Electrical and Chemical Tuning of Exciton Lifetime in Monolayer MoS₂ for Field-Effect Transistors

Pradeepa H L, Praloy Mondal, Aveek Bid, and Jaydeep K. Basu*

Cite This: *ACS Appl. Nano Mater.* 2020, 3, 641–647

Read Online

ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: We report the room temperature tuning of excitonic lifetime in pristine and hole-doped monolayer MoS₂ based field effect transistor (FET) devices by systematically controlling the free carrier density. We observed that in pristine MoS₂ devices, with intrinsic electron doping, an exciton dominant regime with an exciton lifetime of 3 ns exists, when doped electrostatically with holes. Interestingly we observe a sharp decrease in exciton lifetime and population with an increase of the electron density by electrostatic doping, with a corresponding increase in negative trion population. With increased hole doping by a chemical method, the exciton lifetime decreases, but it remains almost constant with electrostatic carrier density tuning. This decrease in lifetime, compared to that of the pristine case, might be due to the exciton–exciton annihilation mechanism which is proposed to be existent in a high exciton density regime. Further hole doping by a chemical method leads to a transition to a positive trion dominated regime, in which the exciton lifetime decreases further due to nonradiative energy transfer to the positive trions. We observe a slight increase in exciton lifetime due to partial neutralization of positive trions at high electrostatic electron doping and a corresponding increase in the probability of excitons. We suggest that when calculating the lifetime of excitons, the exciton-to-trions formation and exciton–exciton annihilation mechanisms should be considered. These fine-tunings of excitons in monolayer MoS₂ can provide a platform for probing the excitonic physics and photonic applications.

KEYWORDS: MoS₂, TRPL, exciton, trion, exciton–exciton annihilation, trion formation, FET

INTRODUCTION

Monolayer transition metal dichalcogenides (TMDC) are known to have several interesting optical and electronic properties, including a transition from indirect to direct bandgap when exfoliated from a few layers to a single layer.^{1–10} These materials have potential application in optoelectronic devices such as photodetectors and light-emitting diodes (LED) etc.^{11,12} As a result of this reduced dimension of monolayer (thickness 6 Å) and dielectric screening, the binding energy of various quasiparticles such as excitons and trions can be significantly higher than their bulk counterparts. For example in molybdenum disulfide (MoS₂), a widely studied TMDC, the binding energy for exciton and trion are reported to be ~600 meV and ~40 meV, respectively.^{13–18} This implies that these quasiparticles are stable even at room temperature, and it becomes convenient to

study their dynamics at higher temperatures. The understanding and control of the lifetime of the quasiparticles in these materials is important from both a fundamental and applied physics approach.

Despite several efforts in this direction the dynamics of these quasiparticles are not well understood. While detailed theoretical models have been published recently to study the temperature and free carrier density dependence of exciton and trion dynamics,^{20–24} no systematic experimental study exists, to the best of our knowledge. This is partly because in real devices, excitons, trions, and free carriers usually coexist,

Received: November 5, 2019

Accepted: December 24, 2019

Published: December 24, 2019

Figure 1. (a) Schematic of the experimental setup. (b) Raman spectrum of the monolayer. Inset: Optical image of the device.

leading to difficulties in understanding the inherent dynamics of individual quasiparticles. Moreover, the properties are significantly dependent on the unavoidable intrinsic defects and contamination during exfoliation and subsequent device fabrication.²⁵ This further complicates the interpretation of experimental results with theory. A theoretical calculation shows that the lifetime of excitons increases with increasing the doping at all temperatures.²⁰ However, these calculations estimate the lifetime of excitons or trions only in the presence of free carriers and neglect the simultaneous presence of either trions or excitons, respectively, in the system.

It was shown that positive and negative trions show a similar photoluminescence intensity profile with carrier density (n_e) at low temperature.¹⁵ The carrier density dependency of optical properties is of particular interest in these 2D materials; however, the electrical way of tuning n_e by using the standard field effect transistor (FET) configuration restricts the tunability range. This limitation constrains the study of both positive and negative trions at room temperature. Along with FET the chemical doping is identified to be an alternative, efficient, and suitable technique to amend the carrier density of the monolayer materials, including graphene.^{26,27} Recently it was shown that the nonradiative channels can be suppressed by applying gate voltage. In addition when the quantum yield (QY) is near unity, it is possible to demonstrate exciton and positive as well as negative trion recombination simply by measuring the QY.¹⁹ Laser power dependence can also alter the exciton–trion ratio by altering the exciton density. However, the possibility to alter free carrier density is not possible with such purely optical methods. On the other hand optical studies on FET devices allow the possibility to vary the free carrier density (both electrons or holes) for a given density of excitons which can be further tuned through appropriate chemical doping. Thus, such optoelectronic measurements allow for more detailed study of quasiparticle excitation dynamics due to alteration of the free carrier density. In general for samples in which QY is lower detailed analysis of PL lifetime along with steady state PL spectroscopy is necessary to obtain a comprehensive picture of exciton–trion interplay. More importantly, details of the dynamics of excitons and trions or of the recombination processes including nonradiative channels such as exciton to trion formation and exciton–exciton annihilation due to alteration of free carrier density through electrostatic doping in an FET device can only be explored with a combination of time-resolved and steady state PL spectroscopy.

In this manuscript, we report a transition between quasiparticle states using time-resolved (TRPL) and steady state PL spectroscopy by tuning the carrier density of MoS₂ monolayer in a FET configuration. Chemical doping along with electrostatic doping through back gate voltage variation in the FET device allows us to tune the free carrier and quasiparticle density. Electrostatic doping for a given level of chemical doping helps us to reach the predominantly neutral exciton, negative trion, and positive trion regimes. This combination is advantageous over the individual electrical or chemical method of controlling the exciton population as it can tune the free carrier density over a much broader regime. Our results show a decrease in exciton lifetime with an increase of the doping, which is opposite to the trend suggested in recent theoretical results. We show that the presence of an exciton–trion conversion channel can significantly influence the exciton lifetime. Present theoretical calculations ignore this exciton–trion formation process in estimations of the influence of free carriers on exciton and trion lifetime. We suggest that while calculating the lifetime of excitons or trions, the exciton–trion formation and exciton–exciton annihilation mechanisms probably need to be considered for more accurate estimates of quasiparticle carrier dynamics.

RESULTS AND DISCUSSION

MoS₂ monolayer flakes were prepared by using a standard exfoliation technique on polydimethylsiloxane (PDMS) sheets and then transferred on prepatterned contact pads on a 300 nm SiO₂ substrate to make a FET for back gate configuration as shown in Figure 1a. Optical microscopy and Raman spectroscopy were used to identify the monolayers. Figure 1b shows the Raman shift of the monolayer, with the inset showing the optical image of the device. PL spectra were collected using the Horiba (LabRam model) instrument, using 532 nm continuous wave (CW) laser to excite the sample, keeping the laser power at $\sim 5 \mu\text{W}$. Signals were collected using a charge coupled device (CCD). The 300 g/mm grating and 1800 g/mm grating were used to collect the PL and the Raman spectra, respectively. TRPL spectra were collected using PicoQuant MicroTime 200 system. The temporal resolution of the system was 25 ps. A 507 nm laser with 40 MHz repetition rate was used to excite the sample keeping the power at $\sim 5 \mu\text{W}$. A 50 $\times$ (Olympus NA-0.45) objective was used to collect both PL and TRPL data. Keithly (model 2400) source meters were used to apply back gate voltage and to measure channel current. Chemical hole doping was done by following

Figure 2. The PL of monolayer MoS₂ at selected gate-voltages V_g for different hole-doping levels achieved via chemical treatment: (a) pristine sample ($n_e = 1.0 \times 10^{12} \text{ cm}^{-2}$); (b) medium-hole-doped sample ($n_e = 7.6 \times 10^{11} \text{ cm}^{-2}$); (c) high-hole-doped sample ($n_e = 2.4 \times 10^{11} \text{ cm}^{-2}$). In all cases, the data for $V_g = -70$ V have been fitted with multiple Lorentzian functions (the red line shows the cumulative fit) to resolve neutral A-exciton (X^0 , shown in brown lines) and trion (X , shown in blue lines). (d) Ratio of the amplitudes of A-excitons and trions versus V_g measured at the different chemically doped regimes. The notations h-doped and e⁻-doped indicate, respectively, regions of V_g in which the sample becomes electrostatically doped with holes and electrons due to the back-gate, over and above the chemical doping. P, M, and H indicate pristine, medium-hole-doped, and high-hole-doped cases, respectively.

the work of Mouri et al.²⁶ Hole doping via the chemical method was achieved by drop casting 0.04 $\mu\text{mol/mL}$ dopant solution of TCNQ on pristine MoS₂. This step was repeated multiple times to achieve higher doping of the pristine MoS₂.

The emission spectra of monolayer MoS₂ consists of two peaks at around 1.88 eV (A exciton) and 2.0 eV (B exciton), which are related to the direct bandgap transition at K (K') point with the energy difference between the A and B peaks corresponding to the valence band splitting due to the strong spin orbital.^{28–30}

Figure 2a–c represents the PL spectra of the pristine and various chemically hole dopant MoS₂ FET at different gate voltages. The PL spectra were fitted with Lorentzian curves, using eq 1. The exciton peak is denoted by X^0 and the trion peak is denoted by X . X can be negative or positive depending on the doping condition. The exciton and trion peak characteristic values such as intensity, energy, etc. were extracted from these fits. The Lorentzian equation used for the fittings can be written as

$$y = y_0 + \frac{I_{\text{exciton}}}{\left[\frac{2(E - E_{\text{ex}})}{W_{\text{ex}}} \right]^2 + 1} + \frac{I_{\text{trion}}}{\left[\frac{2(E - E_{\text{tr}})}{W_{\text{tr}}} \right]^2 + 1} + \frac{I_{\text{Bex}}}{\left[\frac{2(E - E_{\text{Bex}})}{W_{\text{Bex}}} \right]^2 + 1} \quad (1)$$

where I_{exciton} , E_{ex} , and W_{ex} are the intensity, the energy position, and the full width at half-maximum (fwhm) of A exciton, respectively. I_{trion} , E_{tr} , and W_{tr} are the intensity, the energy position, and the fwhm of trion, respectively. I_{Bex} , E_{Bex} , and W_{Bex}

are the intensity, the energy position and the fwhm of B exciton, respectively. Detail fitting is available in section 4 of Supporting Information (SI).

Figure 2a shows the PL spectra of pristine MoS₂. In this case, it is observed that the trion PL intensity is affected much less by doping done by applying back gate voltage V_g (changing the carrier density n_e), whereas the exciton PL intensity is relatively more sensitive to the n_e . With the increase in V_g , both the intensity of exciton and the total PL decreases. As we increase V_g to positive, the electron density increases, which will increase the probability of negative trion formation from excitons which will lead to a decrease in the intensity of excitons. Figure 2b shows the PL spectra of medium-hole-doped MoS₂. In this case, it is observed that the total PL intensity is higher than that of the pristine. This enhancement is due to the suppression of negative trions by chemical doping. With the high-hole-doped by chemical treatment case we observe the PL intensity to drop considerably. We observe a very less gating sensitive PL spectra (Figure 2c), similar to the observation of a PL less sensitive to gating or reduction in exciton density in the liquid top gate configuration reported for the high-hole-doped case.³¹ Further details of PL intensity is available in section 4 of the SI.

Figure 2d shows the V_g dependent amplitude ratio of exciton to the trion peak $I_{\text{exciton}}/I_{\text{trion}}$ of MoS₂ at different chemical doped regimes. In the pristine case, $I_{\text{exciton}}/I_{\text{trion}}$ decreases monotonically with the increase in gate voltage toward the positive direction. This phenomenon can be explained by considering the well-known fact that the as prepared MoS₂ is n doped, due to the presence of unavoidable defects or substrate unintentional doping.^{32,33} In such cases, the exciton at higher

Figure 3. TRPL of monolayer MoS₂ at selected gate-voltages V_g for different hole-doping levels achieved via chemical treatment. (a) Pristine sample ($n_e = 1.0 \times 10^{12} \text{ cm}^{-2}$); the black line is a single exponential fit to the data at $V_g = 70 \text{ V}$. (b) Medium-hole-doped sample ($n_e = 7.6 \times 10^{11} \text{ cm}^{-2}$); the black line is a fit using eq 2 to the data at $V_g = 70 \text{ V}$. (c) High-hole-doped sample ($n_e = 2.4 \times 10^{11} \text{ cm}^{-2}$); the black line is a double exponential fit to the data at $V_g = 70 \text{ V}$. In all three graphs the total weighted average lifetime is shown in respective colors. (d) The ratio of the amplitudes of A-excitons and trions versus V_g measured at the different chemically doped regimes. The notations h-doped and e⁻-doped indicate, respectively, regions of V_g in which the sample gets electrostatically doped with holes and electrons due to the back-gate, over and above the chemical doping. P, M, and H indicate pristine, medium-hole-doped, and high-hole-doped cases, respectively.

Figure 4. Lifetime of A-exciton (solid-red circles) and trions (solid-blue circles) versus back gate voltages at different doping levels achieved via chemical treatment: (a) pristine sample; (b) medium-hole-doped sample; (c) high-hole-doped sample. In all cases the trion lifetime is seen not to vary significantly with V_g . The lifetime of the A-exciton depends strongly on V_g for the pristine sample, the dependence becomes much shallower with increasing hole doping. (d) Schematic of the exciton interaction at different regimes. P, M, and H indicate pristine, medium-hole-doped, and high-hole-doped cases, respectively..

positive V_g would bind with excess electrons to form negative trions, and that effectively decreases the density of exciton and an increase in the density of negative trion. In the medium-hole-doped case $I_{\text{exciton}}/I_{\text{trion}}$ is higher than that in the pristine

case. This is because the chemical treatment will reduce the electrons in the system which will decrease the negative trion density and increase the exciton density in the system. In the high-hole-doped regime, we observe that $I_{\text{exciton}}/I_{\text{trion}}$ is less

than that of pristine and medium-hole-doped cases, and we did not observe a significant change of the $I_{\text{exciton}}/I_{\text{trion}}$ with V_g . This decrease in the ratio occurs because, when the excess electrons are taken out from the system, the system is approaching the hole dominating regime. In that case, the exciton will bind with the holes and form positive trions, which decreases the density of excitons and increases the density of the positive trions.

The gate dependent measurements along with the chemical doping technique explicitly demonstrate the electrical and chemical way to control exciton species in MoS₂. The conversion from exciton to trion can be represented as $e(h) + X^0 \rightarrow X$, where e and h indicate an electron or a hole, respectively, X^0 indicates an exciton, and X indicates negative or positive trions. In the pristine case, V_g is positive favoring negative trions to form, and in this regime X takes a negative sign. In the medium-hole-doped case neither the electron density nor hole density is high enough to favor more negative or positive trions formation. In the highly chemical doped case, as V_g decreases more holes are injected into the sample, and X^0 starts converting into a positive trion to form a positive trion gas with X taking a positive sign. The carrier density n_e was estimated to be $1.0 \times 10^{12} \text{ cm}^{-2}$, $7.4 \times 10^{11} \text{ cm}^{-2}$, and $2.4 \times 10^{11} \text{ cm}^{-2}$ for pristine, medium-hole-doped, and high-hole-doped cases, respectively. The details of the carrier density calculation and resistance v/s gate voltage measurements are available in section 5 of the SI.

To study the dynamics of the quasiparticles and the interplay of excitons, trions, and free carrier density and their respective decay dynamics, the TRPL data of the monolayer MoS₂ were studied. Figure 3 panels a–c show the time-resolved photoluminescence dynamics at different gate voltages and at different hole doping steps of the MoS₂ monolayer sample. The decay profile was fitted most persuasively by the double or single exponential as

$$y = y_0 + A_{\text{exciton}} e^{-(t-t_0)/\tau_{\text{ex}}} + A_{\text{trion}} e^{-(t-t_0)/\tau_{\text{tr}}} \quad (2)$$

where A_{exciton} and τ_{ex} are the amplitude and the lifetime of excitons, respectively. A_{trion} and τ_{tr} are the amplitude and the lifetime of trions, respectively.

Figure 3a shows the decay profiles of the PL emission of the intrinsic monolayer MoS₂ at different gate voltages. When the negative gate voltage is applied to the pristine monolayer MoS₂ FET, the TRPL intensity shows two exponential decays with time, one with longer lifetime, and the other one with a shorter lifetime. When a positive gate voltage has been applied beyond a certain range, TRPL follows a single exponential decay (Figure 4a). Since the longer lifetime disappears as we dope more electrons to the system, we assign it to the exciton,²⁵ say τ_{ex} . The shorter lifetime, which we assign to trion (say τ_{tr}) almost remains constant at ~ 0.25 ns at all gate voltages unlike the longer lifetime (i.e., τ_{ex}) which varies with gate voltage. The τ_{ex} is a short ~ 0.5 ns when the monolayer is electrostatically doped with electrons. With the increase in negative gate voltage (hole doping) the lifetime increases to ~ 3 ns at $V_g = -10$ V and then saturates. At room temperature, the TRPL decay time is affected by both radiative recombination as well as by nonradiative recombination channels, such as trion formation, defect assisted transition, etc. As we increase V_g to positive, the electron density increases, which will increase the probability of negative trion formation. It has been shown that trion formation is a major nonradiative decay channel for

excitons.³⁴ So the τ_{ex} starts decreasing and eventually becomes undetectable with further increase in V_g .

In Figure 3b the decay profile of the MoS₂ monolayer has been shown at medium hole doping condition. Here, it has been observed that at all the gate voltages the photoluminescence decay follows the biexponential (eq 2) decay path. Both τ_{tr} at ~ 0.25 ns and τ_{ex} at ~ 2 ns almost remains constant (Figure 4b). But with further high hole doping via chemical method, the nature of decay with gate voltages has been changed, as shown in Figure 3c and Figure 4c. In this case, τ_{tr} similar to the other two conditions almost remains constant at ~ 0.25 ns at all gate voltages, whereas τ_{ex} varies with gate voltage. With the increase in negative gate voltage (hole doping) τ_{ex} decreases from ~ 1.6 ns to ~ 0.8 ns at $V_g = +50$ V and then saturates.

To further understand this observation and to correlate with the PL observations, the exciton-to-trion amplitude ratio $A_{\text{exciton}}/A_{\text{trion}}$ at different gate voltages of the different chemically doped regimes is shown in Figure 3d. In the pristine case, $A_{\text{exciton}}/A_{\text{trion}}$ monotonically decreases with the increase in gate voltage toward a positive direction from ~ 0.025 to 0; the trend is similar to the PL spectral intensity ratio. In the medium-hole-doped case, the ratio is almost constant at ~ 0.005 . In the high-hole-doped case, the ratio monotonically increases with the increase in gate voltage toward the positive direction from ~ 0.01 to 0.03.

Now, at room temperature, the PL decay time is regularly not only dominated by pure radiative recombination but also by nonradiative recombination channels. The longer decay time of monolayer MoS₂ is affected by different quantities such as the effective exciton radiative recombination time,^{35–39} the nonradiative recombination channels including the exciton–exciton annihilation rate, and trion formation from excitons.^{34,40–43} The Fermi level in the system will control this dominant recombination pathway.¹⁹

Considering the above phenomenon we attempt to explain the difference in nature of exciton lifetime for various chemical doping levels. For the pristine monolayer MoS₂, it is found that when the V_g is above +10 V, the probability of exciton to negative trion formation increases because of the increase in electron density. Since trion formation is a major nonradiative decay channel for excitons, the exciton lifetime starts disappearing. When the V_g is around 10 V, lifetime is 0.5 ns and with increase in negative gate voltage, the magnitude of τ_{ex} reaches to 3.5 ns (Figure 4a). This could take place due to the enhancement of the electrostatic hole doping which reduces the probability of formation of trions from exciton.

For the medium-hole-doped case, the exciton density becomes highly populated which can cause exciton–exciton annihilation (EEA),^{42–48} due to strong interaction between excitons in this confined system. It is possible that the EEA mechanism might be responsible for the observed decrease in the lifetime amplitude ratio with increasing exciton density. It is also probable that the observed decrease of the lifetime from the pristine case to the medium-hole-doped case (Figure 4b) is caused by this EEA mechanism.

Further, high-hole-doping will start favoring positive trion formation from excitons. Again the probability of exciton to positive trion formation increases. This positive trion formation will be a major nonradiative channel for excitons. So we observe the decrease in a lifetime of exciton (Figure 4c), which begins to increase marginally at the highest electron doping, suggesting reduction in decay through nonradiative

channel via exciton to positive trion energy transfer. We also observe the monotonic decrease of the exciton to trion lifetime amplitude ratio with decrease in electron density. The interaction of excitons at different doping regimes is shown in Figure 4d. In the pristine case, when V_g is positive, the exciton mostly interacts with electrons. In the medium-hole-doped case, electrostatic doping induces a small fraction of charges in the vicinity of the exciton. For the exciton mostly in the high-hole-doped case, when V_g starts going toward the positive direction the exciton mostly interacts with the holes.

CONCLUSION

In summary using TRPL and PL, and by controlling the carrier density using electrostatic doping, we observe a predominantly exciton regime and trion regime in the pristine case ($n_e = 1.0 \times 10^{12} \text{ cm}^{-2}$). In the medium-hole-doped case ($n_e = 7.6 \times 10^{11} \text{ cm}^{-2}$), we observe a predominantly exciton regime with a decrease in exciton lifetime compared to the pristine case, probably by EEA mechanism. For the high-hole-doped case ($n_e = 2.4 \times 10^{11} \text{ cm}^{-2}$), we observe a predominantly positive trion regime and exciton regime. Although it is possible to demonstrate exciton as well as positive and negative trion interconversion by QY measurements when QY approaches unity, time-resolved and steady state PL measurements provide a more detailed insight into the recombination processes including nonradiative channels such as exciton-to-trion formation and exciton–exciton annihilation as well as individual quasiparticle dynamics. Our results suggest that the nonradiative decay channel for excitons such as exciton–exciton annihilation and exciton-to-trion formation are dominant and can influence exciton lifetime. At present theoretical calculations do not consider these important factors and calculations show that the lifetime of excitons increases with increasing carrier density at all temperatures, which is not consistent with our results. Further, our results suggest that the interplay of various quasiparticles and carrier density can be used to control the dynamics of exciton which can provide a versatile platform for probing the excitonic physics and photonic applications.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is added separately. The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.9b02170>.

Device fabrication; PL data fittings; photoluminescence; electrical measurements (PDF)

AUTHOR INFORMATION

Corresponding Author

Jaydeep K. Basu – Indian Institute of Science, Bangalore, India; orcid.org/0000-0002-6683-4732;
Email: basu@iisc.ac.in

Other Authors

Pradeepa H L – Indian Institute of Science, Bangalore, India

Praloy Mondal – Indian Institute of Science, Bangalore, India

Aveek Bid – Indian Institute of Science, Bangalore, India

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsanm.9b02170>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

H.L.P. thanks CSIR-UGC for financial support. The authors thank DST Nanomission for funding. The authors thank SERB, India, for funding.

REFERENCES

- (1) Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging photoluminescence in monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275.
- (2) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, I. V.; Kis, A. Single-layer MoS₂ transistors. *Nat. Nanotechnol.* **2011**, *6*, 147.
- (3) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically thin MoS₂: a new direct-gap semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.
- (4) Schell, A. W.; Svedendahl, M.; Quidant, R. Quantum emitters in hexagonal boron nitride have spectrally tunable quantum efficiency. *Adv. Mater.* **2018**, *30*, 1704237.
- (5) Tran, T. T.; Wang, D.; Xu, Z.-Q.; Yang, A.; Toth, M.; Odom, T. W.; Aharonovich, I. Deterministic coupling of quantum emitters in 2D materials to plasmonic nanocavity arrays. *Nano Lett.* **2017**, *17*, 2634–2639.
- (6) Stender, C. L.; Greyson, E. C.; Babayan, Y.; Odom, T. W. Patterned MoS₂ nanostructures over centimeter-square areas. *Adv. Mater.* **2005**, *17*, 2837–2841.
- (7) Goodman, A. J.; Willard, A. P.; Tisdale, W. A. Exciton trapping is responsible for the long apparent lifetime in acid-treated MoS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96*, 121404.
- (8) Amani, M.; Lien, D.-H.; Kiriya, D.; Xiao, J.; Azcatl, A.; Noh, J.; Madhvapathy, S. R.; Addou, R.; Santosh, K.; Dubey, M.; Kyeongjae, C.; Wallace, Robert M.; Lee, Si-Chen; He, Jr-Hau; Ager, Joel W., III; Zhang, Xiang; Yablonovitch, Eli; Javey, Ali Near-unity photoluminescence quantum yield in MoS₂. *Science* **2015**, *350*, 1065–1068.
- (9) Wang, G.; Chernikov, A.; Glazov, M. M.; Heinz, T. F.; Marie, X.; Amand, T.; Urbaszek, B. Colloquium: Excitons in atomically thin transition metal dichalcogenides. *Rev. Mod. Phys.* **2018**, *90*, No. 021001.
- (10) Mueller, T.; Malic, E. Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors. *npj 2D Materials and Applications* **2018**, *2*, 1–12.
- (11) Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive photodetectors based on monolayer MoS₂. *Nat. Nanotechnol.* **2013**, *8*, 497.
- (12) Withers, F.; Del Pozo-Zamudio, O.; Mishchenko, A.; Rooney, A.; Gholinia, A.; Watanabe, K.; Taniguchi, T.; Haigh, S.; Geim, A.; Tartakovskii, A.; Novoselov, K. S. Light-emitting diodes by band-structure engineering in van der Waals heterostructures. *Nat. Mater.* **2015**, *14*, 301.
- (13) Ramasubramanian, A. Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 115409.
- (14) Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J. Tightly bound trions in monolayer MoS₂. *Nat. Mater.* **2013**, *12*, 207.
- (15) Ross, J. S.; Wu, S.; Yu, H.; Ghimire, N. J.; Jones, A. M.; Aivazian, G.; Yan, J.; Mandrus, D. G.; Xiao, D.; Yao, W.; Xiaodong, X. Electrical control of neutral and charged excitons in a monolayer semiconductor. *Nat. Commun.* **2013**, *4*, 1474.
- (16) He, K.; Kumar, N.; Zhao, L.; Wang, Z.; Mak, K. F.; Zhao, H.; Shan, J. Tightly bound excitons in monolayer WSe₂. *Phys. Rev. Lett.* **2014**, *113*, No. 026803.
- (17) Ye, Z.; Cao, T.; O'Brien, K.; Zhu, H.; Yin, X.; Wang, Y.; Louie, S. G.; Zhang, X. Probing excitonic dark states in single-layer tungsten disulfide. *Nature* **2014**, *513*, 214.

- (18) Chernikov, A.; Berkelbach, T. C.; Hill, H. M.; Rigosi, A.; Li, Y.; Aslan, O. B.; Reichman, D. R.; Hybertsen, M. S.; Heinz, T. F. Exciton binding energy and nonhydrogenic Rydberg series in monolayer WS₂. *Phys. Rev. Lett.* **2014**, *113*, No. 076802.
- (19) Lien, D.-H.; Uddin, S. Z.; Yeh, M.; Amani, M.; Kim, H.; Ager, J. W.; Yablonoitch, E.; Javey, A. Electrical suppression of all nonradiative recombination pathways in monolayer semiconductors. *Science* **2019**, *364*, 468–471.
- (20) Wang, H.; Zhang, C.; Chan, W.; Manolatou, C.; Tiwari, S.; Rana, F. Radiative lifetimes of excitons and trions in monolayers of the metal dichalcogenide MoS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, No. 045407.
- (21) Selig, M.; Berghäuser, G.; Raja, A.; Nagler, P.; Schüller, C.; Heinz, T. F.; Korn, T.; Chernikov, A.; Malic, E.; Knorr, A. Excitonic linewidth and coherence lifetime in monolayer transition metal dichalcogenides. *Nat. Commun.* **2016**, *7*, 13279.
- (22) Steinhoff, A.; Kim, J.-H.; Jahnke, F.; Rosner, M.; Kim, D.-S.; Lee, C.; Han, G. H.; Jeong, M. S.; Wehling, T.; Gies, C. Efficient excitonic photoluminescence in direct and indirect band gap monolayer MoS₂. *Nano Lett.* **2015**, *15*, 6841–6847.
- (23) Steinhoff, A.; Rosner, M.; Jahnke, F.; Wehling, T.; Gies, C. Influence of excited carriers on the optical and electronic properties of MoS₂. *Nano Lett.* **2014**, *14*, 3743–3748.
- (24) Naik, M. H.; Jain, M. Substrate screening effects on the quasiparticle band gap and defect charge transition levels in MoS₂. *Physical Review Materials* **2018**, *2*, No. 084002.
- (25) Yan, T.; Qiao, X.; Liu, X.; Tan, P.; Zhang, X. Photoluminescence properties and exciton dynamics in monolayer WSe₂. *Appl. Phys. Lett.* **2014**, *105*, 101901.
- (26) Mouri, S.; Miyauchi, Y.; Matsuda, K. Tunable photoluminescence of monolayer MoS₂ via chemical doping. *Nano Lett.* **2013**, *13*, 5944–5948.
- (27) Chen, W.; Chen, S.; Qi, D. C.; Gao, X. Y.; Wee, A. T. S. Surface transfer p-type doping of epitaxial graphene. *J. Am. Chem. Soc.* **2007**, *129*, 10418–10422.
- (28) Xiao, D.; Liu, G.-B.; Feng, W.; Xu, X.; Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides. *Phys. Rev. Lett.* **2012**, *108*, 196802.
- (29) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R. Theory of neutral and charged excitons in monolayer transition metal dichalcogenides. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, No. 045318.
- (30) Kormányos, A.; Burkard, G.; Gmitra, M.; Fabian, J.; Zólyomi, V.; Drummond, N. D.; Fal'ko, V. k. p theory for two-dimensional transition metal dichalcogenide semiconductors. *2D Mater.* **2015**, *2*, No. 022001.
- (31) Ponomarev, E.; Pásztor, Á.; Waelchli, A.; Scarfato, A.; Ubrig, N.; Renner, C.; Morpurgo, A. F. Hole Transport in Exfoliated Monolayer MoS₂. *ACS Nano* **2018**, *12*, 2669–2676.
- (32) Santosh, K.; Longo, R. C.; Addou, R.; Wallace, R. M.; Cho, K. Impact of intrinsic atomic defects on the electronic structure of MoS₂ monolayers. *Nanotechnology* **2014**, *25*, 375703.
- (33) Baugher, B. W.; Churchill, H. O.; Yang, Y.; Jarillo-Herrero, P. Intrinsic electronic transport properties of high-quality monolayer and bilayer MoS₂. *Nano Lett.* **2013**, *13*, 4212–4216.
- (34) Godde, T.; Schmidt, D.; Schmutzler, J.; Afmann, M.; Debus, J.; Withers, F.; Alexeev, E.; Del Pozo-Zamudio, O.; Skrypka, O.; Novoselov, K.; Bayer, M.; Tartakovsky, A. I. Exciton and trion dynamics in atomically thin MoSe₂ and WSe₂: effect of localization. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *94*, 165301.
- (35) Withers, F.; Del Pozo-Zamudio, O.; Schwarz, S.; Dufferwiel, S.; Walker, P.; Godde, T.; Rooney, A.; Gholinia, A.; Woods, C.; Blake, P.; S. J. Haigh, K.; Watanabe, T.; Taniguchi, I.; Aleiner, L.; Geim, A. K.; Fal'ko, V. I.; Tartakovsky, A. I.; Novoselov, K. S. WSe₂ light-emitting tunneling transistors with enhanced brightness at room temperature. *Nano Lett.* **2015**, *15*, 8223–8228.
- (36) Arora, A.; Nogajewski, K.; Molas, M.; Koperski, M.; Potemski, M. Exciton band structure in layered MoSe₂: from a monolayer to the bulk limit. *Nanoscale* **2015**, *7*, 20769–20775.
- (37) Wang, G.; Robert, C.; Suslu, A.; Chen, B.; Yang, S.; Alamdari, S.; Gerber, I. C.; Amand, T.; Marie, X.; Tongay, S.; Urbaszek, B. Spin-orbit engineering in transition metal dichalcogenide alloy monolayers. *Nat. Commun.* **2015**, *6*, 10110.
- (38) Eizagirre Barker, S.; Wang, S.; Godiksen, R. H.; Castellanos, G. W.; Berghuis, M.; Raziman, T.; Curto, A. G.; Gómez Rivas, J. Preserving the Emission Lifetime and Efficiency of a Monolayer Semiconductor upon Transfer. *Adv. Opt. Mater.* **2019**, 1900351.
- (39) Lin, Y.; Ling, X.; Yu, L.; Huang, S.; Hsu, A. L.; Lee, Y.-H.; Kong, J.; Dresselhaus, M. S.; Palacios, T. Dielectric screening of excitons and trions in single-layer MoS₂. *Nano Lett.* **2014**, *14*, 5569–5576.
- (40) Singh, A.; Moody, G.; Tran, K.; Scott, M. E.; Overbeck, V.; Berghäuser, G.; Schaibley, J.; Seifert, E. J.; Pleskot, D.; Gabor, N. M.; Jiaqiang, Y.; David, G. M.; Marten, R.; Ermin, M.; Xiaodong, X.; Xiaoqin, L.; et al. Trion formation dynamics in monolayer transition metal dichalcogenides. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, No. 041401.
- (41) Lee, Y.; Ghimire, G.; Roy, S.; Kim, Y.; Seo, C.; Sood, A. K.; Jang, J. I.; Kim, J. Impeding Exciton–Exciton Annihilation in Monolayer WS₂ by Laser Irradiation. *ACS Photonics* **2018**, *5*, 2904–2911.
- (42) Sun, D.; Rao, Y.; Reider, G. A.; Chen, G.; You, Y.; Brezin, L.; Harutyunyan, A. R.; Heinz, T. F. Observation of rapid exciton–exciton annihilation in monolayer molybdenum disulfide. *Nano Lett.* **2014**, *14*, 5625–5629.
- (43) Mouri, S.; Miyauchi, Y.; Toh, M.; Zhao, W.; Eda, G.; Matsuda, K. Nonlinear photoluminescence in atomically thin layered WSe₂ arising from diffusion-assisted exciton–exciton annihilation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *90*, 155449.
- (44) Kumar, N.; Cui, Q.; Ceballos, F.; He, D.; Wang, Y.; Zhao, H. Exciton–exciton annihilation in MoSe₂ monolayers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 125427.
- (45) Plechinger, G.; Nagler, P.; Kraus, J.; Paradiso, N.; Strunk, C.; Schüller, C.; Korn, T. Identification of excitons, trions and biexcitons in single-layer WS₂. *Phys. Status Solidi RRL* **2015**, *9*, 457–461.
- (46) Shang, J.; Shen, X.; Cong, C.; Peimyoo, N.; Cao, B.; Eginligil, M.; Yu, T. Observation of excitonic fine structure in a 2D transition-metal dichalcogenide semiconductor. *ACS Nano* **2015**, *9*, 647–655.
- (47) You, Y.; Zhang, X.-X.; Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R.; Heinz, T. F. Observation of biexcitons in monolayer WSe₂. *Nat. Phys.* **2015**, *11*, 477.
- (48) Yuan, L.; Wang, T.; Zhu, T.; Zhou, M.; Huang, L. Exciton dynamics, transport, and annihilation in atomically thin two-dimensional semiconductors. *J. Phys. Chem. Lett.* **2017**, *8*, 3371–3379.