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**Unraveling Spatially Heterogeneous Ultrafast Carrier Dynamics of Single-Layer WSe₂ by
Femtosecond Time-Resolved Photoemission Electron Microscopy**

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Abstract

Studies of the ultrafast carrier dynamics of transition metal dichalcogenides have employed spatially-averaged measurements, which obfuscate the rich variety of dynamics that originate from the structural heterogeneity of these materials. Here, we employ femtosecond time-resolved photoemission electron microscopy (TR-PEEM) with sub-80-nm spatial resolution to image the ultrafast sub-picosecond to picosecond carrier dynamics of monolayer tungsten diselenide (WSe₂). The dynamics observed following 2.41-eV pump and 3.61-eV probe occurs on two distinct timescales. The 0.1-ps process is assigned to electron cooling via intervalley scattering, whereas the picosecond dynamics is attributed to exciton-exciton annihilation. The 70-fs decay dynamics observed at negative time delay reflects electronic relaxation from the Γ point. Analysis of the TR-PEEM data furnishes the spatial distributions of the various time constants within a single WSe₂ flake. The spatial heterogeneity of the lifetime maps is consistent with increased disorder along the edges of the flake and the presence of nanoscale charge puddles in the interior. Our results motivate the need to go beyond spatially-averaged time-resolved measurements to understand the influence of structural heterogeneities on the elementary carrier dynamics of two-dimensional materials.

TOC graphic

Keywords: photoemission electron microscopy, ultrafast carrier dynamics, 2D materials, pump-probe, structural defects, lifetime imaging

Transition metal dichalcogenides (TMDs) exhibit exotic properties such as the emergence of a direct bandgap in monolayer samples,¹⁻² valley polarization,³ and the existence of a large range of bandgaps associated with the extensive library of TMDs.⁴ TMDs have found applications in light harvesting,⁵ sensitive photodetectors,⁶ field-effect transistors⁷ and light-emitting diodes.⁸ However, the quantum efficiencies of TMDs-based light detector and emitter are poor despite its direct bandgap.^{6, 9-10} The low efficiency is attributed to the nonradiative recombination and/or trapping of electrons and holes that are mediated by defects in TMDs.¹¹⁻¹² While chemical vapor deposition (CVD) can furnish wafer-scale samples,¹³ CVD-grown samples have a higher density of defects compared with those obtained from the mechanical exfoliation.¹⁴

Ultrafast spectroscopy provides a route to understanding the fundamental properties of semiconductors by elucidating their ultrafast carrier dynamics.¹⁵ In the case of TMDs, ultrafast spectroscopy measurements reveal dynamics such as the formation of excitons,¹⁶⁻¹⁷ biexcitons¹⁸ and trions.¹⁹ Studies performed with sub-10-fs pulses reveal sub-20-fs carrier thermalization and sub-picosecond carrier cooling.²⁰ Ultrafast dynamics of band-selective carrier relaxation,²¹ valley depolarization,²²⁻²³ defect-assisted carrier trapping,²⁴⁻²⁶ and exciton-exciton annihilation^{12,27-28} have also been reported. Optically initialized valley-polarized holes²⁹ and exciton valley coherence³⁰ in monolayer WSe₂ are discovered.

The majority of time-resolved studies of TMD materials reported to date employ spatially-averaged measurements. By combining pump-probe spectroscopy with optical microscopy, different regions of interest within a TMD sample can be selectively probed in time-resolved experiments.³¹⁻³² The time-resolved optical microscopy investigation of exciton dynamics of an exfoliated MoS₂ sample with regions of different layer numbers reveals that intravalley relaxation rates can be enhanced 40-fold in a monolayer sample relative to a thick sample.²⁵ However time-

resolved optical microscopy has its drawbacks. First, the spatial resolution of conventional optical microscopy is limited by diffraction to several hundred nanometers. Second, the higher-order dispersion introduced by high numerical-aperture microscope objectives limits the typical achievable temporal resolution to ~ 100 fs, although the combination of a single aspheric lens for excitation and a high numerical-aperture objective for collection has recently resulted in the dramatic improvement of the time resolution to ~ 15 fs.^{33,34} Third, producing a differential transmission map of the sample requires raster scanning. Imaging techniques such as tip-enhanced microscopy³⁵ and scanning near-field optical microscopy (SNOM)³⁶ offer few tens-of-nanometer spatial resolution, although their pump-probe implementation remains to be applied to TMD materials.

Here, we employ femtosecond time-resolved photoemission electron microscopy (TR-PEEM) to investigate the sub-picosecond to picosecond carrier dynamics of monolayer WSe₂. In TR-PEEM, a pump pulse of photon energy $\hbar\omega_{\text{pu}}$ injects electrons into the conduction band, following which electrons that lie within the probe window are ejected into the continuum³⁷⁻⁴⁰ after a variable time delay. The ejected photoelectrons pass through several electrostatic lenses to form a magnified image of the sample surface at the two-dimensional array detector. Recording the PEEM image as function of pump-probe time delay yields the time evolution of the population of conduction band electrons. TR-PEEM has recently been applied to image carrier transport and recombination occurring on the 1 – 10-ps timescale in both bulk⁴¹ and atomically-thin semiconductors.⁴² In the present work, we focus on imaging the sub-picosecond to picosecond carrier dynamics of TMDs with 80-nm spatial- and 60-fs time resolution. Spatially integrated analysis of single flakes yields a timescale of 0.12 ± 0.01 ps for carrier cooling via intervalley scattering and a second-order rate constant of 0.075 ± 0.001 cm²/s for Auger-mediated trapping

Figure 1. (a) Static PEEM image of monolayer WSe₂ illuminated by 3.61-eV light. (b) Photoemission signal plotted as a function of fluence of 3.61-eV light, showing a quadratic dependence. (c) Band structure of monolayer WSe₂. The shaded region shows the 2×3.61 eV two-photon probe window, taking into account momentum conservation in the photoionization process. The vertical green lines denote the 2.41-eV photoexcitation of electrons from the valence band to the conduction band at the K valley.

and/or recombination. Fitting the time traces obtained at different positions within a single flake yields a spatial map of the ultrafast carrier relaxation time constants. The pronounced spatial heterogeneities of these time constant maps suggest the need to go beyond spatially-averaged measurements in the study of the ultrafast carrier dynamics of TMDs.

Figure 1a shows the static PEEM image of a monolayer WSe₂ flake that is acquired by irradiating the sample with 40-fs, 3.61-eV UV laser pulses. The WSe₂ flake has a triangular shape, characteristic of TMDs. The observed spatial heterogeneity will be addressed below. Photoelectron spectroscopy of WSe₂ yields a range of 4.5 – 5.5 eV for the ionization potential,⁴³ dependent on the type of substrate. The absorption of a single 3.61-eV photon is therefore insufficient to eject an electron from the valence band maximum of the WSe₂ sample. Fluence dependence measurements show that the photoemission signal scales quadratically with fluence (Figure 1b), suggesting the formation of the static PEEM image via two-photon photoionization. Taking into

Figure 2. (a) Spatially-integrated time traces of the single flake at different pump fluences. Note that the traces have been offset for clarity. (b) Time constants of the fast decay at negative times (τ_-), along with the fast (τ_1) and slow (τ_2) decays at positive times, plotted as a function of pump fluence.

account the conservation of lateral momentum in photoionization, Figure 1c shows the region of the band structure that is accessible by the two-photon photoionization probe.

To investigate the ultrafast dynamics of the monolayer WSe₂ flakes, we employ 46-fs, 2.41-eV visible laser pulses for single-photon photoexcitation of electrons from the valence band to the conduction band. Following a variable time delay, 40-fs, 3.61-eV UV pulses eject electrons from the conduction band via a two-photon process to yield the photoemission signal (see the Supporting Information). TR-PEEM resolves the photoemission signal in both space and time, hence furnishing the temporal evolution of the photoemission signal for different spatial regions of the WSe₂ flake. To compare the ultrafast dynamics observed herein with those obtained from spatially-averaged measurements, however, we first plot the spatially-integrated photoemission signal as a function of time delay. Figure 2a shows the time traces obtained at pump fluences of 11 to 21 $\mu\text{J}/\text{cm}^2$; the probe fluence in all cases is fixed at 2 $\mu\text{J}/\text{cm}^2$. The time traces can be fit to a double-sided exponential decay convolved with the instrument response function; the TR-PEEM

signal at negative time undergoes a single exponential decay, whereas the signal at positive time exhibits a biphasic decay. The resultant time constants obtained at different pump excitation fluences are summarized in Figure 2b. The decay dynamics observed at negative times is characterized by a time constant τ_- of ~ 70 fs, independent of pump fluence. In the positive time regime, the ~ 0.1 -ps decay component τ_1 is relatively independent of pump fluence, whereas the picosecond decay component τ_2 decreases monotonically from 2.61 ps to 2.29 ps with increasing pump fluence.

The biphasic decay dynamics observed at positive time delays can be explained as follows. The 2.41-eV photon energy of the pump pulse spans the band gap of monolayer WSe₂ and lies beyond its A and B exciton transition energies of 1.6 and 2.1 eV, respectively.⁴⁴⁻⁴⁵ Photoexcitation therefore initially furnishes a non-thermal distribution of free carriers, initially localized in the K valley. Such a non-thermal distribution was shown to undergo carrier thermalization on the ~ 10 -fs timescale via carrier-carrier and carrier-phonon scattering.²⁰ The latter serves as a plausible mechanism for transferring electrons from the K valley to the neighboring Q valley within the 60-fs instrument response of our experimental setup, although we note that such a phenomenon requires further investigation, perhaps by time-resolved angle-resolved photoemission electron spectroscopy. The Q valley resides within the window of the 2×3.61 eV probe process, hence giving rise to the large photoemission signal at time zero. The 0.1-ps decay component (τ_1) is attributed to carrier cooling via intervalley electron-phonon scattering of electrons from the Q valley, which lies within the probe window, to the K valley, where the minimum of the conduction band resides. The observed fluence dependence for τ_2 , on the other hand, suggests that the picosecond decay originates from exciton-exciton annihilation. It is noteworthy that the time

constants do not exhibit any significant variation across different flakes (see the Supporting Information).

The above assignments are supported by previous time-resolved two-photon photoemission (2PPE) and optical pump-probe studies of TMDs, which reveal sub-picosecond and picosecond timescales for electron cooling and exciton-exciton annihilation, respectively. Furthermore, the time-dependent photoemission signal follows second-order kinetics for time delays beyond 0.5 ps (see the Supporting Information). Global analysis of time traces collected for multiple pump fluences over the range of 0.5 – 5 ps yields an exciton-exciton annihilation rate of $0.075 \pm 0.001 \text{ cm}^2/\text{s}$, similar to the exciton-exciton annihilation rates reported previously for MoS₂ ($0.043 \pm 0.011 \text{ cm}^2/\text{s}$)¹² and WS₂ ($0.089 \pm 0.001 \text{ cm}^2/\text{s}$).²⁸ Compared to these earlier studies, which probe the dynamics of excitons confined at the K valley, however, it is important to note that the exciton-exciton annihilation dynamics most likely involves intervalley excitons, i.e., excitons with non-zero center-of-mass momenta. The deviation in the present study arises from the finite probe window of the two-photon ionization probe and the insufficient excess energy of the hole to populate regions beyond the K valley in the carrier thermalization process. In our case, the intervalley exciton comprises an electron in the Q valley bound to a hole in the K valley. The formation of such intervalley excitons in monolayer WSe₂ was recently inferred from time-resolved mid-infrared probing of intraband electron dynamics.¹¹ There, it was found that intervalley excitons, being optically dark, could undergo rapid nonradiative relaxation via Auger-type exciton-exciton annihilation. In fact, the reported annihilation rate of $0.065 \pm 0.005 \text{ cm}^2/\text{s}$ is in excellent agreement with the results of our measurements.

At negative time delays, the sequence in which the visible and UV pulses are incident on the sample is reversed compared to positive time delays. The TR-PEEM signal at negative time

delays therefore reports on the dynamics that are induced by 3.61-eV UV excitation and probed by the 2.41-eV visible pulse. As can be seen from the band structure of monolayer WSe₂, high-energy UV photoexcitation can occur across multiple regions in the Brillouin zone, including the vicinity of the Γ point (see blue arrow in Fig. 1c), which resides in the probe window for 2.41-eV, single-photon ionization (see hatched area in Fig. 1c). The 70-fs decay therefore characterizes the timescale for the scattering of electrons away from the Γ point, out of the probe window, to lower-energy regions of the conduction band. The large density of electronic states that exists in high-energy region of the conduction band facilitates the observed ultrafast electron relaxation dynamics.

Analyzing the time traces acquired at the individual pixels of the TR-PEEM image yields information on the spatially resolved ultrafast dynamics of single-layer WSe₂. Some representative time traces are shown in Figure 3a. The resultant spatial distributions of the time constants, analogous to lifetime maps obtained from fluorescence lifetime imaging microscopy, are shown in Figures 3b and 3c for the fast (τ_1) and slow (τ_2) decay components, respectively. These lifetime maps are obtained with a pump (probe) fluence of 10 $\mu\text{J}/\text{cm}^2$ (2 $\mu\text{J}/\text{cm}^2$). Due to the lower count rates for the single-pixel time traces (Figure 3a) compared to the spatially-integrated time traces (Figure 2a), the standard errors for τ_1 and τ_2 obtained from the fits to the single-pixel time traces are typically in the range of $\sim 30 - 70\%$ of the fit values, comparable to the difference in the lifetimes along the edge and the interior of the flake. While the large standard errors of the fits might affect the quantitative accuracy of the lifetime maps, we nevertheless note that the pronounced segregation of the fast and slow dynamics between different regions of the flake (see below) strongly suggests that the observed spatial heterogeneity in the carrier dynamics is at least qualitatively correct. The corresponding histograms of the fast- (τ_1) and slow-decay (τ_2) time

Figure 3. (a) Representative time traces obtained for single pixels located at different positions of the WSe₂ flake. The PEEM image in the inset shows the positions from which the time traces are extracted. Note that the traces have been offset for clarity. Time constant mapping of the (b) fast component and (c) slow component, along with their corresponding histograms, shown in (d) and (e), respectively.

constants are shown in Figures 3d and 3e, respectively. The spatial heterogeneity of the observed

ultrafast dynamics is evident from the lifetime maps and their associated histograms. For the fast (slow) decay component, we obtain an average time constant of 108 fs (2.90 ps) and a standard deviation of 43 fs (1.28 ps). The amplitude-weighted fast- and slow-decay time constants of 107 fs and 2.67 ps, respectively, are in good agreement with those furnished by the spatially integrated analysis (123 ± 6 fs and 2.61 ± 0.17 ps for the fast and slow decay, respectively).

The most striking features of the lifetime maps are the smaller τ_1 and larger τ_2 lifetimes that appear along the edges of the flakes. Because the WSe₂ sample used in the present work were transferred onto the SiO₂/Si substrate, a procedure that is known to release the tensile strain that accumulates during CVD growth,⁴⁶⁻⁴⁷ we eliminate strain fields as a source of heterogeneity. Instead, we ascribe these observations to the presence of increased disorder along the peripheral edges of the WSe₂ flake. Structural disorder is known to yield new zone-edge phonon modes in the Raman spectra⁴⁸⁻⁴⁹ of TMDs as well as increased linewidths for the A_{1g} and E_{2g}^1 phonon peaks due to phonon confinement. In addition, ab initio simulations reveal the broadening of the phonon density of states due to structural disorder.⁵⁰ The appearance of disorder-induced phonon modes accelerates electron-phonon scattering rates, thereby facilitating electronic relaxation and resulting in smaller τ_1 values along the edges of the WSe₂ flake. The larger τ_2 lifetimes along the edges can also be explained in terms of slower exciton diffusion⁵¹ resulting from increased disorder, which in turn leads to longer timescales for exciton-exciton annihilation.

The observed differences in the ultrafast carrier dynamics between the peripheral edge and the interior of the WSe₂ flake are consistent with previous results obtained from hyperspectral imaging of TMDs by near-field photoluminescence (PL) microscopy.³⁵⁻³⁶ Those studies reveal that the edges of TMD flakes exhibit significantly different spectral characteristics from the interior of the flakes. The edges are characterized by reduced PL intensities and the appearance of a high-

energy tail in the PL spectra, both of which are signatures of a disordered, inhomogeneously broadened ensemble of emitters, such as those encountered in organic conjugated polymers⁵² and quantum dot solids.⁵³

Aside from the pronounced differences in electron lifetimes between the edge and interior of the WSe₂ flake, it is noteworthy that the interior of the flake itself also exhibits noticeably heterogeneous carrier dynamics. Previous studies by hyperspectral PL imaging⁵⁴ and Raman microscopy⁵⁵ have attributed the observed heterogeneity to the presence of substrate-induced charge puddles, originally uncovered for graphene.⁵⁶ Charge puddles form as a result of the inhomogeneous doping of the substrate or charge transfer from impurities that are trapped between the TMD monolayer and the substrate. In addition, a combination of atomic force microscopy and scanning tunneling spectroscopy have elucidated the existence of bandgap puddles that arise from nanoscale distortions of the TMD flake induced by the ~ 1 -nm surface roughness of the SiO₂/Si substrate.⁵⁷ The spatially heterogeneous carrier density and band gap of WSe₂ modulates electron-phonon coupling strengths and exciton transport. The former explains the heterogeneity observed in the electron cooling dynamics (τ_1), whereas the latter yields a distribution of exciton-exciton annihilation times (τ_2). Future experiments that correlate hyperspectral PL and Raman microscopy with TR-PEEM microscopy will enable us to ascertain the effect of charge puddles on the ultrafast carrier dynamics.

Finally, we address the spatial heterogeneity observed in the case of the static PEEM image (Figure 1a). The PEEM image is collected under two-photon UV irradiation conditions. It is important to note that the two-photon ionization process is resonantly enhanced because the absorption of a single 3.61-eV photon accesses the conduction band at the Γ point. If the lifetime of the electron at the Γ point of the conduction band is longer than the 40-fs temporal duration of

Figure 4. Time constants at negative times (τ_-) of each pixel plotted as a function of their corresponding static image counts. A linear correlation with a Pearson correlation coefficient of 0.35 is observed (red line).

the UV pulse, the absorption of an additional photon by the intermediate state would result in ionization of the sample. On the other hand, if the intermediate state undergoes ultrafast relaxation to a region of the conduction band that lies beyond the probe window, ionization would be suppressed. The ionization yield, and hence the PEEM signal, is therefore expected to increase with the lifetime of the electron at the Γ point. This lifetime is reflected in the dynamics observed at negative time delays (see above), when the UV pulse precedes the visible pulse. Figure 4 shows that the photoemission signal is indeed correlated with the lifetime τ_- , with a Pearson correlation coefficient of 0.35. Similar correlation coefficients are obtained for the other WSe₂ flakes examined in this study (see the Supporting Information).

In summary, we have employed femtosecond TR-PEEM to image the ultrafast carrier dynamics of monolayer WSe₂ on SiO₂/Si with ~ 50 -fs time resolution and sub-diffraction-limited spatial resolution. The observed dynamics are assigned to carrier cooling via intervalley electron-phonon scattering of electrons from the Q valley to the K valley, exciton-exciton annihilation

involving indirect excitons, and electronic relaxation from the Γ point of the conduction band. The lifetime maps of the ultrafast dynamics exhibit pronounced spatial heterogeneity, most likely associated with structural disorder along the peripheral edges of the WSe₂ flake and the existence of charge puddles in the interior. While the presence of such structural and electronic heterogeneity have been inferred from previous studies of TMDs by time-integrated hyperspectral PL and Raman imaging, our present work directly reveals their effect on the ultrafast carrier dynamics. Future studies that combine TR-PEEM with an array of hyperspectral electron and optical imaging techniques is envisioned to provide insight into how various classes of structural heterogeneities and defects influence the ultrafast elementary carrier dynamics of TMD materials.

Methods

Sample Fabrication. WO₃ powder (0.1 g) was put in a quartz boat and placed in the heating zone center of the furnace. Se powder was prepared in a separate quartz boat at the upstream side of the furnace. The sapphire substrates for growing WSe₂ were put at the downstream side, next to the quartz boat that contains WO₃. The gas flow was brought by an Ar/H₂ flowing gas (Ar = 60 sccm, H₂ = 5 sccm) and the chamber pressure was set at 20 Torr. The central heating zone was heated to 925 °C, and the temperature of the Se boat was maintained at 260 °C by heating tape during the reaction. After reaching 925 °C, the temperature was held at 15 minutes for reaction before the furnace was naturally cooled down to room temperature. To transfer the WSe₂ sample onto the SiO₂/Si substrate, the as-grown WSe₂ on sapphire was first coated with a layer of PMMA and then dipped into a HF solution (HF : H₂O = 1 : 3) for 15 min. After sapphire-etching by HF, the PMMA/WSe₂ film was transferred into DI water twice to dilute the HF etching solution, following

which PMMA/WSe₂ was transferred onto the SiO₂/Si substrate and heated at 100 °C on a hotplate for 30 min to evaporate the water at the interface. The sample was then put into acetone at 60 °C for 30 min to remove the PMMA. Finally, the sample was rinsed with isopropanol and water, and dried under a stream of N₂ gas.

Femtosecond TR-PEEM. The light source that is employed in the femtosecond TR-PEEM is based on a Yb fiber laser (Amplitude Systemes) with an output pulse energy of 50 μ J, pulse duration of 320 fs FWHM, and center wavelength of 1030 nm. The 0.6-MHz repetition rate supports a high signal count rate while suppressing space charge-induced degradation of the spatial resolution. The laser output is spectrally broadened in a xenon-filled hollow-core fiber before recompression by chirped mirrors to yield 50 fs pulses. The fundamental wavelength is converted to the second- and third-harmonic in a series of BBO crystals to yield 2.41-eV and 3.61-eV pulses with measured FWHM durations of 46 fs and 40 fs, respectively. A computer-controlled motorized translation stage introduces a variable time delay between pump and probe pulses before both beams are loosely focused onto the sample. Under our experimental conditions, the PEEM (Focus GmbH) furnishes a spatial resolution of 77 nm (16-84% criterion). At each time delay, the image acquisition time was set at 10 s. The time-sequenced images are processed by a home-built MATLAB program to obtain the lifetime maps.

Supporting Information

Supporting Information Available: Optical and fluorescence image of WSe₂ sample, large field-of-view static PEEM image of the WSe₂ sample, power dependence measurement results, determination of spatial resolution of the PEEM microscope, analysis of second-order kinetics, and analysis of other WSe₂ flakes.

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The authors declare no competing financial interest.

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