excitons in monolayer MoS₂ could be categorized into three types, as shown in Figure 1. The band

Figure 1. (a) Illustration of A and B excitons in the band structure of the MoS₂ monolayer. Eᵥ: direct bandgap; Eₓ: exciton binding energy; Eᵥ−A: optical transition of the A exciton; Eᵥ−B: optical transition of the B exciton; Δ: spin-orbit splitting. (b) Illustration of the C exciton in the band structure of the MoS₂ monolayer. Eᵥ−C: optical transition of the C exciton.

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structure of monolayer MoS$_2$ at the K point in the Brillouin zone with the direct electronic bandgap ($E_g$) is illustrated in Figure 1a. The valence band splitting ($\Delta$) induced by spin-orbit coupling results in two types of excitons, so-called A and B excitons. The optical transition energies of A ($E_A$) and B ($E_B$) excitons correspond to the photoluminescence (PL) peak positions of monolayer MoS$_2$.\textsuperscript{10} Therefore, the exciton binding energy ($E_b$) can be expressed as $E_b = E_g - E_A$ or $E_b = E_g - (E_B - \Delta)$, as shown in Figure 1a. In addition, the C exciton is created from the band-nes ting region, where the slope of the conduction band is parallel to that of the valence band, as shown in Figure 1b.\textsuperscript{11}

A detailed relaxation process in monolayer and bulk MoS$_2$ was announced by Shi et al. in 2013.\textsuperscript{12} The intraband relaxation in bulk MoS$_2$ is dominated by both carrier–carrier and carrier–phonon scattering, while in monolayer MoS$_2$ is dominated by defect-assisted scattering. The interband relaxation processes in monolayer MoS$_2$ are much shorter than those in bulk MoS$_2$. This suggests that nonradiative relaxation processes rather than radiative ones dominate the exciton dynamics in monolayer MoS$_2$. In addition, the carrier lifetime of MoS$_2$ increases with the number of layers since the defect-assisted recombination at the surface becomes significant as the thickness is reduced.\textsuperscript{13} There are two carrier transport modes, hot-carrier diffusion and band-edge carrier transport, in monolayer MoS$_2$. The former is the transport mode of the C exciton, and the latter is that of the A/B exciton.\textsuperscript{14} Although many studies concerning this topic have been conducted, the MoS$_2$ used in these studies was mostly obtained by either exfoliation from the bulk or chemical vapor deposition (CVD). The thickness and area of exfoliated MoS$_2$ cannot be precisely controlled. The optical microscopy (OM) and/or atomic force microscopy (AFM) images of MoS$_2$ triangular flakes obtained by CVD growth indicate that the MoS$_2$ films are non-continuous, even if the dimension is larger than 100 $\mu$m. The noncontinuous film limits real applications in the semiconductor industry.\textsuperscript{15} In this report, the exciton dynamics in monolayer MoS$_2$ synthesized by metal sulfurization,\textsuperscript{16} achieving large-scale, continuous, and uniform MoS$_2$ thin films with controllable numbers of layers, is investigated and discussed. The metal sulfurization method is advantageous in the construction of large-scale vertical heterojunctions of TMDs.\textsuperscript{17} In order to further investigate the interlayer exciton (moire exciton) in the 2D layer-by-layer heterostructure and design MoS$_2$ optoelectronic devices in the future, it is important to first comprehend the relaxation mechanism of electron–hole pairs in monolayer MoS$_2$.

### RESULTS AND DISCUSSION

Mo thin films with particular thicknesses were first deposited on double-side polished sapphire wafers using a radio-frequency (RF) sputtering system. Then, sulfur powder was used to sulfurize the Mo films into MoS$_2$ layers at 800 $^\circ$C. For the bilayer, the layer removal procedure was conducted using oxygen plasma under 0.4 Torr to obtain monolayer MoS$_2$. After water dipping, sulfurization was implemented again to resulfurize the partially oxidized MoS$_2$ monolayer. More details are provided in studies by Chen and Wu et al.\textsuperscript{16,17} A transmission electron microscope (TEM, FEI Tecnai G2 F20) with an accelerating voltage of 200 kV was used to monitor the nanoscale layer structure. A spectrometer (HORIBA, LabRAM, HR800 UV) with a laser of 488 nm wavelength and 60 mW power was employed for Raman analysis to initially check the crystal quality of the MoS$_2$ layers. The PL spectra were obtained by switching the mode from Raman to PL in the same spectrometer. The UV–Vis absorption spectra were measured using a spectrometer (JASCO V-670). Pump-probe transient absorption measurements to analyze the exciton dynamics in monolayer MoS$_2$ synthesized by metal sulfurization were performed using a commercial transient absorption spectrometer (FemtoFrame II, IB Photonics). The instrument response function (IRF) was determined using a laser system and the spectrum shows a FWHM of 1.5 times longer than the pump pulse width. The excitation source was a 400 nm pulsed laser with a pulsed duration of 100 fs and a repetition rate of 1 kHz, which was generated from a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami) with an optical parametric amplifier (OPA, TOPAS-C, Light Conversion) system. The pulsed laser bandwidth was 100 fs, and the focal spot sizes of the pump and probe beams were $\sim 7 \times 10^{-4}$ and $\sim 1.6 \times 10^{-4}$ cm$^2$, respectively. The pump laser beam with a wavelength of 400 nm was produced using an OPA system, while a broadband (450–800 nm) white-light probe beam with a pulse width of 30 fs was generated via supercontinuum generation from a thick sapphire plate with a thickness of 2–3 mm by focusing the 1 kHz Ti:Sapphire amplified laser (Spitfire, Spectra Physics). The pump densities were within $\sim 25–205 \mu J/cm^2$. All of the optical measurements were performed at room temperature.

The crystallinity of the MoS$_2$ layers was first inspected by Raman analysis before an in-depth investigation of carrier dynamics. To confirm the uniformity of the MoS$_2$ film prepared by using this growth technique, large-area Raman measurements were performed over the sample area, and almost identical Raman peaks were observed on different locations of the MoS$_2$ film.\textsuperscript{16} The results reveal that the prepared MoS$_2$ samples exhibit good large-scale uniformity. Figure 2a shows the Raman spectra of the MoS$_2$ layers synthesized by sulfurization of the sputtered Mo films with different thicknesses.\textsuperscript{16,17} The Raman bands of MoS$_2$, which resulted from the lattice vibration modes, were located at $\sim$384 and 408 cm$^{-1}$. As can be seen in the inset of Figure 2a, the $E_{2g}$ and $A_{2g}$ peaks correspond to the in-plane and out-of-plane vibration modes in the MoS$_2$ crystal, respectively.\textsuperscript{10,12} The difference in the Raman shift between the two peaks slightly increases as the number of layers increases from 1 to 5. A weak band emerging at $\sim$417 cm$^{-1}$ originated from the sapphire substrate. The continuous monolayer MoS$_2$ on the sapphire can be clearly observed in the TEM image of Figure 2b. According to the results mentioned above, the synthesis method can achieve large-scale, continuous, and uniform MoS$_2$ and can precisely control the number of layers,\textsuperscript{16} as shown in the photograph of Figure 2c.

The room-temperature PL spectrum of monolayer MoS$_2$ in Figure 3a shows an intense peak ($\sim$1.86 eV) and a weaker shoulder ($\sim$2 eV) corresponding to the optical transition energies of A ($E_A$) and B ($E_B$) excitons, respectively,\textsuperscript{14,18} indicating that the energy of valence band splitting, $\Delta$, is 0.14 eV. The intensity of the PL signal was greatly reduced with the increasing layer number because of the direct-to-indirect bandgap transition. The PL enhancement is close to 600% as the number of layers decreases from 3 to 1. The sharp Raman peak appearing close to the position of 1.77 eV comes from the sapphire substrate.\textsuperscript{15} The absorption spectra of 1-, 3-, and 5-layered MoS$_2$ show three respective absorption bands corresponding to A ($\sim$1.88 eV), B ($\sim$2.03 eV), and C
In contrast to the PL spectra, the absorbance increases with the thickness of MoS$_2$ since more photons are absorbed by more molecules. It is noted that the absorption bands of the A and B excitons do not shift significantly with the number of layers but that of the C exciton redshifts with it. This is attributed to the bandgap variations at the K point and band-nesting region as the number of layers changes. According to the band structures of MoS$_2$ with different thicknesses, the bandgap in the band-nesting region slightly decreases with the number of layers, resulting in the redshift of the absorption band of the C exciton. On the other hand, the bandgap at the K point remains nearly the same value independent of the number of layers; hence, the absorption bands of the A and B excitons remain at almost the same position.

In Figure 3b, the pump-probe TA spectra of the MoS$_2$ layers show that there are two bleach features (valleys) representing the two transient absorption signals of the A and B excitons. It is worth noting that the intensity of the PL signal as shown in Figure 3a is greatly enhanced with the decrease of the layer number to the monolayer because of the indirect-to-direct bandgap transition. The corresponding steady-state absorption spectra show that the absorption signal increases with the number of layers, which is because there are more atoms to absorb the incoming light. However, the transient absorption signals of A and B excitons (ground-state bleach features) at a time delay of 0.5 ps for different number of layers in Figure 3b do not show systematic variation within the same order of magnitude ($<10^{-3}$). This can be illustrated by the carrier thermalization, and cooling (energy relaxation) would affect the observed transient absorption signal.

To understand the fundamental charge carrier dynamics in the MoS$_2$ synthesized by a novel metal sulfurization method, we performed pump-probe TA measurements to study the carrier relaxation time in the monolayer MoS$_2$. The pump-probe TA spectra of monolayer MoS$_2$ under different pump energy densities at a delay time of 0.5 ps are shown in Figure 4a. Initially, the photoinduced absorption band ($\sim$1.82 eV) does not vary at low pump energy densities ($\leq$38 $\mu$J/cm$^2$). Then, it remains broader and more intense as the pump energy
density is increased. Another photoinduced absorption band (∼2.4 eV) gradually becomes stronger as the pump energy density increases, probably resulting from the creation of hot carriers.\textsuperscript{14} For the bleach features, the intensity increases (more negative) as the pump energy density increases up to 140 μJ/cm\(^2\). However, if the pump energy density is higher, it starts to decrease (become more positive). It is reasonable that the photoinduced absorption band and bleach features become stronger with the increasing pump energy density since the higher energy excites more free carriers. However, the broadening of the photoinduced absorption band and the reduction of the intensity of bleach features at higher pump energy densities (≥140 μJ/cm\(^2\)) might be caused by the spectral overlap with the stronger excited-state absorption and/ or other signals from new photogenerated transient species.\textsuperscript{24,25} Furthermore, the overall redshift with the pump energy density could be associated with the renormalization of the electronic structure.\textsuperscript{24–26}

Figure 4B shows the delay-time evolution of the pump-probe TA spectra of monolayer MoS\(_2\) at a pump energy density of 42 μJ/cm\(^2\). The blueshift of signals may be induced by the Stark effect as the delay time is increased.\textsuperscript{26,27}

The decay curves of the A and B excitons shown in Figure 5 were fitted using a multieponential decay function,

\[
y = y_0 + \sum_{i=1}^{3} A_i \times \exp\left(\frac{-x}{\tau_i}\right) \times \left(1 - \text{erf}\left(\frac{\sigma^2 - x \times \tau_i}{\sqrt{2} \times \sigma \times \tau_i}\right)\right)
\]

. Here erf (x) is the error function, and the real decay time can be determined along with a parameter σ that corresponds to the instrument response function (IRF). In the fit, the temporal IRF was taken into account (σ ∼150 fs).\textsuperscript{28,29} We observed three different lifetimes corresponding to various carrier relaxation processes for the A and B excitons. The shortest lifetime (τ\(_1\)) is assigned to be the exciton–exciton annihilation.\textsuperscript{14} The intermediate lifetime (τ\(_2\)) belongs to the process concerning the trapping of the excitons by surface states and the long lifetime (τ\(_3\)) is associated with the interband carrier-phonon scattering.\textsuperscript{12} A linear-log plot of the decay curve easily shows the lifetimes (τ\(_1\), τ\(_2\), and τ\(_3\)) in three different timescales (Figure S1). Among these mechanisms, the first two processes belong to the intraband relaxation in which the carriers are not relaxed via the optical transition between conduction and valence bands. In contrast, the last process is interband relaxation leading to carrier recombination via the optical transition between conduction and valence bands. The normalized transient absorption changes for various pump fluences of the A exciton state and B exciton state, revealing nonsystematic variation with pump fluences (Figure S2). This can be illustrated by the high fluences-induced sample damage with fluences exceeding 113 μJ/cm\(^2\). The three time constants (τ\(_1\), τ\(_2\), and τ\(_3\)) of excitons (Table S1), which were obtained by fitting the time decay curves in Figure S2, do not show systematic variation with pump fluences. Although the measured lifetimes stay in reasonable ranges but do not show significant changes with the pump power density under the chosen experimental conditions, this behavior also has been reported in the literature.\textsuperscript{30} There is no strong or systematic variation of time constants with the pump fluence. It is worth noting that the measured carrier relaxation times in monolayer MoS\(_2\) synthesized by sulfurization at a low pump fluence of 42 μJ/cm\(^2\) are reliable (Figure S2). A simple model based on exciton–exciton annihilation was also applied to fit the decay curves within the first 40 ps for obtaining the annihilation rate constants of A (k\(_A\)) and B (k\(_B\)) excitons.\textsuperscript{30} The calculated k\(_A\) and k\(_B\) values are equal to 6.7 × 10\(^{-3}\) and 3.7 × 10\(^{-3}\) cm\(^2\)/s, respectively, and are comparable to those obtained in the study by Sun et al.\textsuperscript{30} It is noted that the carrier relaxation times obtained from this large-scale monolayer MoS\(_2\) possess the characteristics of exciton dynamics similar to literature reports (Table S2). Moreover, induced absorption due to the mid-gap defects,\textsuperscript{31–33} characterized by a faster decay due to electron capture by defects, is not observed for our MoS\(_2\) synthesized by metal sulfuration (Figure S3). This result indicates that the monolayer MoS\(_2\) synthesized by metal sulfuration has better material quality compared to the CVD-grown monolayer MoS\(_2\).

**CONCLUSIONS**

The exciton dynamics in wafer-size, continuous, and uniform monolayer MoS\(_2\) synthesized by metal sulfuration has been studied for the first time. Raman spectra and TEM images reveal that the metal sulfuration-synthesized monolayer MoS\(_2\) films have high uniformity and that the number of layers can be precisely controlled. The exciton fine structure in monolayer MoS\(_2\) obtained in this work is successfully characterized by optical measurements, including PL, UV–Vis absorption, and pump-probe TA spectroscopy. In particular, the carrier dynamics measured by using the pump-probe TA technique has an ultrafast temporal resolution of 150 fs, consistent with the fast exciton dynamics in typical 2D materials. The carrier relaxation processes are exciton–exciton annihilation (hundreds of femtoseconds), the trapping of the excitons (a few picoseconds) by surface states, and interband...
carrier-phonon scattering (tens of picoseconds). In particular, the mid-gap defects induced absorption, which is often observed in the CVD-grown film and is not observed for the continuous and uniform monolayer MoS2 synthesized by metal sulfurization. A fundamental understanding of the charge carrier dynamics in the scalable and uniform monolayer MoS2 synthesized by the metal sulfurization method is important for advancing its applications in high-performance optoelectronic devices based on TMDs.

**ASSOCIATED CONTENT**

1. Supporting Information
   The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00187.

   Detailed analysis of the carrier dynamics (PDF).

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