Abstract: Using ultrafast degenerate pump–probe spectroscopy, we have investigated the ultrafast exciton dynamics of monolayer MoSe2 at different pump fluences. The exciton–exciton annihilation, typically occurring tens of picoseconds after pump excitation, has been found to have a substantial correlation with the initial relaxation process dominated by the defect trapping of excitons. A new exciton–exciton annihilation model has been proposed by introducing a coupling term that accounts for the initial relaxation contribution. This coupling term can be tuned by varying the pump excitation intensity and at a high intensity it vanishes due to the full occupation of the defect states. At the same time, the final electron–hole recombination is found to be affected by the heat accumulation effect originating from the high intensity pump pulses.
Coupled relaxation channels of excitons in monolayer MoSe$_2$

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Using ultrafast degenerate pump-probe spectroscopy, we have investigated the ultrafast exciton dynamics of monolayer MoSe$_2$ at different pump fluences. The exciton-exciton annihilation, typically taking effect tens of picoseconds after pump excitation, has been found to have a substantial correlation with the initial relaxation process dominated by the defect trapping of excitons. A new exciton-exciton annihilation model has been proposed by introducing a coupling term that accounts for the initial relaxation contribution. This coupling term can be tuned by varying pump excitation intensity and at high intensity it vanishes due to the full occupation of the defect states. At the same time, the final electron-hole recombination is found to be affected by heat accumulation effect originating from the high intensity pump pulses.

1 Introduction

Photo-generated excitons in monolayer transition metal dichalcogenides (TMDCs) are widely investigated in recent years due to their excellent optical properties. Emerging TMDCs materials such as MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$, have sizable bandgaps that change from indirect bandgap to direct bandgap when reduced to monolayer. This electronic bandgap change leads to an extreme enhancement of photoluminescence (PL), which makes these atomically thin materials well suited to a variety of optoelectronic applications, such as LEDs, photodetectors, and photovoltaics. In addition, due to the high exciton binding energy (on the order of hundreds of meV), these materials have good stability even at room temperature for the application of optoelectronic devices. To apply TMDCs in future optoelectronic devices, it is very important to understand the dynamical behavior of excitons or carriers excited by light. The temporal characteristics of excitons or carriers will determine the performance of the LEDs or photodetectors. Recently, the exciton dynamics in monolayer TMDCs have been investigated via both time-resolved PL and transient pump-probe spectroscopy techniques. According to the time-resolved PL measurements as well as the theoretical calculations, the average radiative lifetime of excitons in TMDCs vary from a few picoseconds at low temperature to hundreds of picoseconds or even nanoseconds at room temperature. In addition to the radiative recombination, various exciton scattering mechanisms are revealed through the pump-probe spectroscopy. Exciton-exciton annihilation, an efficient exciton relaxation mechanism occurring within a few tens of ps, has been observed in atomically thin MoS$_2$ and MoSe$_2$. Several groups that attribute the initial relaxation process within a few ps in single layer MoS$_2$ to defect states trapping, and Nie et al. interpret the same span as the carrier cooling. Although different kinds of scattering mechanisms have been proposed, the microscopic mechanisms governing the relaxation process of excitons (or carriers) in TMDCs is still not fully clear. In these previous works, each of the relaxation stages was found to be dominated by a specific relaxation mechanism. It is important to explore if any of these mechanisms are coupled or not, as these mechanisms might take effect in a wide time scale leading to their possible overlaps. Addressing such an aspect will be critical in understanding the relatively complex photo-physics and manipulating the exciton lifetime in TMDCs.

In this article, by employing degenerate pump-probe spectroscopy, we find clear evidence of the correlation between two exciton relaxation channels, where the initial fast decay component facilitates the subsequent exciton-exciton annihilation process in monolayer MoSe$_2$. A coupling term is introduced to account for the influence of the initial defect trapping process on the following exciton-exciton annihilation. The contribution of this coupling term is found to decrease with the increase of the pump...
fluence until the saturation of the defect states at high fluences. The final stage of relaxation, which lasts hundreds of picoseconds, is attributed to electron hole recombination as no dependence of the relaxation time on pump injected exciton density is found at low pump fluence.

2 Experimental Section

We performed the degenerate pump-probe spectroscopy of which the experimental configuration is shown in Fig.1 (a), with the pump and probe wavelengths being the same. To avoid the pump beam scattering into the detectors, the probe beam is at normal incidence while the pump beam is around 40 degrees away from the normal direction of the sample plane. This configuration allows us to spatially separate the reflected pump and probe beams. The probe beam is focused on the sample by an aspheric lens with the spot size of about 20 \( \mu m \) in diameter. Whereas the pump beam is focused by another lens and its spot size is about 38 \( \mu m \).

Fig.1 (b) shows the diagram of the conduction and valence band of monolayer MoSe\(_2\) at K valley. The red arrows represent the degenerate pump-probe excitation at A-exciton resonance. The MoSe\(_2\) samples are grown by chemical vapor deposition (CVD) method with the size larger than 100 \( \times \) 100 \( \mu m \) and all the measurements are performed at room temperature. In this measurement, the polarization of pump and probe beams is orthogonal to each other to further avoid the scattering of pump beams. Under excitation of a 532 nm laser, strong photoluminescence with a central wavelength of 800 nm, a fingerprint of the monolayer MoSe\(_2\), is observed, as shown in Fig.1 (d) (black solid line). Fig.1 (c) presents the Raman spectrum of monolayer MoSe\(_2\) and the peak at the wave vector of 239.72 \( cm^{-1} \) corresponds to the out-of-plane \( A_{1g} \) phonon mode. The similar Raman spectra behavior of monolayer MoSe\(_2\) is also reported in many other works. The in-plane mode \( E_{2g} \) is not obvious, which may be due to the defect impact. The optical image in the inset of Fig.1 (c) shows a typical MoSe\(_2\) flake used in our measurement.

3 Results and discussion

Fig.2 (a) shows the transient reflectivity of monolayer MoSe\(_2\) measured at different values of the pump fluence. We perform these measurements under the wavelength of 800nm. For clarity, we only present the data below the pump fluence of 1.16 \( \mu J/cm^2 \). The zoom in of the first 30 ps of the data shown in (a), (c) transient reflectivity amplitude \( \Delta R/R \) at \( \Delta T = 0.27 \) ps under different pump excitations. The saturation trend above 2.20 \( \mu J/cm^2 \) is obvious. The relaxation time \( \tau_1 \), \( \tau_2 \) and \( \tau_3 \) as a function of excitation intensity are shown in (d), (e) and (f), respectively. The red solid lines in (a), (b) and (c) are fitting lines and the red dash lines in (d), (e) and (f) are eye guiding lines.

The dynamic curves are well described by tri-exponential decay function, indicating three distinct exciton relaxation channels characterized by \( \tau_1 \), \( \tau_2 \) and \( \tau_3 \) are discovered. Note that one should be aware of that each different time constant does not necessarily mean a different relaxation pathway. As reported by Cooney et al, in QD system, 2-3 different channels contribute to the rate process of electron or hole...
cooling. Here, our result reveals one more relaxation stage than that reported by Kumar et al.\textsuperscript{18,23} who only observed two relaxation channels in monolayer MoSe\textsubscript{2}. A possible reason for this distinction may be that the intra-valley relaxation can be minimized through our degenerate pump probe configuration and thus more refined relaxation dynamics can be observed. More specifically, in the case of non-degenerate pump probe configuration, the pump-generated excitons are not observed until their transition energy can be accessed by the probe wavelength. In addition to the detailed relaxation processes, the resonant A-exciton transition also allows a very fast exciton generation via photoabsorption process\textsuperscript{2,18,29} as shown in Fig.2 (b) where the rise-up time is as short as 0.27 ps or less.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(a) Transient reflectivity traces at different pump fluences between $\Delta T = 59$ ps and 169 ps. The fitting lines are obtained by the modified exciton-exciton annihilation model (Eq.2). (b) The coupling term $N_0/d^2$ increases within the fluence range between 0.58 $\mu$J/cm$^2$ and 2.9 $\mu$J/cm$^2$. The values above the 1.62 $\mu$J/cm$^2$ approximately equal to zero.
}
\end{figure}

Figure 2 (c) shows the transient reflectivity amplitude at $\Delta T = 0.27$ ps under different pump excitation intensity. The values of $\Delta R/R$ at $\Delta T = 0.27$ ps increase by a factor of four in the measured pump fluence range, saturating at the highest fluence, which is likely due to the state filling effect near the band edge\textsuperscript{30}. To quantify the pump injected excitons, we employ a saturable absorption model\textsuperscript{31} to fit to these peak values and obtain the saturation pump fluence density of 3.5 $\mu$J/cm$^2$. The red solid line in Fig.2 (c) represents the fitting line. Using the absorption coefficient of MoSe\textsubscript{2} reported in previous work\textsuperscript{32} and the measured pump fluence, we estimate the saturant excitation exciton density to be 1.96 $\times 10^{11}$/cm$^2$ which is comparable to the reported values of monolayer MoSe\textsubscript{2} in other works\textsuperscript{23,33}. The nonlinear behavior of the peak values of $\Delta R/R$ above 1.74 $\mu$J/cm$^2$ also suggests that the photon generated exciton density is close to the highest capacity density. To obtain accurate photon generated exciton density, we calibrated the conversion process of pump power to the pump fluence by measuring the beam spot size carefully (see supporting information). This process helps to optimize the quantitative analysis discussed later. The $\tau_1$ shown in Fig.2 (d) is found to be increased by two times. The similar fluence dependent relaxation component of free carrier is also reported by Nie et al\textsuperscript{21} in few-layer MoS\textsubscript{2}, which is assigned to the hot phonon effect. But in the case of excitons rather than the free carriers, as reported by Robert et al\textsuperscript{34}, the thermalization time is about a few tens of ps. Thus, we could exclude the hot phonon effect here. The contribution of intrinsic radiative exciton lifetime to this short time scale should be ruled out as in low fluence range it is expected to be independent of excitation fluence\textsuperscript{35}. A possible mechanism accounting for the prolonged fast exciton decay part under high pump fluence is the surface defects scattering. Since at low pump fluences photo-excited carriers can quickly relax into the defect states, while with the pump fluence being high, these defect states are filled gradually, leading to the increase of and its stabilization eventually. As can be seen in Fig.2 (d), the $\tau_1$ remains constant above 1.62 $\mu$J/cm$^2$. We also notice that some other group\textsuperscript{30} reported similar pump fluence dependence of exciton relaxation within the timescale of a few ps, claiming that the defect trapping process dominate this behavior. To visualize this exciton relaxation mechanism, we draw the cartoon picture of this process shown in Fig.4 (a) where the density is introduced. After initial fast relaxation into the surface defect states, the populations of excitons are further decreased via exciton-exciton annihilation (EEA) as shown in Fig.2 (e) where the relaxation time decreases with increasing the pump fluences. To verify this assignment, we fit a subrange of the transient traces to an exciton-exciton annihilation model that is expressed as the following:\textsuperscript{17}

\begin{equation}
N(t) = \frac{N_0}{1 + \gamma N_0 t}
\end{equation}

where $N_0$ is the initial photo-generated exciton density and $\gamma$ is the exciton-exciton annihilation rate. We carefully select the time zone between $\Delta T = 5.6$ ps and $\Delta T = 169$ ps as the relaxation process of $\tau_2$ and fit the data to Eq. 1. According to the fitting results obtained under various pump fluences, we found that the fitted parameter $\gamma$ above 1.62 $\mu$J/cm$^2$ remained almost unchanged indicating that the exciton-exciton annihilation dominated the exciton relaxation at this high pump fluence range. However, for excitation fluences below 1.62 $\mu$J/cm$^2$, the fitted $\gamma$ values increase with the decrease of excitation intensity (see in Fig.S2), which suggests that higher annihilation rate would be required to reduce the population of excitons in the low pump fluence regime. While as reported before by other groups\textsuperscript{17,18}, the annihilation rate between excitons in specific material is constant. Thus, we infer that, in addition to the exciton-exciton annihilation mechanism, one more factor should contribute to the $\tau_2$ decay channel in the low pump excitation range. Meanwhile, it’s clearly observed that the pump excitation threshold (1.62 $\mu$J/cm$^2$) below which the $\gamma$ begins to increase is the same as that where $\tau_1$ begins to decrease (as shown in Fig.2 (d)). Inspired by the similar dependence of $\tau_1$ and $\gamma$ on pump fluence, we correlate the defect trapping process of $\tau_1$ with the $\tau_2$ relaxation channel. A generalized rate equation describing the exciton dynamics, where both EEA process and radiative exciton lifetimes are considered, has been reported\textsuperscript{17,36}. In addition, Yu et al\textsuperscript{37} also employed the basic EEA differential equation with additional incident power density term to describe the effect of EEA on luminescence in monolayer TMDs. To better understand the pump fluence dependent coupling strength between the defect trapping and EEA process, we introduce con-
fitted result of the excitation intensity as shown in Fig.S3. From the independence of electron hole recombination processes with the pump fluence (as shown in Fig.3), the traces are almost overlapped between all the fluences as expected. Whereas after around $\tau_1$, the traces that correspond to the fluences above 1.62 $\mu J/cm^2$ begin to separate. The up-going trend after $\Delta T = 400$ ps under high pump fluences indicates an additional factor makes it difficult for the excitons to relax. Generally, the heat diffusion is possible in the sample is not efficient enough as discussed by Shi et al.\cite{Shi2017}. This finding also suggests that if one wants to avoid the impact of defects on exciton-exciton annihilation, a proper selection of pump fluence would work. Similar experimental results have been reported previously in QD system. Tyson et al.\cite{Tyson2017,Tyson2018} have found that, due to surface trapping, high pump fluence can affect exciton dynamics and the exciton annihilation can be controlled via surface treatment. These results also uncovered the correlation between defect trapping and EEA.

After being trapped by the defect states that followed by the bi-exciton interaction relaxation, the excitons of monolayer MoSe$_2$ finally relax to an equilibrium state within a long-time scale of a few hundreds of picoseconds, which is usually assigned to both the electron-hole recombination process.\cite{Tyson2017,Tyson2018}. At the same time, after $\tau_1$ and $\tau_2$ relaxation processes, the remained exciton population is far below the threshold where exciton-exciton interaction begins to be dominated. Therefore, many body interaction of excitons can be ignored and we contribute the $\tau_3$ relaxation regime to an isolated exciton recombination process. As shown in Fig.4 (c), both the radiative and non-radiative exciton recombination processes may contribute to the exciton recombination. The wavy line denotes photon emission during the radiative electron-hole recombination. The time scale of the electron-hole recombination in our measurement is consistent with that reported by other groups.\cite{Deng2015,Deng2017}.

However, as shown in Fig.2 (f), the $\tau_3$ values are influenced by pump fluence at relatively high intensity range, which contradicts the independence of electron hole recombination lifetime with pump excitation intensity as reported by Cui et al.\cite{Cui2017}. Considering this, we infer that the $\tau_3$ values are also affected by other factors in high fluence range. Back to the original experimental data as shown in Fig.S3, it is clearly observed that the transient $\Delta R/R$ traces are almost overlapped between $\Delta T = 200$ and 400 ps. This period can be safely assigned to the time window of the $\tau_3$ relaxation process as the $\tau_1$ and $\tau_2$ relaxation processes correspond to the high repetition rate of pump. Since the transient $\Delta R/R$ traces are overlapped at the beginning of $\tau_3$ relaxation process, the $\tau_3$ relaxation time should be constant for all the fluences as expected. Whereas after around $\Delta T = 400$ ps, the traces that correspond to the fluences above 1.62 $\mu J/cm^2$ begin to separate. The up-going trend after $\Delta T = 400$ ps under high pump fluences indicates an additional factor makes it difficult for the excitons to relax. Generally, the heat diffusion is possible in such a time scale. We also note that the high repetition rate of laser system would have the possibility to lead to a significant heat accumulation effect if the thermal dissipation in the sample is not efficient enough as discussed by Shi et al.\cite{Shi2017}. Thus, a possible explanation accounting for the behavior of $\tau_3$ under high pump fluence is the effect of accumulated heat from the pulse laser. Our results indicate that any possible different diffusion rates for different substrates may have different impacts on the behavior of $\tau_3$. 

![Diagram](image-url)
4 Conclusions

In conclusion, we have studied three distinct relaxation channels in monolayer MoSe$\textsubscript{2}$ by varying the pump intensity using the degenerate ultrafast pump-probe spectroscopy. Our results reveal for the first time the correlation between the different exciton relaxation channels in MoSe$\textsubscript{2}$. The exciton-exciton annihilation process is found to be mediated by the defect trapping process that accounts for the initial fast excitons decay at low pump fluence. We have employed an improved exciton-exciton annihilation model with the introduction of a pump-fluence dependent coupling term and it agrees well with the experimental observations. The final electron-hole recombination is demonstrated to be independent on pump-injected excitons, although it is affected by the heat accumulation under high excitation intensity. Our findings provide new insights into the exciton relaxation dynamics in terms of the coupled relationship between different decay channels, and at the same time, demonstrate that the pump fluence can be utilized to tune the specific relaxation process, which is important to potential optoelectronic applications of the TMDC materials.

Author contributions

X.Z.R., F.W., and Y.B.X. conceived the project and Y.B.X supervised the project. Y.Z.M. and F.Q.S. prepared the monolayer MoSe$\textsubscript{2}$ samples by CVD method. B.L. performed ultrafast pump-probe experiments. B.L., X.Z.R., F.W., Q.S., W.Q.L., X.F.W., and J.W., L.H., R.Z. and Y.B.X. contributed to the analysis of the experiment data. B.L. wrote the paper with all authors contributing to discussion and preparation of the manuscript.

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