Photo-induced doping effect and dynamic process in monolayer MoSe$_2$

Qian Yang[1, 2], Yongzhou Xue[1, 2], Hao Chen[1, 2], Xiuming Dou[1, 2, †], and Baoquan Sun[1, 2, †]

[1]State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

[2]College of Materials Science and Optoelectronic Technology, University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Dynamic processes of electron transfer by optical doping in monolayer MoSe$_2$ at 6 K are investigated via measuring time resolved photoluminescence (PL) traces under different excitation powers. Time-dependent electron transfer process can be analyzed by a power-law distribution of t^{-a} with a = 0.1–0.24, depending on the laser excitation power. The average electron transfer time of approximately 27.65 s is obtained in the excitation power range of 0.5 to 100 μW. As the temperature increases from 20 to 44 K, the energy difference between the neutral and charged excitons is observed to decrease.

Key words: photodoping; monolayer MoSe$_2$; dynamic process; temperature

1. Introduction

The monolayer transition metal dichalcogenides (TMDCs) have great potential in the manufacture of optoelectronic devices such as exciton lasers[1–3], light-emitting diodes[4, 5], and single-photon sources[6, 7] because they are direct band gap materials[8]. The laser irradiation will increase the number of free electrons in this monolayer materials, causing the conversion of neutral exciton to trion[9–11]. This photodoping effect provides the possibility of developing devices due to its advantages of being able to dope specified areas without the need for photoresist[12], long time stability in a vacuum and low temperature environment[13], and electrical tunability[14]. Since this effect is susceptible to environment, it is necessary to fully characterize the influence of environmental factors on the photodoping effect. People have studied the influences of electric field[14], substrate[15], gas environment[16] and other factors. However, the dynamics of photodoping and the effect of temperature on the doping effect have not been studied in detail. It is easy to distinguish the PL emission peaks of neutral exciton and trion in monolayer MoSe$_2$ at low temperature, which is an ideal material to study the photodoping effect.

In this letter, we report on observations of the laser excitation power dependences of neutral exciton (X) and negatively charged exciton (X$^-$) PL peak intensities at low temperature of 6 K with increasing excitation power from 0.2 to 872 μW, showing a typical irreversible switching over between X and X$^-$ PL peak intensities. The dynamic process of the switching over can be described by a power-law distribution of t^{-a} with a = 0.1–0.24, depending on the laser excitation powers. The derived average photo-induced electron

transfer time is approximately 27.65 s. As the temperature increases from 20 to 44 K, the energy difference between X and X$^-$ shows a downward trend.

2. Experimental section

2.1. Samples and setup

Monolayer MoSe$_2$ sample is grown on a 300 nm SiO$_2$/Si substrate by chemical vapor deposition (CVD) (products by 6 carbon technology). Fig. 1(a) shows the micrographs of the as grown and the transferred monolayer MoSe$_2$ sample, respectively, by 100× objective. Fig. 1(b) shows a typical PL spectrum of the as grown sample measured at 6 K and excitation of 37 μW. Here, owing to a larger lattice mismatch between MoSe$_2$ and substrate as well as a rapid change of the growth temperature[17], the strain is generated in the monolayer MoSe$_2$. So the exciton PL peaks are red-shifted. However, after transferring the monolayer MoSe$_2$ to another SiO$_2$/Si substrate via the viscoelastic stamping technique, the internal strain of sample can be released. The transfer process is: first, the as grown sample covered by PDMS is immersed in 1 mol/L KOH solution for 1.5 h, and then monolayer MoSe$_2$ is transferred to the polydimethylsiloxane (PDMS) film; second, monolayer MoSe$_2$ on the PDMS is transferred into a 300 nm SiO$_2$/Si substrate by dry transfer method. After the monolayer MoSe$_2$ is transferred, the observed cracks in Fig. 1(a) and the X PL peak blue-shift in Fig. 1(b) reveal a release of internal strain in monolayer MoSe$_2$[18]. Raman spectrum of transferred monolayer MoSe$_2$ is used to confirm sample quality[18] as shown in Fig. 1(c). In the experiment, PL spectra are measured by a home-built optical confocal microscopy setup. A 532 nm laser is focused to the monolayer samples for exciting the samples, the PL is spectrally analyzed by a 0.5 m monochromator equipped with a silicon charge-coupled device (CCD). An acoustic-optical modulator (AOM) with a time resolution of about tens of ns, a silicon avalanche photodiode (APD) detector, and a multi-channel scaler (MCS) are em-
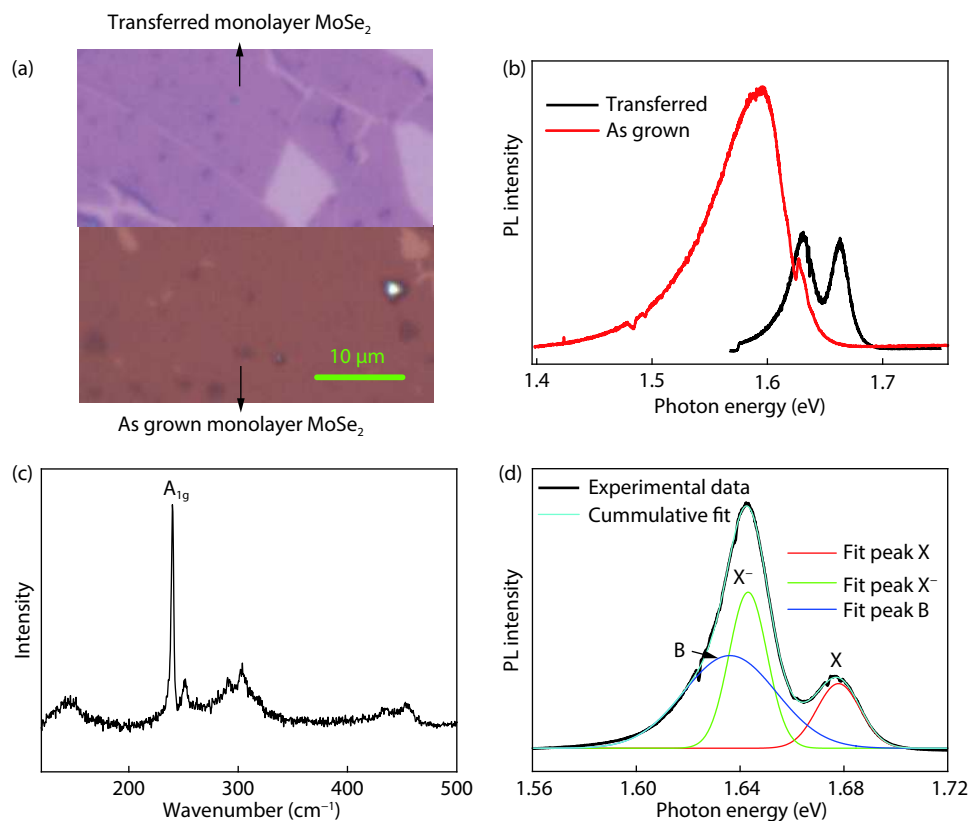
Fig. 1. (Color online) (a) Micrograph of transferred monolayer $MoSe_2$ sample (upper part) and as grown monolayer $MoSe_2$ sample (lower part). (b) PL spectra of monolayer $MoSe_2$ measured at 6 K for as grown (red line) and after transferring to a SiO_2/Si substrate (black line). (c) Raman spectrum of the transferred sample. (d) PL spectrum of the transferred monolayer $MoSe_2$ measured at an excitation power of 872 μW. The curve can be fitted by using three Gauss functions.

ployed to measure the time evolution of the exciton PL peak intensity. Fig. 1(d) shows the PL spectrum of a transferred monolayer $MoSe_2$ measured at 6 K and an excitation power of 872 μW. Here three Gauss functions are used to analyze the PL data and the obtained PL peak energies of 1.678 eV for X emission, 1.643 eV for X^- emission and 1.636 eV for B emission, where the lower energy PL peak B maybe related to the biexciton emission[19].

2.2. Power dependence of $MoSe_2$ photoluminescence

The detailed PL spectra as a function of the excitation power from 0.2 to 872 μW for X and X^- emissions are presented in Fig. 2(a), where the PL spectra are measured when the X PL peak intensity become to be steady evidently. As can be seen in Fig. 2(a), when the excitation power is smaller, such as 0.2 μW, X exciton emission is dominant. However, with increasing the excitation power, X^- PL peak intensity gradually increases and become to be dominant. Furthermore, X PL peak exhibits a blue-shift, whereas X^- PL peak shows a red-shift. Fig. 2(c) summarizes the PL peak shift as a function of the excitation power. Here X PL peak blue-shift and X^- PL peak red-shift are attributed to the increase of electron densities[20]. Fig. 2(e) summarizes the increase of the PL peak intensities for X and X^- emissions as a function of excitation power by a log-log plot, showing that X^- PL intensity increases faster than the X PL intensity and the X^- PL peak becomes to be dominant at larger excitation power of 872 μW.

In order to further study the power-dependent PL intensity changes of X and X^- after the first round laser excitation

up to the largest power of 872 μW. We restart to measure the power-dependent PL on the same excitation spot of the sample at 6 K under excitation power from 1 to 760 μW, as shown in Fig. 2(b). It clearly demonstrates that X^- PL intensity is always larger than the X, even at the minimum excitation power of 1 μW. Furthermore, it is different from the power-dependence of X and X^- characteristics, as shown in Figs. 2(a), 2(c), and 2(e). Here X and X^- peak energies, as shown in Fig. 2(d), are basically unchanged with increasing the excitation power, and the PL peak intensities have nearly the same rate of increase, as shown in Fig. 2(f). For the second-round power changing measurements, the X^- emission is dominant even at the minimum excitation power after the sample is irradiated by large laser power. This implies that in both round measurements, the equilibrium state of the conduction band is different. In the first round, the conduction band has no electrons, while the second round has redundant electrons. This phenomenon has been reported and is interpreted by photo-doping effect[13], i.e., optical ionization of donor centers in the substrate or the substrate–monolayer interface[20].

2.3. Time-resolved measurements

To study the dynamics of photo-induced electrons, the time evolution of X PL peak intensity is measured by using a modulated cw laser excitation. Here AOM is used as a fast switch of the cw laser. In the experiment, as soon as the laser is turned on, the X PL peak intensity is detected by an APD and the time evolution is recorded by an MCS with a time bin of 100 ms and time range of 60 s. The recorded data are plot-
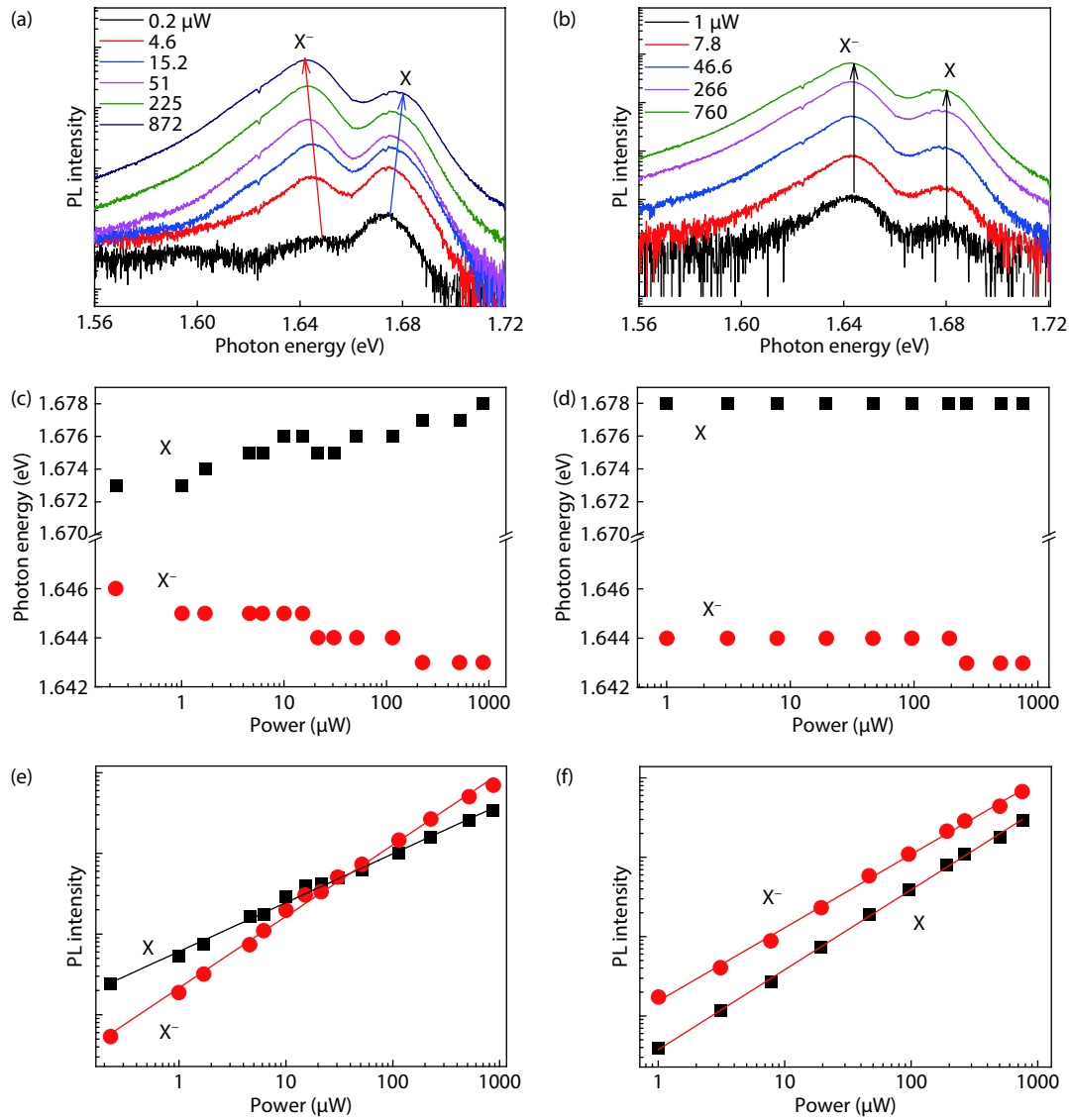
Fig. 2. (Color online) (a) PL spectra of the transferred monolayer $MoSe_2$ for the first-round measurements with increasing excitation power from 0.2 to 872 μW at 6 K. The corresponding X and X$^-$ PL peak energies and intensities are summarized in (c) and (e), respectively. (b) PL spectra for the second-round measurements with increasing excitation power from 1 to 760 μW at 6 K after the excitation power up to 872 μW. The corresponding X and X$^-$ PL peak energies and intensities are summarized in (d) and (f), respectively.

ted in Fig. 3(a) under different laser excitation powers, where the ordinate is logarithmic and the curves of different powers are shifted relatively for clarity. It is found that for the excitation power ranges from 0.5 to 100 μW, the decay law of X PL peak intensity can be described by power-law distribution of $I(t) - t^{-\alpha}$, as analyzed by log–log plot at the excitation power of 0.5 and 10 μW, as shown in Figs. 3(c) and 3(d), respectively. By linear fitting to the curves, it is found that one α value can fit to the data for the excitation power less than 10 μW, whereas two α values are needed to fit the data for the power larger than 10 μW. The obtained α values as a function of power are summarized in Fig. 3(b), indicating a distribution of α values range from 0.1 to 0.24.

As can be seen in Figs. 3(c) and 3(d), as time increases, a change of the X PL peak intensity can be fitted by power-law function. Assuming that the total PL intensity of X and X$^-$ remains constant at a fixed excitation power, the decrease of the X PL intensity with time delay implies that more electrons transfer into X$^-$ energy level which is lower than X. This

results in an increase of X$^-$ PL intensity. Then the average electron transfer time <t> from X to X$^-$ band can be obtained with power-law distribution. Here the luminescence intensity $I(t)$ of X emission is:

$$I(t) = I(0)\left(\frac{t}{\tau}\right)^{-\alpha}. \tag{1}$$

Thus the average electron transfer time based on of Eq. (1) is:

$$\tau_{ave} =< t >= \frac{\int_0^\infty I(0)\left(\frac{t}{\tau}\right)^{-\alpha} t dt}{\int_0^\infty I(0)\left(\frac{t}{\tau}\right)^{-\alpha} dt} = \frac{\int_0^\infty t^{-\alpha} t dt}{\int_0^\infty t^{-\alpha} dt}. \tag{2}$$

Based on the experimental curves as shown in Fig. 3(a), we can calculate the numerical integral of the denominator
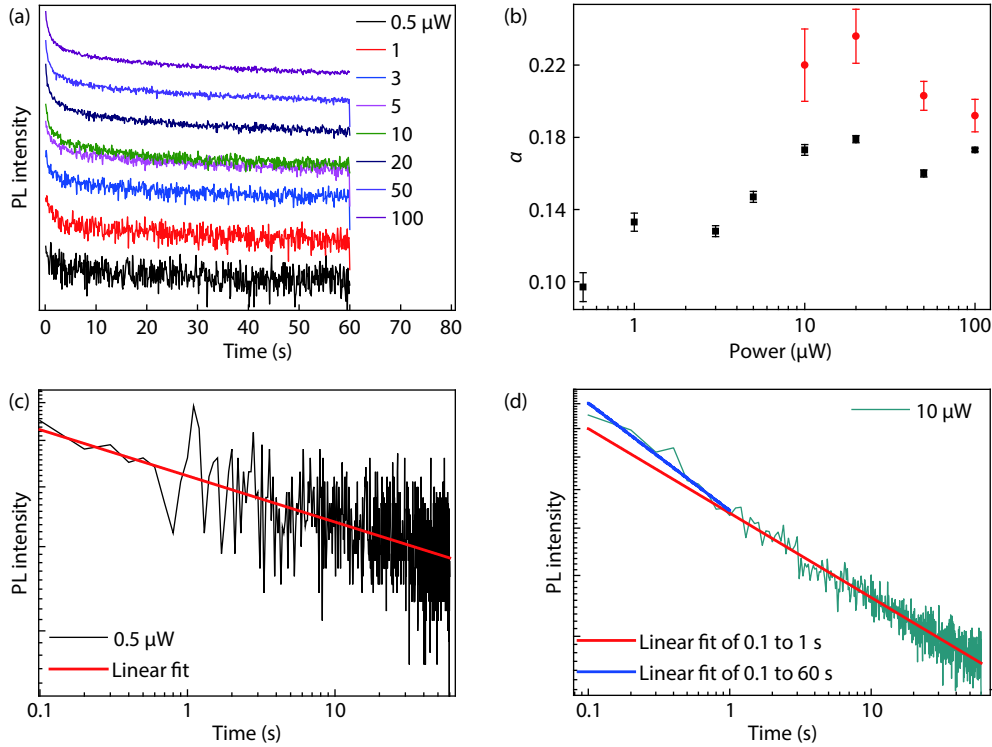
Fig. 3. (Color online) (a) PL intensity of X as a function of time measured by a modulated cw laser excitation with power from 0.5 to 100 μW. The ordinate is logarithmic and the curves of different power are shifted relatively for clarity. (b) Fitting values of α as a function of excitation power from 0.5 to 100 μW, where α values are derived by linear fitting to the curves by log–log plot, as shown in (c) at 0.5 and (d) 10 μW, respectively.
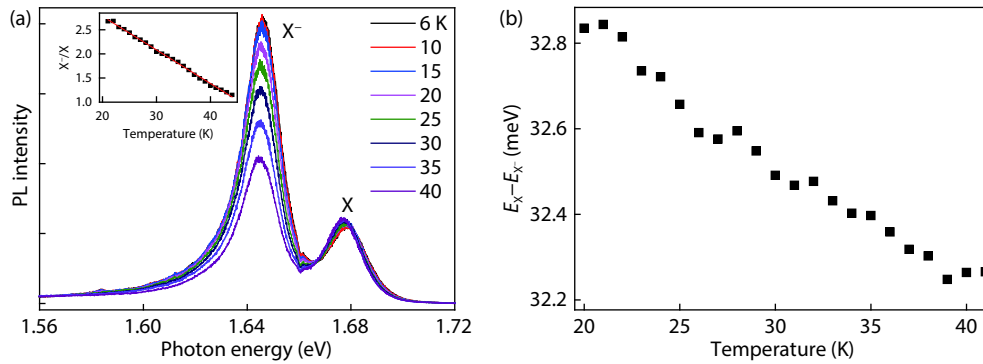

Fig. 4. (Color online) (a) The PL spectra of the transferred monolayer MoSe$_2$ with the temperature increased from 6 to 44 K, under the 42 μW laser irradiation. Inset: the ratio of PL peak intensity of X$^-$ and X as a function of temperature, a linear law is used to fit the experimental data. (b) The energy difference between X and X$^-$ as a function of temperature.

of Eq. (2)[21], i.e., the integral of the curve under different excitation powers. A numerical integral of the numerator term of Eq. (2) is equal to the function of Eq. (1) multiplied by t and then the integral is obtained, where $I(t)$ plays the role of the probability density of a time interval t[21]. The obtained electron transfer times τ_{ave} are 28.52, 27.90, 27.98, 27.67, 27.28, 27.17, 27.47, 27.21 s, respectively, for excitation power from 0.5 to 10 μW. Therefore, in the measured power range of 0.5 to 100 μW, the average electron transfer time is approximately 27.65 s. Note that considering the time scale of energy level relaxation of non-equilibrium carriers in semiconductors, such a long electron transfer time can't just correspond to the transfer of electrons from X to X$^-$ band by pumping electrons from the valence band to the conduction band. It was reported that the optical ionization of donor centers in the substrate or the substrate–monolayer interface is suggested to re-

sponsible for the change in PL peak intensity[15]. We believe that the photo-induced electron doping may be related to the deep donor levels in monolayer MoSe$_2$ owing to the time-dependent diffusion of localized electrons is governed by power-law distribution[22, 23].

2.4. Temperature dependence of MoSe$_2$ photoluminescence

In order to obtain a stable spectrum in a short time, the laser power is first set to 118 μW to irradiate the sample, and then the power is kept at 42 μW for temperature dependent PL measurements. As shown in Fig. 4(a), when T < 15 K, it can be found that the PL intensity of the monolayer MoSe$_2$ sample keep almost unchanged. In the range of 20 K < T < 40 K, the temperature is increased slowly at 1 K intervals, the intensity of X is relatively stable, and the intensity of X$^-$ de-

creases evenly with the increase of temperature. As shown in inset of Fig. 4(a), the ratio of PL peak intensity of X⁻ and X shows a good negative linear law with temperature, and the linear fitting slope is obtained to be –0.07. The energy difference between the two peaks shows a downward trend as the temperature increases from 20 to 44 K (Fig. 4(b)). They imply that the increasing of temperature (20–40 K) may have a negative influence on the photo doping effect in monolayer $MoSe_2$.

3. Conclusion

In summary, we have studied the excitation power dependence of the X and X⁻ PL intensities for the transferred monolayer $MoSe_2$ at 6 K. When the laser excites the sample with a power of tens of μW, an irreversible switching over between X and X⁻ PL peak intensities occurs. After laser irradiation, X⁻ emission will be dominated even if the excitation power is reduced by less than μW. This indicates the generation of additional electrons by optical excitation or photodoping process. Dynamic process of electron transfer can be described by power-law distribution $t^{-\alpha}$ with $\alpha = 0.1$–0.24 depending on the laser excitation powers. The obtained average electron transfer time is approximately 27.65 s. In the temperature range of $20 < T < 44$ K, the increase of temperature induces the reduction of the ratio of the PL peak intensity of X⁻ and X, also, the reduction of the two peak energy difference. The photodoping effect provides a convenient way of local doping of electrons, which may be useful for new device fabrication.

Acknowledgements

References

[1] Salehzadeh O, Djavid M, Tran N H, et al. Optically pumped two-dimensional MoS_2 lasers operating at room-temperature. Nano Lett, 2015, 15, 5302

[2] Ye Y, Wong Z J, Lu X F, et al. Monolayer excitonic laser. Nat Photon, 2015, 9, 733

[3] Wu S, Buckley S, Schaibley J R, et al. Monolayer semiconductor nanocavity lasers with ultralow thresholds. Nature, 2015, 520, 69

[4] Pospischil A, Furchi M M, Mueller T. Solar-energy conversion and light emission in an atomic monolayer p–n diode. Nat Nanotechnol, 2014, 9, 257

[5] Withers F, del Pozo-Zamudio O, Mishchenko A, et al. Light-emitting diodes by band-structure engineering in van der Waals heterostructures. Nat Mater, 2015, 14, 301

[6] Koperski M, Nogajewski K, Arora A, et al. Single photon emitters in exfoliated WSe_2 structures. Nat Nanotechnol, 2015, 10, 503

[7] He Y M, Clark G, Schaibley J R, et al. Single quantum emitters in monolayer semiconductors. Nat Nanotechnol, 2015, 10, 497

[8] Roldán R, Silva-Guillén J A, López-Sancho M P, et al. Electronic properties of single-layer and multilayer transition metal dichalcogenides MX_2 (M = Mo, W and X = S, Se). Ann Der Physik, 2014, 526, 347

[9] Currie M, Hanbicki A T, Kioseoglou G, et al. Optical control of charged exciton states in tungsten disulfide. Appl Phys Lett, 2015, 106, 201907

[10] Singh A, Moody G, Tran K, et al. Trion formation dynamics in monolayer transition metal dichalcogenides. Phys Rev B, 2016, 93, 041401

[11] Godde T, Schmidt D, Schmutzler J, et al. Exciton and trion dynamics in atomically thin $MoSe_2$ and WSe_2: Effect of localization. Phys Rev B, 2016, 94, 165301

[12] Liu T, Xiang D, Zheng Y, et al. Nonvolatile and programmable photodoping in $MoTe_2$ for photoresist-free complementary electronic devices. Adv Mater, 2018, 30, 1804470

[13] Quereda J, Ghiasi T S, van der Wal C H, et al. Semiconductor channel-mediated photodoping in h-BN encapsulated monolayer $MoSe_2$ phototransistors. 2D Mater, 2019, 6, 025040

[14] Ross J S, Wu S F, Yu H Y, et al. Electrical control of neutral and charged excitons in a monolayer semiconductor. Nat Commun, 2013, 4, 1474

[15] Cadiz F, Robert C, Wang G, et al. Ultra-low power threshold for laser induced changes in optical properties of 2D molybdenum dichalcogenides. 2D Mater, 2016, 3, 045008

[16] Atkin P, Lau D M, Zhang Q, et al. Laser exposure induced alteration of WS_2 monolayers in the presence of ambient moisture. 2D Mater, 2017, 5, 015013

[17] Liu Z, Amani M, Najmaei S, et al. Strain and structure heterogeneity in MoS_2 atomic layers grown by chemical vapour deposition. Nat Commun, 2014, 5, 5246

[18] Fu X, Li F, Lin J F, et al. Pressure-dependent light emission of charged and neutral excitons in monolayer $MoSe_2$. J Phys Chem Lett, 2017, 8, 3556

[19] Pei J, Yang J, Wang X, et al. Excited state biexcitons in atomically thin $MoSe_2$. ACS Nano, 2017, 11, 7468

[20] Lundt N, Cherotchenko E, Iff O, et al. The interplay between excitons and trions in a monolayer of $MoSe_2$. Appl Phys Lett, 2018, 112, 031107

[21] Pelant I, Valenta J. Luminescence spectroscopy of semiconductors. London: Oxford University Press, 2012

[22] Scher H, Montroll E W. Anomalous transit-time dispersion in amorphous solids. Phys Rev B, 1975, 12, 2455

[23] Kakalios J, Street R A, Jackson W B. Stretched-exponential relaxation arising from dispersive diffusion of hydrogen in amorphous silicon. Phys Rev Lett, 1987, 59, 1037