Observation of Excitonic Fine Structure in a 2D Transition-Metal Dichalcogenide Semiconductor

Jingzhi Shang, † Xiaonan Shen, ‡ Chunxiao Cong, † Namphung Peimyoo, † Bingchen Cao, † Mustafa Eginligil, † and Ting Yu *,†,‡,§

† Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, ‡ Department of Physics, Faculty of Science, National University of Singapore, Singapore 117542, and § Graphene Research Centre, National University of Singapore, 2 Science Drive 3, Singapore 117542

ABSTRACT Two-dimensional (2D) semiconductors, such as transition-metal dichalcogenide monolayers (TMD 1Ls), have attracted increasing attention owing to the underlying fundamental physics (e.g., many body effects) and the promising optoelectronic applications such as light-emitting diodes. Though much progress has been made, intrinsic excitonic states of TMD 1Ls are still highly debated in theory, which thirsts for direct experimental determination. Here, we report unconventional emission and excitonic fine structure in 1L WS₂ revealed by electrical doping and photoexcitation, which reflects the interplay of exciton, trion, and other excitonic states. Tunable excitonic emission has been realized in a controllable manner via electrical and/or optical injection of charge carriers. Remarkably enough, the superlinear (i.e., quadratic) emission is unambiguously observed which is attributed to biexciton states, indicating the strong Coulomb interactions in such a 2D material. In a nearly neutral 1L WS₂, trions and biexcitons possess large binding energies of ~10 – 15 and 45 meV, respectively. Moreover, our finding of electrically induced robust emission opens up a possibility to boost the luminescent efficiency of emerging 1L TMD light emitting diodes.

KEYWORDS: two-dimensional semiconductor, transition-metal dichalcogenide, photoluminescence, trion, biexciton

Atomically thin transition-metal dichalcogenides (TMDs) have aroused great attention because of their intriguing physical properties and promising optoelectronic applications.¹⁻³ In particular, monolayers (1Ls) of MoS₂, MoSe₂, W S₂, and WSe₂ as a group of direct-band two-dimensional (2D) semiconductors provide a new platform to realize electronic and optical functionalities in ultrathin, flexible, and/or transparent devices, such as transistors⁴⁻⁵ and light-emitting diodes⁶⁻⁸ which could potentially be superior alternatives of conventional Si and III–V based semiconductors. Distinct from the conventional bulk and quasi-2D semiconducting materials, quantum confinement and reduced dielectric screening in 2D semiconductors enhance quasiparticle interactions and result in large binding energies of excitons and trions⁹⁻¹³ where many-body effects need to be taken into account for the electronic and excitonic band structures. The compelling optical properties of TMD 1Ls are strongly correlated to their quasiparticle band structures and significantly influenced by the large excitonic effects.¹⁴,¹⁵

Due to the existence of quantum confinement and large excitonic effects in 2D semiconductors, investigations of many-body physics become a very exciting research field for exploring fundamentals of quantum mechanics. In particular, the information on elementary excitations is essential to study many-body interactions. Precise determination of basic quantities of binding energies is critical for clarifying the current theoretical debate on quasiparticle band structures of 1L TMDs.¹⁴,¹⁵ Through experimental probes such as scanning tunnelling spectroscopy (STS), temperature-dependent photoluminescence (PL) and/or nonlinear optical spectroscopy, the binding energies of A excitons in 1L MoS₂,¹⁶ MoSe₂,¹⁷ WSe₂,¹⁸ and WS₂¹⁹⁻²² were measured to be in a...
range of 0.2 to 0.8 eV. However, the exact values are still under discussion probably due to the spectral overlapping of near-band-edge electronic and excitonic transitions. In nearly neutral 1Ls of MoS$_2$,$^9$ MoSe$_2$,$^{23}$ and WSe$_2$,$^{24}$ the binding energies (18–30 meV) of trions were recovered. For 1L WS$_2$, the binding energy of negative trions is still controversial,$^{19,20,25}$ and the information on the positive trions is less known. In addition to the exciton and trion states confirmed by the previous studies,$^{9,23,24}$ for 2D semiconductors of MoS$_2$ and a more favorable emission energy (visible) transitions possessing much stronger light emission than 1L MoS$_2$,7,27 this direct observation of biexciton emission in TMD 1Ls is still highly desired.

The excitonic emission and the dissociation energies of trions in TMD 1Ls have been found to be sensitive to the electrical doping$^{9,23,24}$ and photoexcitation.$^{25}$ These studies have been focused on electrical or photoinduced doping effect independently. By contrast, how the excitonic emission responds to both electrical doping and excitation power simultaneously remains unclear in 1L TMDs, especially for 1L WS$_2$, a very promising candidate for optoelectronic applications possessing much stronger light emission than 1L MoS$_2$ and a more favorable emission energy (visible) than 1L Mo/WSe$_2$ (near-infrared). Exciting enough, the electroluminescence from 1L diodes of MoS$_2$,$^{7,27}$ WSe$_2$,$^6$ and WS$_2$,$^8$ was demonstrated, yet the low efficiency (typically less than 1%) might be a bottleneck for further practical applications. Hence, thoroughly understanding and further modulating the excitonic emission become a basis for solving such issues. In this work, by separately and jointly controlling the electrical doping and the photoexcitation, we have observed the intrinsic excitonic states and achieved the tunable emission in 1L WS$_2$. The roles of unconventional excitonic states are identified in the near-band edge emission of 1L WS$_2$. The basic quantities of binding energies of both positive and negative trions have been extracted from a nearly neutral 1L WS$_2$. In particular, the striking biexciton emission is electrically controllable, which promises a bright future of significantly improving luminous efficiency in 1L WS$_2$ diodes.

**RESULTS AND DISCUSSION**

Here, all of the PL measurements were performed at the excitation power of 65 $\mu$W unless otherwise specified. Figure 1a shows PL spectra from a field effect device of exfoliated 1L-WS$_2$ taken at the back-gate voltages from $-40$ to $+40$ V, which reflect the excitonic emission near the band edge at room temperature (rt). On the whole, the emission band consists of two components, where the high/low energy peak becomes dominant at $-40/40$ V and is assigned to a exciton ($X_A$)/negative trion ($X_A^-$) emission, as seen in Figure 1b. On the one hand, from $-40$ to $+40$ V, the peak position of $X_A^-$ apparently redshifts and that of $X_A$ slightly blueshifts (Figure 1c). Consequently, the energy difference of $X_A$ and $X_A^-$ increases, which is strongly related to phase space blocking$^{28}$ and many body effects.$^{29}$ We define this energy splitting as the dissociation energy of trion, which consists of the trion binding energy ($E_{tb}$) and the Fermi level ($E_F$). In a simplified model,$^{9,30}$ the dissociation energy of trion is $E_{tb} + E_F$, where $E_{tb}$ is considered to be a constant. The increase of the dissociation energy of trion with electron doping is mainly due to the rising of Fermi level. In case the trion binding energy varies with doping,$^{28}$ further theoretical investigation is needed to fully address the observed trend. The exciton energy can be estimated by $E_g - E_{extb}$, where $E_g$ and $E_{extb}$ are the band gap and the exciton binding energy, respectively. The blueshift of exciton energy may be due to the decrease in the exciton binding energy with electron doping or the band gap renormalization. A recent theoretical study$^{28}$ supports the former, where the electron doping causes the reduction of phase space due to Pauli exclusion and decreases the exciton binding energy. Meanwhile, the electron doping typically causes the reduction of band gap$^{29,31,32}$ and thus tends to decrease the exciton energy. Therefore, the blueshift of exciton energy here is attributed to the decrease in the exciton binding energy with electron doping. On the other hand, the total integrated intensity and that of $X_A$ gradually decrease with the increase in the back-gate voltage, while the intensity of $X_A^-$ increases from $-40$ to $0$ V and then remains stable between 0 and 30 V and slightly decreases after 30 V (Figure 1d). The stable feature has been seen in heavily doped 1L MoS$_2$,$^9$ and the intensity changes of $X_A^-$ have been observed in the nearly neutral 1L MoSe$_2$.$^{22}$ The different responses of these three devices could be due to the different grades of native doping in the original TMD flakes. Special care should be paid to such a study. Figure 1e shows the PL spectra of the CVD-grown 1L WS$_2$ at varied back-gate voltages (curves) and the total integrated intensity as a function of gate voltage (dots). The emission band mainly contains one component, and its intensity decreases with more electron doping as seen in Figure 1f. Comparing such gate dependence of intensity with that of $X_A$, shown in Figure 1d, we assign this strong peak to the $X_A$ emission. The general agreement of the peak width ($\sim 0.04$ eV) of the present band with that of $X_A$ in the exfoliated 1L WS$_2$ further confirms this assignment (see Figure S1a, Supporting Information). At positive voltages larger than 20 V, the emission profile widens and extends to the lower energies (Figure S1b, Supporting Information). With the increasing electron doping, the presence of the emission component of trions and its redshift are expected as seen in Figure 1a, which take responsibility
for the observed broadening and the low energy tail at 40 V (Figure S1b, Supporting Information).

As noticed in graphene, in addition to the electrical doping, the carrier concentration can also be tuned by light illumination. Here, we studied the influence of excitation power on the excitonic emission in 1L WS₂ at both room and cryogenic temperatures and explored the possibility of controlling the excitonic emission optically. Figure 2a shows the representative PL spectra of an exfoliated 1L WS₂ device taken under four excitation powers. The overall emission band profile evolves from the two-component feature at low excitation powers into a single peak at high powers. To further reveal the response of excitons and trions to photoexcitation, their emission energies and strengths are plotted as functions of the excitation power. As shown in Figure 2b, with the increase in the excitation power, the Xₐ peak blueshifts while the Xₐ⁻ peak redshifts; the integrated intensity of Xₐ⁻ increases linearly while that of Xₐ sublinearly increases at lower excitation powers (<1000 μW) and saturates at higher excitation powers (>1000 μW). These peak shifts and the rising intensity ratio of Xₐ⁻/Xₐ are in line with our electrical doping measurements (see Figure S2, Supporting Information) and are mainly attributed to the photoinduced electron doping, which is further evidenced by the electrical transport measurements under photoexcitation (Figure S3, Supporting Information). In the n-type exfoliated 1L WS₂, at a low temperature (4 K) such photoinduced doping effect has also been observed. Note that the possible lattice heating induced by photoexcitation will cause the redshift of exciton band while the blueshift presents here. It indicates that the laser heating is a minor factor in our cases. Figure 2c shows the PL spectra of the CVD-grown 1L WS₂ at different excitation powers. The peak...
shape maintains at the first three excitation powers and becomes asymmetric at the highest excitation power. In detail (Figure 2d), the total integrated intensity of PL linearly increases with the excitation power (<2500 μW) and slightly deviates at high excitation powers (>2500 μW). The width of PL is nearly constant at the excitation power less than 2500 μW. At higher excitation powers, the band broadens toward lower photon energies and becomes more asymmetric, which is analogous to the PL evolution induced by electrical doping (Figure S1b, Supporting Information) and results from the presence of excitonic emission from negative trions induced by strong photoexcitation.

As presented above, the PL spectrum of CVD-grown 1L WS₂ at rt mainly shows one single component of Xₐ(Figure 1e). When the temperature cools down to a cryogenic temperature of 4.2 K, one broad band appears at the low energies and the other high-energy band becomes asymmetric at the excitation powers of 7 and 65 μW as shown in the upper and middle panels of Figure 3a, respectively. The corresponding emission spectra can be well deconvoluted by three Lorentzian peaks, assigned to Xₐ, Xₐ/X₀, and localized states (LS). The LS are probably due to shadow impurities, defects, and/or disorder effects, which deserves further investigation. Similar emission bands with the lower energies than those of exciton and trion states have often been observed in other TMD 1Ls of MoS₂, MoSe₂, and WSe₂. The typical crossover of exciton and biexciton intensities at high excitation power of 9570 μW, the Xₐ/X₀ peak becomes more obvious and another new band appears (Figure 3a, bottom panel). The new band is assigned to the biexciton emission in 1L WS₂, denoted as XₐXₐ, which will be further discussed later. More clearly, the gradual evolution of the emission bands with the excitation power is seen in the PL intensity mapping versus excitation power and photon energy (Figure 3b). Figure 3c presents the peak positions of four components as a function of excitation power. As shown in Figure S4 (Supporting Information), the dissociation energies of negative trions are 13–15 meV, which slightly increases with the excitation power due to photoinduced doping; for XₐXₐ, the extracted dissociation energies are between 50 and 60 meV. In the electrical transport measurements of the CVD-grown 1L WS₂ device (Figure S5, Supporting Information), the turn-on voltage shifts to negative gate voltages with the increasing excitation power, which verifies the increasing electron doping at 4.2 K by photoexcitation. Figure 3d presents the integrated intensities of Xₐ, Xₐ/X₀, XₐXₐ, and LS as functions of the excitation power. With the increase in the excitation power, the emission from exciton and trion states linearly increases over the whole studied range. The emission from LS shows a sublinear dependence (<2200 μW, α ~ 0.6). The defect-induced emission band in 1L MoS₂ also presents a sublinear behavior, which is consistent with our data. Remarkably, the integrated intensity of XₐXₐ grows quadratically with the excitation powers (<2000 μW, α ~ 1.9), which is a strong evidence for biexciton emission. Meanwhile, the typical crossover of exciton and biexciton intensities
has also been observed with the increasing excitation power. Moreover, it is found that the fwhm of the XA peak is \( \sim 2.1 \) times of that of XA (Figure S4d, Supporting Information). In ideal cases, the spectral width reflects the quasiparticle decay rate\(^\text{39–41}\) and the biexciton lifetime is expected to be half of the exciton lifetime\(^\text{42,43}\). Assuming the homogeneous broadening\(^\text{39,40}\) dominating for the observed PL at 4.2 K, the observed width ratio of XA to XA \( \sim 2.1 \) could be another signature for the biexciton emission in 1L WS\(_2\). Furthermore, the linear polarization dependences of photon energies of XA, XA/C0, XA/XA, and LS have been measured at three excitation powers (Figure S6, Supporting Information). The sinusoidal modulation has been found for XA, XA/C0 and XA/XA components, while there are no periodic trends for the LS component. In particular, the opposite linear polarization behaviors of photon energies have been observed for XA and XA/XA, which is a unique characteristic for identifying the XA/XA.\(^\text{44}\) Theoretically, in 2D case, the binding energy ratio of biexcitons to excitons is \( \sim 0.08 \) according to an exciton basis model\(^\text{48}\) when the effective masses of electrons and holes in 1L WS\(_2\) are taken as 0.27 and 0.32,\(^\text{49}\) respectively. Recent works have extracted the exciton binding energies of 0.53–0.71 eV for 1L WS\(_2\).\(^\text{20–22}\) As a result, the calculated biexciton binding energies of 42–57 meV agree well with our observations above. In addition, transient absorption measurements of the similar material of 1L MoS\(_2\) have been correlated to biexciton formation, where the extracted binding energies of 70 at 74K\(^\text{26}\) and 35 meV at 10 K\(^\text{50}\) for the biexcitons of XA/XA are in the same order as the data for biexcitons here. Note that the previous transient absorption measurements\(^\text{26,50}\) mainly imply biexciton formation via upward transitions (absorption), while our present steady-state data directly reflect biexciton emission via downward transitions between exciton and biexciton states. Both kinds of techniques are parallel but complementary for uncovering biexciton states in 1L TMDs. On the basis of the discussion above, the observed superlinear emission of XA/XA is attributed to biexciton states in 1L WS\(_2\). Further experimental investigations by transient four-wave mixing and time-resolved fluorescence spectroscopy together with selective polarizations should be very helpful to elucidate the nature of biexciton and possible multiexciton states in such 2D semiconductors.

Finally, the superposition effect of electrical doping and optical excitation has been further studied, and tunable excitonic emission in a 1L WS\(_2\) field-effect device has been demonstrated in a controllable manner. Figure 4a shows the PL spectra of the CVD-grown 1L WS\(_2\) device at different back-gate voltages and the excitation power of 65 \( \mu \)W. At 0 V, there are mainly two broad bands: the higher energy one from the combination of XA and XA/C0 and the other from the LS at lower energies which could be modified during device fabrication\(^\text{6,23,51}\) and not the focus here. With the increase of the positive back-gate voltage, the emission

---

**Figure 3.** Exciton, trion and biexciton states in a CVD-grown 1L WS\(_2\) at 4.2 K. (a) Photoluminescence spectra at various excitation powers. The total fit curve and subpeaks are shown in red and green, respectively. (b) Photoluminescence intensity mapping versus excitation power and photon energy, where dash curves are guide lines to indicate the spectral evolution. (c) Photon energies of four emission components versus excitation power. (d) Log–log plots of integrated intensities of four emission components versus excitation power. Solid lines are the linear fit curves, and the corresponding \( \alpha \) values are the slopes.
from negative trion and biexciton states becomes more obvious. At negative voltages, the enlarged spectra of the higher energy band have been shown in Figure S7 (Supporting Information), which consist of the emission from exciton ($X_A$) and positive trion states labeled by $X_A^+$. The evolution of emission states is clearly observed in the PL intensity mapping as a function of photon energy and gate voltage (Figure 4b). The center of exciton emission locates near zero or a small negative gate voltage, which indicates that the sample is nearly neutral or slightly n-doped. The emission zones of positive and negative trions behave like two wings, spreading from the exciton emission center, redshift with the carrier injection. The similar features of trion and exciton bands have been observed in the field effect devices based on 1Ls of WSe$_2$ and MoSe$_2$. More importantly, the $X_AX_A^-$ emission comes to be pronounced at positive back-gate voltages. As shown in the gate-tuned PL intensity maps at higher excitation powers (Figure 4c,d), the overall feature shifts down with respect to that in Figure 4b due to induced electron doping by strong photoexcitation. In a nearly neutral state of 1L WS$_2$, the binding energies of $\sim 12$, $10$, and $45$ meV are extracted for negative ($X_A^-$), positive trions ($X_A^+$) and biexcitons ($X_AX_A^-$), respectively. Note that, on the one hand, the binding energies of trions are much smaller than the thermal energy at rt ($k_BT = 26$ meV, $k_B$ is the Boltzmann constant); thus, the trion is instable in such a nearly neutral 1L WS$_2$ at rt which will be thermally activated to lose one electron or hole and form one exciton. This is supported by the almost absence of trion emission in the nearly neutral CVD-grown 1L WS$_2$ at rt (Figure 1e). On the other hand, the biexciton emission with a binding energy of...
energy of \( \sim 45 \text{ meV} \) is observed at 4.2 K but vanished at rt. This is explained as follows: At 4.2 K, the excited exciton state absorption in the spectral range of bieixciton transitions is dominant which is in favor of bieicxiton formation. This scene is consistent with the recent studies on bieicxiton formation in 1L MoS2 at 10 K.50 At rt, the exciton decay becomes faster than those at low temperatures so that the excited states of bieicxitons are hardly formed, and thus, the bieicxiton emission is absent. The accelerated exciton relaxation has been observed with the lifted temperature in 1L WS2,52 which is in line with the explanation above.

Figure 4e shows the gate-tuned PL spectra at the high excitation power of 6000 \( \mu \text{W} \), where the \( X_eX_e \) emission is dominant and sensitive to the modulated back-gate voltage. Figure 4f shows the schematics of the electronic and excitonic transitions at low (e.g., 65 \( \mu \text{W} \)) and high excitation powers (e.g., 6000 \( \mu \text{W} \)). Theoretical calculations14 and recent experiments19–21 have shown that the electronic band gap of 1L WS2 is larger than 2.4 eV. Under our laser excitation energy of 2.33 eV, the electrons are pumped up to the lower excitonic levels rather than the continuum. At rt and a low excitation power, the dominant emission is due to biexcitons rather than the continuum. At 4.2 K, the preferred emission is through exciton, trion and localized states for a moderate doped sample and trion states for a heavily doped sample, where the trion emission becomes more important at high excitation powers. At a low temperature of 4.2 K, the preferred emission is through exciton, trion and localized states at a low excitation power. The high excitation power and the excited exciton state absorption will cause the photon-induced n-doping and formation of bieicxiton states. With the increase in the electron doping and the excitation power, the \( X_eX_e \) emission starts to be dominant over the other three emission channels by exciton, trion, and localized states.

**CONCLUSIONS**

In summary, we have studied the intrinsic excitonic emission of a 2D semiconductor 1L-WS2. By applying the electrical back-gate and varying the excitation power, tunable emission from exciton, trion, bieicxiton, and localized states has been obtained. At rt, the roles of excitons and trions in PL emission are clearly identified under electrical doping and photoexcitation. At 4.2 K, the emission from localized states appears. With the increase in electron doping and/or excitation power, the superlinear (i.e., quadratic) emission due to bieicxitons occurs and becomes dominant. In a nearly neutral 1L WS2, the binding energies of \( \sim 10–15 \text{ meV} \) have been extracted for positive and negative trions. Here, the observed bieicxiton emission in 1L WS2 reflects strong electron–hole interactions in single-layer semiconductor, which is calling more attention to the research of many-body physics in atomically thin TMD layers. Our studies also develop an efficient strategy for manipulating the excitonic emission, which is valuable to 2D light-emitting applications.

**METHODS**

Two kinds of 1L WS2 samples were used here: one was mechanically exfoliated from a synthesized WS2 crystal (2D semiconductors Inc.) onto SiO2 (300 nm)/Si (500 \( \mu \text{m} \), p-type) substrates; the other was directly grown on the same SiO2/Si substrates by chemical vapor deposition as described previously.22,53 For the field effect devices, the electron beam lithography and evaporator were used to make the electrodes of Ni/Au (5 nm/80 nm) as source and drain contacts.34 The back-gate voltage was applied between the p-type Si substrate and the source/drain electrode.

The prepared 1L WS2 samples were bonded to a printed circuit board (PCB) attached to a three-dimensional piezo-stage in a confocal micro-Raman/PL spectroscopic system with a liquid helium cryostat. An 532 nm Nd:YAG laser was used to excite the samples through a \( 600 \times 600 \) objective lens, and the PL signals were collected by a grating (600/mm) spectrometer with a cooled charge-coupled device camera. The electrical transport data were measured by a commercial Keithley 4200 parameter analyzer.

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

**Acknowledgement:** This work is mainly supported by the Singapore National Research Foundation under NRF RF Award No. NRFRF2010-07, MOE Tier 2 MOE2012-T2-2-049, and A*Star SERC, PSF grant 1321202101. Shang thanks Dr. Rui Chen, Dr. Tingchao He, and Ms. Lin Ma for helpful discussions.

**Supporting Information Available:** Supplementary figures (Figures S1–S8) and the corresponding discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES AND NOTES**


