Ultrafast Carrier Thermalization and Cooling Dynamics in Few-Layer MoS$_2$

Zhaogang Nie,$^{†}$ Run Long,$^{3,5}$ Linfeng Sun,$^{†}$ Chung-Che Huang,$^{†}$ Jun Zhang,$^{*,†}$ Qihua Xiong,$^{*,†}$ Daniel W. Hewak,$^{†}$ Zexiang Shen,$^{†,8}$ Oleg V. Prezhdo,*$^{†}$ and Zhi-Heng Loh$^{*,†,#}$

1Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore, 2Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States, 3School of Physics, Complex Adaptive Systems Laboratory, University College Dublin, Belfield, Dublin 4, Ireland, 4Centre for Disruptive Photonic Technologies, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore, 5Optoelectronics Research Centre, University of Southampton, Southampton SO17 183, United Kingdom, 6Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore, 7NOVITAS, Nanoelectronics Centre of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore, and 8Division of Materials Technology, School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

ABSTRACT  Femtosecond optical pump—probe spectroscopy with 10 fs visible pulses is employed to elucidate the ultrafast carrier dynamics of few-layer MoS$_2$. A nonthermal carrier distribution is observed immediately following the photoexcitation of the A and B excitonic transitions by the ultrashort, broadband laser pulse. Carrier thermalization occurs within 20 fs and proceeds via both carrier—carrier and carrier—phonon scattering, as evidenced by the observed dependence of the thermalization time on the carrier density and the sample temperature. The $n^{-0.37±0.03}$ scaling of the thermalization time with carrier density suggests that equilibration of the nonthermal carrier distribution occurs via non-Markovian quantum kinetics. Subsequent cooling of the hot Fermi—Dirac carrier distribution occurs on the ∼0.6 ps time scale via carrier—phonon scattering. Temperature- and fluence-dependence studies reveal the involvement of hot phonons in the carrier cooling process. Nonadiabatic $ab$ $initio$ molecular dynamics simulations, which predict carrier—carrier and carrier—phonon scattering time scales of 40 fs and 0.5 ps, respectively, lend support to the assignment of the observed carrier dynamics.

KEYWORDS: MoS$_2$ · ultrafast dynamics · nonthermal · carrier—carrier scattering · carrier—phonon scattering · quantum kinetics

Inspired by the remarkable electronic properties of graphene,1,2 explorations of other two-dimensional (2D) materials3,4 have led to the emergence of few-layer transition metal dichalcogenides as promising candidates for a new generation of optoelectronic materials.5,6 Of the various few-layer transition metal dichalcogenides, molybdenum disulfide (MoS$_2$) is the most extensively studied to date.7 The indirect band gap of bulk MoS$_2$ (1.3 eV)8 increases with decreasing number of layers, eventually culminating in the emergence of a 1.8 eV direct band gap semiconductor in the case of single-layer MoS$_2$.5,10 The transition from indirect to direct band gap is evidenced by the $>100$-fold enhancement of the photoluminescence quantum yield for single-layer MoS$_2$ compared to bulk MoS$_2$. The existence of a direct band gap in the visible and its relatively strong photoluminescence make single-layer MoS$_2$ well-suited to a variety of optoelectronic applications.11,12 Moreover, as a result of the broken inversion symmetry, single-layer MoS$_2$ possesses two nonequivalent, energetically degenerate valleys at the corners of the first Brillouin zone, labeled K and K'. Coupled with the opposite spin projection of the two spin—orbit—split valence bands, selective photoexcitation of either the K or K' valley can be achieved with circularly polarized light.13–16 The ability to address the valley degree of freedom optically suggests a possible route to optoelectronic devices based on valleytronics.13,17

The application of few- to single-layer MoS$_2$ in optoelectronics necessitates a detailed understanding of its fundamental carrier dynamics. For example, ultrafast carrier dynamics are known to determine the electronic transport and optical properties of semiconductors.18 For applications in
valleytronics, it is also important to understand how carrier–carrier and carrier–phonon scattering events impact the valley polarization. Motivated by the above considerations, the ultrafast dynamics of single- and few-layer MoS₂ has recently been investigated by several groups. Time-resolved photoluminescence measurements show carrier recombination on a few-picosecond time scale and insignificant polarization decay over the entire emission duration.¹⁹,²⁰ Pump–probe microscopy allows carrier diffusion to be resolved in real space,²¹ in addition to the observation of carrier recombination and the trapping of excitons by surface defects.²² Helicity-resolved optical pump–probe spectroscopy reveals subpicosecond loss of conduction band valley polarization and a slower, ~10 ps time scale for valence band valley depolarization.²³,²⁴ The observed loss of valley polarization is attributed to trapping of excitons by defect states and Coulomb-induced coupling to dark excitonic states. Finally, a 500 fs decay component observed directly via transient absorption spectroscopy has been assigned to exciton–exciton scattering.²⁵ The above studies on single- to few-layer MoS₂ are complemented by investigations of the ultrafast dynamics of bulk MoS₂. Two-photon photomission of bulk MoS₂ reveals <100 fs hot-carrier relaxation dynamics,²⁶ whereas intervalley scattering, carrier cooling, and carrier recombination are observed by transient reflectivity microscopy to occur with time constants of 0.35, 50, and 180 ps, respectively.²⁷

Here, we report the application of optical pump–probe spectroscopy with 10 fs, linearly polarized pulses to investigate the earliest ultrafast carrier dynamics that follow the photoexcitation of few-layer MoS₂. The five-layer MoS₂ sample was prepared by chemical vapor deposition and shown by Raman and atomic force microscopies to be highly homogeneous (Supporting Information Figure S1). The large spectral bandwidth of the pump pulse (560–740 nm at −10 dB) allows simultaneous excitation of the A and B excitonic transitions of MoS₂ (Figure 1a and Supporting Information Figure S2), which, for the case of linearly polarized

Figure 1. (a) UV/visible absorption spectrum of five-layer MoS₂ sample at 77 K (solid line). The A and B excitonic transitions are located at 665 and 612 nm, respectively. The normalized spectral density of the 10 fs laser pulses employed for pump and probe is also shown (dashed line). (b) The A and B excitonic transitions in MoS₂ correspond to the transitions from the spin–orbit–split Kᵥ and Kᵥ valence bands, respectively, to the conduction band Kᵥ at the K and K’ points.

RESULTS AND DISCUSSION

The temporal evolution of the differential transmis-

The temporal evolution of the differential transmission (ΔT/T) spectrum obtained following photoexcitation of five-layer MoS₂ by 10 fs visible pulses is shown in Figure 2. The positive ΔT/T reflects ground state bleaching of the A and B excitonic transitions and stimulated emission from the excited states. In addition, a negative ΔT/T feature, corresponding to excited state absorption, is observed to the low-energy side of the A exciton transition, as well as in between the two excitonic transitions. Recently reported optical pump–probe data obtained after selective excitation of the B exciton transition shows qualitatively similar features.²⁵ The excited state absorption has been attributed to carrier-induced broadening of the excitonic transitions,²⁵ or alternatively, to exciton-biexciton transitions.²⁴ The ultrafast dynamics appear to be biphasic on the time scale of our measurements, which spans <10 fs to 5 ps (see below). In the remainder of this section, the time constants for the fast and slow
processes are denoted $\tau_f$ and $\tau_s$, respectively. It is important to note here that the free-carrier origin of the ultrafast dynamics entails time constants that are slightly dependent on the probe frequency $\omega_{pr}$. This is because a given $\omega_{pr}$ interrogates the carrier dynamics in a specific region of $k$ space where the resonance condition $\hbar \omega_{pr} = E_i(k) - E_f(k)$ is fulfilled; $E_i(k)$ and $E_f(k)$ are the $k$-dependent energies of the final and initial states that are coupled by the probe transition, respectively. Within the context of carrier thermalization and cooling, the time-dependent differential transmission signal at a given probe wavelength gives the time-evolution of a specific region of the carrier distribution functions.

At short pump–probe time delays ($\tau < 50$ fs), the differential transmission spectra have predominantly positive $\Delta T/T$ values (Figure 3a) and resemble the calculated absorbed laser spectrum (Supporting Information Figure S3). The appearance of these spectra is indicative of saturable absorption and provides strong evidence for the existence of nonthermal carrier distributions. Unlike traditional spectral hole-burning that is effected by narrowband lasers, the broadband excitation employed in this work yields a broad spectral hole that overlaps with the ground state bleaching. Moreover, the multitude of ultrafast phenomena—carrier—carrier and carrier—phonon scattering, band gap renormalization, and band filling, all of which are simultaneously operative following the pump excitation, results in complex differential transmission spectra at short time delays. The decomposition of the spectral features in terms of the various ultrafast processes requires further experimental and theoretical investigations that are beyond the scope of this study. Here, we focus on the feature at 655 nm in order to extract time constants that are representative of the ultrafast dynamics at short time delays. A pronounced hole-burning response is expected at this probe wavelength due to its close proximity to the 660 nm center wavelength of the pump pulse. This feature becomes stronger with increasing excitation pump fluence. Its temporal evolution comprises an ultrafast <20 fs decay component $\tau_f$ and a slower $\sim 0.6$ ps component $\tau_s$ (Figure 3b). The former is hitherto unobserved due to the limited $\gtrsim 100$ fs time resolution employed in previous time-resolved studies, although a recent Z-scan measurement of liquid-phase-exfoliated MoS$_2$ nanosheets suggests carrier relaxation times of $\sim 30$ fs. The time constant for the fast decay $\tau_f$ decreases with increasing excitation pump fluence $F$ according to the power law $\tau_f \propto F^{-0.37 \pm 0.03}$ (Figure 3c).

The power law can be rewritten as $\tau_f \propto n^{-0.37 \pm 0.03}$ because the differential transmission signal, and hence the carrier density $n$, varies linearly with $F$ over the entire range of excitation fluences employed in the experiments (Supporting Information Figure S4). Moreover, temperature-dependence measurements show that $\tau_f$ initially decreases with $T$ according to the relation $\tau_f \propto T^{-0.08 \pm 0.03}$ up to a sample temperature of $T \sim 300$ K, beyond which it exhibits a rapid decrease following $T^{-1.49 \pm 0.23}$ (Figure 3d).

The appearance of the <20 fs decay component $\tau_f$ is assigned to the evolution of the initial nonthermal distribution of carrier energies toward a hot quasi-equilibrium Fermi—Dirac distribution. The measured carrier thermalization time is comparable to those of graphene and graphite, which were found to be $<50$ and $13 \pm 3$ fs, respectively. At sufficiently high carrier densities, carrier thermalization is mediated primarily by carrier—carrier scattering, for which ab initio nonadiabatic molecular dynamics simulations predict a characteristic time scale of 37 fs (Figure 3e). As a result of its contribution from carrier—carrier scattering, the thermalization rate is expected to increase with carrier density, as observed in our experimental data (Figure 3c).

The quantitative scaling of carrier—carrier scattering time constants with carrier density for samples of different dimensionality has been a subject of considerable debate. Femtosecond photon echo measurements performed on bulk GaAs and two-dimensional Al$_x$Ga$_{1-x}$As quantum wells suggests that carrier—carrier scattering times should scale as $n^{-1/2}$, where $D$ is the dimensionality of the sample. This result is consistent with a model that assumes a short-ranged and strongly screened Coulomb interaction that allows carrier—carrier scattering only between nearest neighbors. Within this framework, the carrier—carrier scattering rate scales as $n^{-1/2}$ for a $D$-dimensional sample. The stronger carrier—density dependence observed for a 2D material is rationalized in terms of carrier confinement leading to less effective screening of the carrier—carrier Coulombic interaction. The localization of carriers in MoS$_2$ to a 2D plane, with negligible extension of the carrier wave functions along the interlayer direction in the case of multilayer samples, is therefore expected to yield an $n^{-1/2}$-dependence for the carrier—carrier scattering time constant, in contrast to the $n^{-1/3}$-scaling that is suggested by our experimental results. This expectation, however, is inconsistent with the identical carrier
thermalization rates found for In$_{0.47}$Ga$_{0.53}$As quantum wells with thicknesses spanning the one-dimensional quantum confinement to bulk regimes. Furthermore, recent experimental measurements performed on Al$_x$Ga$_{1-x}$As quantum wells over a larger range of carrier densities than that accessed in ref 37 show unequivocally that carrier–carrier scattering time constants scale as $n^{1/3}$ even in 2D systems. The $n^{1/3}$-dependence observed in the MoS$_2$ sample is suggestive of non-Markovian quantum kinetics. In contrast to Boltzmann kinetics, which treats carrier–carrier scattering events as irreversible processes of negligible durations that are local in both space and time, non-Markovian quantum kinetics considers the phase-coherent, wave-like nature of the carriers on short time scales, from which finite scattering durations and memory effects emerge, as well as the finite time for the buildup of screening. In the presence of carrier phase coherence, the duration of a carrier–carrier scattering event $T_{coh}$ is given by the relation $T_{coh} = \hbar/\Delta E_{coh}$, where $\Delta E_{coh}$ is the energy separation between the initial and final states. When $T_{coh}$ becomes comparable to or longer than the interval between successive scattering events, the Fermi Golden Rule-type description of scattering in terms of a single rate, as in semiclassical Boltzmann kinetics, is no longer valid.

Figure 3. (a) $\Delta T/T$ spectra acquired at 15 fs time delay for various excitation pump fluences at 77 K. The $\Delta T/T$ spectrum acquired at a time delay of 100 fs, representative of a thermalized carrier distribution, is also shown for comparison. (b) $\Delta T/T$ time trace obtained at 655 nm probe wavelength with 0.11 mJ/cm$^2$ excitation fluence and 77 K sample temperature. The solid line is a fit to a biexponential decay convolved with the instrument response function. (c) Dependence of the fast decay component $\tau_f$ on excitation fluence $F$ at 77 K. The solid line is a fit to the power law $\tau_f \sim F^{-0.37\pm0.03}$. (d) Dependence of the fast decay component $\tau_f$ on the sample temperature $T$. The time constant $\tau_f$ initially shows a gradual decrease according to $\tau_f \sim T^{-0.06\pm0.05}$ followed by a rapid decrease beyond $T \sim 300$ K that scales as $T^{-1.49\pm0.23}$. The excitation fluence is kept constant at 0.33 mJ/cm$^2$. (e) Time trace for electron–electron scattering obtained from ab initio nonadiabatic molecular dynamics (solid line), which reveals a 37 fs time constant (dashed line exponential fit) for the scattering of carriers. The inset shows the simulated dephasing of carriers (solid line) on a 35 fs time scale (dotted line exponential fit). (f) Zeroth-moment time trace $\langle \chi(0) \rangle$ computed about the A exciton transition, suggestive of <20 fs intervalley scattering. The solid line is a fit to a biexponential decay convolved with the instrument response function. The excitation fluence is 0.33 mJ/cm$^2$, and the sample temperature is 77 K.
applicable. Studies of early time carrier dynamics in the coherent regime must therefore be analyzed within the framework of non-Markovian quantum kinetics. In this work, carrier phase coherence is favored by the coherent excitation of the A and B transitions by broadband 10 fs pulses. Semiclassical evaluation\(^44\) yields an electronic coherence time of 35 fs (Figure 3e inset) that is comparable to the time between successive scattering events. This result lends support to the observation of carrier–carrier scattering in the quantum kinetic regime. The existence of relatively long-lived carrier phase coherence is further complicated by the finite time required for screening to be established, which occurs on the time scale of the inverse plasmon frequency \(\omega_p^{-1}\).\(^45\) In fact, it is the retarded quantum-kinetic screening that results in the observed \(n^{-1/3}\)-dependence of \(\tau\).\(^1\) Contrastingly, scattering times for both 2D and 3D materials,\(^6,46\) by contrast, the initial analysis that gave the \(n^{-1/3}\)-dependence assumes the instantaneous creation of a short-ranged, strongly screened Coulomb potential by the pump pulse.\(^36,37\) It is important to note that the buildup of screening can be slower in 2D than 3D systems, since \(\omega_p\) in the case of the former vanishes in the limit of small wavevector.\(^47\) As such, it is conceivable that non-Markovian quantum kinetics manifests itself more strongly in 2D than in 3D systems.

The observed temperature-dependence of \(\tau\) suggests that carrier–phonon scattering also contributes to carrier thermalization. While the effect of temperature on carrier–phonon scattering in MoS\(_2\) remains unexplored by time-resolved studies, information on electron–phonon scattering can nonetheless be inferred from temperature-dependent electron mobility measurements. Indeed, within the relaxation time approximation, the time interval between scattering \(\tau\) is related to the electron mobility \(\mu\) by the Drude relation \(\mu = e\tau/m^*\), where \(m^*\) is the effective electron mass.\(^48\) Our experimental data shows that the gradual decrease in \(\tau\) at low temperatures is followed by a more rapid increase at higher temperatures (Figure 3d). This behavior is qualitatively similar to the temperature-dependent electron mobility curves exhibited by mono- and bilayer MoS\(_2\) as well as bulk samples.\(^28,49\)–51\) Analogous to the situation encountered in electron mobility, the plateau in the measured thermalization time constant \(\tau\) at low temperatures can be attributed to charged-impurity scattering counteracting the scattering of carriers by acoustic and optical phonons.\(^52\) At higher temperatures, carrier–phonon scattering dominates and results in the power law \(\tau \propto T^{-\gamma}\). Despite the experiment being performed on a five-layer MoS\(_2\) sample, it is noteworthy that the measured exponent \(\gamma\) of 1.49 \(\pm\) 0.23 in the present work is similar to those previously measured \((\gamma = 1.4, 1.7)\)\(^28,49\) and predicted \((\gamma = 1.69)\)\(^52\) for monolayer MoS\(_2\); in comparison, bulk MoS\(_2\) exhibits a significantly higher \(\gamma\) value of 2.6.\(^50,51\) The observed similarity of the \(\gamma\) values could be coincidental, since measurements and simulations of mobility have focused on that of electrons alone, whereas the time constant \(\tau\) obtained from our pump–probe measurements reflects the dynamics of both electrons and holes.

Further evidence for the participation of carrier–phonon scattering in the sub-20 fs carrier thermalization process comes from examining the zeroth-moment time trace for the bleaching band of the A exciton transition (Figure 3f). The zeroth moment, defined as \((\lambda(0)(t)) = \int_0^\infty d\lambda \Delta T(\lambda, t)/\Delta T(\lambda))\), gives the total population of carriers in the region of \(k\) space whose valence and conduction bands are optically coupled by probe wavelengths that span \(\lambda\), to \(\lambda\).\(^54\) The \((\lambda(0)(t))\) time trace computed for the A transition exhibits a biphasic decay. The faster component is characterized by a time constant of 15.4 \(\pm\) 0.2 fs, consistent with that obtained from monitoring the single-wavelength kinetics at 655 nm (14.1 \(\pm\) 0.3 fs). The decrease of the spectrally integrated stimulated emission signal with time delay is indicative of the rapid scattering of carriers away from the initially populated K valley (the Franck–Condon region). Inspection of the calculated band structures for few-layer MoS\(_2\) suggests that electrons can scatter to the Q valley, located midway between the K and \(\Gamma\) points and where the conduction band minimum resides, whereas holes can scatter to the valence band maximum located at the \(\Gamma\) valley.\(^38,55\) Such intervalley scattering must be phonon-mediated in order to satisfy momentum conservation. Among the various phonons that are present in MoS\(_2\), the longitudinal acoustic (LA) phonon has been identified by first-principles calculations to be the dominant source of intervalley carrier–phonon scattering.\(^56\) In fact, the theoretical total intervalley scattering rate of >0.05 fs\(^{-1}\) supports the observed <20 fs thermalization time constant.

Beyond the ultrafast carrier thermalization dynamics, the optical pump–probe data also reveals slower carrier dynamics (Figure 4a). The \(\Delta T/T\) time traces obtained at the A and B excitonic transitions decay monexponentially with time constants \(\tau\) of 0.64 \(\pm\) 0.01 and 0.54 \(\pm\) 0.01 ps, respectively. Both excitation fluence- and temperature-dependence measurements show that the time constant \(\tau\) is prolonged by increasing fluence (Figure 4b) and temperature (Figure 4c). The observed behavior is consistent with the hot phonon effect, whereby a large phonon population that results from either higher lattice temperatures or larger photoexcitation fluences, along with a slow phonon relaxation rate (>10 ps; Supporting Information Figure S5), impedes carrier cooling via phonon emission.\(^57,58\) The origin of the \(\tau\) decay constant can therefore be attributed to carrier cooling, in good agreement with the 0.5 ps cooling time predicted by \textit{ab initio} nonadiabatic molecular dynamics simulations.
The weak oscillatory feature in the simulated electron cooling time trace with a frequency of $400 \text{ cm}^{-1}$ (Figure 4d inset) is suggestive of the participation of the A$_{1g}$ and/or E$_{1g}^2$ LO phonons$^{59}$ in the electron cooling process. We note that the $\sim 0.6$ ps time scale for carrier cooling observed in the present work is comparable to the $0.35$ ps intervalley scattering time constant that was reported for bulk MoS$_2$. Under our experimental conditions, however, the excitation fluence-dependence exhibited by the $0.6$ ps decay component is incompatible with a previously proposed exciton–exciton scattering process.$^{25}$ Contribution from exciton–exciton annihilation, which is expected to accelerate with increasing excitation pump fluence, can similarly be ruled out based on the observed fluence-dependence.

The above assignment of $\tau_s$ to carrier cooling is further supported by the observed blueshift of the spectral first moments of the A and B transitions as a function of time delay. The excitation fluence is $0.33 \text{ mJ/cm}^2$, and the sample temperature is $77$ K. The solid lines are fits to exponential shifts of $1.2 \pm 0.1$ ps. Figure 4(e) is indicative of band filling, or the dynamic Burstein–Moss shift, that accompanies intravalley carrier relaxation to the band edge.$^{50,61}$ On a
To extract reliable time constants the hole at the K point of MoS2, a sp 3 r e d i c t e d by whereby the larger e to the separate electron and hole cooling channels, tentatively attribute the existence of two time constants noticeably di

cerns. The resultant pulses enter a Mach–Zehnder interferometer, which consists of a motorized translation stage incorporated into the probe arm to generate a computer-controlled time delay between pump and probe pulses. The time resolution of the apparatus is 14 fs to generate a computer-controlled time delay between pump pulses centered at 660 nm with a spectral bandwidth of ∼200 nm. These pulses are produced by spectral broadening of the 25 fs output from an amplified Ti:sapphire laser system in a helium-filled hollow-core fiber followed by chirped mirror compression and six bounces off of a broadband dielectric mirror pair with 650 nm center wavelength. A pair of fused silica wedges is used for dispersion fine-tuning. The resultant pulses enter a Mach–Zehnder interferometer, which consists of a motorized translation stage incorporated into the probe arm to generate a computer-controlled time delay between pump and probe pulses. The time resolution of the apparatus is 14 fs (Supporting Information Figure S6), as determined by the width of the second-order intensity cross-correlation between pump and probe pulses. The cross-correlation is performed in a 10-μm-thick BBO crystal located at the position of the sample target. To extract reliable time constants τf for the fast decay component, the measured time traces are fitted to a convolution of the instrument response function with a biexponential decay function. Typical pulse energies for pump and probe beams are 100 and 20 nJ, respectively; both beams have focal spot diameters (1/e²) of 200 μm. The pump and probe beams are orthogonal polarized to minimize the contribution of coherent artifacts to the measured signal, which can be further suppressed by singular-value decomposition of the two-dimensional probe wavelength-time delay data set (Supporting Information Figure S5). The transmitted probe beam is spectrally dispersed in a 300 mm spectrograph and detected on a 1024-element linear array detector. The detector has a read-out rate of 1 kHz and is synchronized to the 500-Hz optical chopper positioned in the path of the pump beam. Fluence-dependence measurements confirm that the differential transmission signal is linear in the range of pulse energies used in the experiments (Supporting Information Figure S4). The MoS2 sample is housed in a vacuum cryostat that is evacuated to <10⁻⁶ mbar to perform the variable temperature measurements. The vacuum environment also minimizes sample degradation by potential atmospheric oxidation over the course of the measurements.

The 5-layer MoS2 sample is prepared by chemical vapor deposition. The MoCl5 precursor (99.6%, Alfa Aesar) is kept in a bubbler at room temperature and its vapor is delivered by argon gas, which acts only as a carrier gas, through a mass flow controller (MFC) to the CVD quartz tube. The reactive gas, H2S, is generated in situ by the reaction of 18% aqueous HCl and FeS (99%, Strem) and delivered diluted with argon gas through a second MFC. The H2S/argon mix is purified by passing through an in-line dryer before entering the CVD reactor. The flow rates for delivering MoCl5 precursor and H2S are 250 and 200 sccm, respectively. After 25 min, the CVD-grown Mo–S thin films are annealed with H2 and H2S mixture gases at 500 °C to remove Cl atoms, followed by an additional annealing process with H2S gas at 900 °C to convert MoS3 to MoS2.

**Theoretical Methods.** We apply *ab initio* nonadiabatic molecular dynamics (NAMD) implemented within time-domain density-functional theory (TDDFT) to model the electron–electron scattering and electron–phonon relaxation in an 108-atom bilayer MoS2. The simulations are carried out using the Vienna *ab initio* simulation package (VASP) enhanced with the NAMD capabilities. The generalized gradient approximation functional of Perdew, Burke and Ernzerhof and the projector augmented wave approximation for the core electrons are used. The system is periodically replicated in three dimensions. To prevent spurious interactions between the bilayer images, 8 Å of vacuum is added perpendicular to the bilayer. The optimized MoS2 bilayer is heated to 300 K by
repeated velocity rescaling. A 5 ps microcanonical MD trajectory is generated in the ground state with a 1 fs time step. van der Waals interactions\(^\text{11}\) are included to stabilize the bilayer system during geometry optimization and MD simulations. The calculated density of states of the bilayer MoS\(_2\) is shown in Figure S8 of Supporting Information.

To model the photoinduced electron–phonon dynamics in the time-domain, we utilize fewest switches surface hopping (FSSH)\(^\text{77}\) implemented within TD-DFT with the classical path approximation.\(^\text{82}\) FSSH is a NAMD methodology that converts the time-dependent Schrödinger equation into a master-type equation with time-dependent transition rates. With a stochastic algorithm, it accounts for correlation of phonon trajectories with different electronic states, gives trajectory branching, and satisfies detailed balance between transitions upward and downward in energy. The latter property ensures that thermodynamic equilibrium is achieved at long times.\(^\text{73}\) The many-electron configurations are expressed using Slater determinants, which are built from the one-electron Kohn–Sham (KS) orbitals. The NA couplings between the many-electron configurations are expressed in terms of the NA couplings between the KS orbitals.\(^\text{66,67}\) They are computed numerically using the approximation.\(^\text{64}\) A detailed description of the algorithm and discussion of its capabilities and limitations can be found elsewhere.\(^\text{67,68}\)

NAMD-TD-DFT generates nonequilibrium electron–phonon trajectories, subject to an initial condition. For each configuration in the bilayer MoS\(_2\) system, the initial state was chosen by selecting the adiabatic configuration with the largest optical transition dipole moment from the ground state, within the relevant energy range. To allow both electron–electron and electron–phonon scattering, the simulations include configurations with one and two active electrons and holes. To characterize the carrier phase coherence during the electron–electron scattering we compute the pure-dephasing function, as described in ref 44. The coherence in the electronic subsystem is destroyed due to elastic interactions with the phonon subsystem.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. This work is supported by a NTU start-up grant, the A*Star Science and Engineering Research Council Public Sector Funding (122-PSF-0011), and the award of a Nanyang Assistant Professorship to Z.-H.L. Z.N. and Z.-H.L. are grateful to T. Kobayashi for useful discussions. R.L. thanks Science Foundation Ireland SIRG Program (11/SIRG/E2172). Q.X. gratefully acknowledges Singapore National Research Foundation through a NRF fellowship grant (NRF-OF2009-06). Ministry of Education via an AcRF Tier 2 grants (MOE2012-T2-2-086), and a start-up grant support (MS8113004) from NTU. O.V.P. acknowledges financial support from the US National Science Foundation (CHE-1300118). Thin film deposition work undertaken at the Optoelectronics Research Centre at the University of Southampton is funded in part by the EPSRC Centre for Innovative Manufacturing in Photonics (EP/H02607X/1) and the Zepler Institute Stimulus fund.

Supporting Information Available: Sample characterization by AFM and Raman microscopy, variable-temperature absorption spectroscopy, calculated photoexcited carrier densities and absorbed laser spectrum, excitation pump fluence-dependence measurements, measurement of phonon relaxation time constants, optical pump–probe cross-correlation, suppression of coherent artifact by singularity-value decomposition, and calculated density of states for bilayer MoS\(_2\). This material is available free of charge on Internet at http://pubs.acs.org.

REFERENCES AND NOTES


