Excited State Biexcitons in Atomically Thin MoSe₂

Jiajie Pei,† Jiong Yang,‡ Xibin Wang,† Fan Wang,§‖ Sudha Mokkapati,§ Tieyu Lü,‡ Jin-Cheng Zheng,# Qinghua Qin,† Dragomir Neshev,⊥ Hark Hoe Tan,§ Chennupati Jagadish,§ and Yuerui Lu*†

†Research School of Engineering, College of Engineering and Computer Science, ‡Department of Electronic Materials Engineering, Research School of Physics and Engineering, and §Nonlinear Physics Centre, Research School of Physics and Engineering, The Australian National University, Canberra, ACT 2601, Australia
‡School of Mechanical Engineering, Beijing Institute of Technology, Beijing 100081, China
‖ARC Centre for Nanoscale BioPhotonics (CNBP), Department of Physics and Astronomy, Faculty of Science, Macquarie University, Sydney, NSW 2109, Australia
§Department of Physics, and Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen University, Xiamen 361005, China

Supporting Information

ABSTRACT: The tightly bound biexcitons found in atomically thin semiconductors have very promising applications for optoelectronic and quantum devices. However, there is a discrepancy between theory and experiment regarding the fundamental structure of these biexcitons. Therefore, the exploration of a biexciton formation mechanism by further experiments is of great importance. Here, we successfully triggered the emission of biexcitons in atomically thin MoSe₂ via the engineering of three critical parameters: dielectric screening, density of trions, and excitation power. The observed binding energy and formation dynamics of these biexcitons strongly support the model that the biexciton consists of a charge attached to a trion (excited state biexciton) instead of four spatially symmetric particles (ground state biexciton). More importantly, we found that the excited state biexcitons not only can exist at cryogenic temperatures but also can be triggered at room temperature in a freestanding bilayer MoSe₂. The demonstrated capability of biexciton engineering in atomically thin MoSe₂ provides a route for exploring fundamental many-body interactions and enabling device applications, such as bright entangled photon sources operating at room temperature.

KEYWORDS: MoSe₂, biexciton, two-dimensional materials, freestanding, room temperature

Atomically thin two-dimensional (2D) layered transition-metal dichalcogenide (TMD) semiconductors have aroused particular interest because of their interesting physical properties and promising applications in both fundamental research and optoelectronic devices.1−7 The highly enhanced Coulomb interactions in these atomically thin layers, arising from the reduced dimensionality and weak dielectric screening, allow the formation of tightly bound excitons,8 trions,9,10 and biexcitons.11−14 Biexcitons have been of particular interest for both fundamental studies of the remarkable many-body interactions15−17 and investigations of novel device applications, such as quantum logic gates,18 biexciton lasing devices19,20 entangled photon sources,21 etc. Recently, tightly bound biexcitons have been observed in monolayer TMDs, such as WSe₂,11 MoS₂12 and WS₂.13 These biexcitons in monolayer TMDs show an ultralarge binding
energy in the range of 50−70 meV, which is more than 1 order of magnitude higher than the values found in III−V quasi-2D quantum wells. This strong binding necessitates the complete understanding of the structures of these biexcitons and their dynamics in 2D materials as well as characterization of their properties and full investigation of their potential functionalities. A few theoretical models, such as the path integral Monte Carlo approach, effective mass model, and variational calculation method, have been used to estimate the binding energies of biexcitons in TMD 2D materials. These models consider a biexciton to be a spatially symmetric four-particle state. However, based on this symmetric four-particle model, the predicted binding energies of biexcitons in TMD monolayers are in the range of 18−24 meV, less than half of the values observed, suggesting a discrepancy between theory and experiment. Recently, Varga et al. using high-accuracy variational calculations, showed that the predicted binding energies of excited state biexcitons in TMD monolayers are in the range of 50−70 meV, which agrees well with the earlier experimental data. In Varga’s model, the excited state biexciton corresponds to a charge attached to a trion, which is energetically favorable than the ground state biexciton consisting of four spatially symmetric particles. How to further experimentally confirm the existence of the trion-charge-bound excited state biexcitons in the Varga’s model is extremely important. This will allow us to fully understand the structures and formation mechanisms of these biexcitons and will enable us to overcome the limitations of previous experiments by engineering the environment of these biexcitons.

RESULTS AND DISCUSSION

Here, we successfully observed tightly bound biexcitons with a binding energy of ~60 meV in atomically thin MoSe2. The measured binding energy matches well with the theoretically predicted value of the excited state biexcitons in MoSe2. We further probed the formation dynamics of these biexcitons and found that the density of biexcitons increases with increasing density of negative trions and decreases with increasing density of excitons. This finding suggests that the biexcitons observed here are excited state biexcitons instead of ground state biexcitons. More importantly, we successfully triggered the emission of excited state biexcitons at room temperature in freestanding bilayer MoSe2 by modulating three independent parameters: (1) dielectric screening, (2) density of trions, and (3) excitation power. The implications of the tightly bound biexcitons at room temperature in 2D materials are far-reaching. It provides a room-temperature 2D platform to explore fundamental many-body interactions, which provides a route for quantum logical devices and entangled photon sources operating at room temperature.

It has been known that many-body effects, which determine the behaviors of excitons, trions, and biexcitons, play important roles in optical transitions in low-dimensional...
materials, including quantum wells, carbon nanotubes, 2D semiconductors, and so on.1,11,26–37 Such a many-body effect, arising mainly from strong Coulomb interactions among charges, can be significantly enhanced with the reduction of dielectric screening from the environment11,26,27,38 (Figure 1a,b). Thus, the biexciton or even higher-order multiple exciton states will typically become more pronounced in an environment with lower dielectric screening. To explore the dielectric screening effect on the many-body interactions in atomically thin semiconductors, we fabricated two types of MoSe2 samples: SiO2-supported and freestanding thin layers. The freestanding MoSe2 sample was fabricated by mechanically transferring the sample onto a prepatterned circular hole on a SiO2/Si substrate, as illustrated in Figure 1c. The freestanding atomically thin layers were confirmed by the contrast difference in optical microscope images (Figure 1d and Figure S1a) and the photoluminescence (PL) intensity difference in the PL mapping images (Figure 1e and Figure S1b). The layer number was identified and confirmed by phase-shifting interferometry39 and PL spectroscopy measurements.

We compared the PL spectra of the MoSe2 samples measured at 6 K and found that for the SiO2-supported bilayer (2L) and monolayer (1L) MoSe2 samples, there are only two distinct PL peaks at approximately 1.615 and 1.645 eV (Figure 1f and Figure S1c). These PL peaks can be identified as trion (T) and exciton (A) peaks according to previous studies.10 Importantly, a new PL emission peak “X” at approximately 1.585 eV was observed from both the freestanding 2L (Figure 1f) and 1L (Figure S1d) MoSe2 samples. We observed this new peak from multiple freestanding 1L and 2L MoSe2 samples (more than 3 samples for each type). For some freestanding 2L MoSe2 samples, this new peak became completely dominant in the PL spectrum, and the exciton (A) and trion (T) peaks were not pronounced at 6 K (Figure 2 and Figure S3), possibly because these samples had slightly different sample-dependent initial doping levels compared with the one shown in Figure 1f.

To determine the origin of this new peak X, we carried out power-dependent PL measurements on one freestanding 2L MoSe2 sample at 6 K (Figure 2a). For a quantitative analysis, the integrated PL intensity of the X peak was plotted as a function of that of the exciton (A) peak (Figure 2b). By fitting the data with a power-law \( I_X \propto I_A^n \), where \( I_X \) is the integrated PL intensity of X peak and \( I_A \) is the integrated PL intensity of A peak,11 it is found that peak X grows superlinearly with the excitation power (\( \alpha \sim 1.23 \)). Based on the measured \( \alpha \) value, peak X is attributed to the emission of bieexcitons. In the ideal case, the \( \alpha \) value of bieexciton emission is expected to be close to 2; however, \( \alpha \) values in the range of 1.2 to 1.9 were typically observed for bieexciton emissions in quantum well systems30,41 and TMD semiconductors11,14 that might be due to the lack of thermal equilibrium between the states.11

Time-resolved PL (TRPL) measurement is another useful approach to identify the emission features in a PL spectrum. We measured the TRPL traces for the peaks A, T, and X (Figure 2c) at a temperature of 6 K. The decay trace curves were deconvoluted with respect to the instrument response and then were fitted with the equation

\[
I = A \exp\left(-\frac{t}{\tau_1}\right) + B \exp\left(-\frac{t}{\tau_2}\right) + C,
\]

where \( I \) is the PL intensity, \( A, B, \) and \( C \) are constants, \( t \) is time, and \( \tau_1 \) is faster decay rate and \( \tau_2 \) is the slower decay rate, indicating emission lifetimes for different decay processes.42 The measured lifetimes of exciton (A), trion (T), and bieexciton (X) were on the same order and comparable with each other, which is consistent with what has been reported in monolayer WSe2,11 indicating that the peak X is indeed from bieexciton rather than localized exciton as the lifetime of localized exciton should be an order longer than that of the exciton and trion.11 Moreover, the peaks A, T, and X from the freestanding 1L MoSe2 sample (Figure S4) possess consistent lifetimes with the respective peaks in
freestanding 2L MoSe$_2$ (Figure 2d), which suggests the same emission features in both freestanding 1L and 2L MoSe$_2$ samples.

In addition, the spectrum of this new emission feature is asymmetric and can be fitted to two peaks, labeled as “X” and “L”, by Lorentzian fitting (Figure S1d and Figure S2). The peak X is from the biexciton emission as discussed above, whereas the lower energy peak L could be from the contribution of defect states and is not the focus of this work. The measured full width at half-maximum (fwhm) value of the biexciton peak X in both freestanding 1L and 2L MoSe$_2$ samples was $\sim$46 meV, which is similar to that of the biexciton peak observed in 1L WS$_2$. From the temperature-dependent PL measurements (Figure S3a), we can clearly see that the intensity of the X peak increased dramatically as the temperature decreased from 63 to 6 K (Figure S3c).

Taken together, the observed power dependence and temporal dynamics properties of the X feature provide strong evidence for its assignment as a biexciton feature. We thus explored the binding energy of biexcitons and their dynamics to obtain a deeper physical insight into the biexcitons in atomically thin MoSe$_2$ layers. The binding energy of biexcitons is given by the energy difference between the exciton and biexciton peaks, assuming that an exciton is produced in the radiative decay of a biexciton. The measured energy difference values between the X and A peaks in freestanding 1L and 2L MoSe$_2$ samples are 60 meV (Figure S1d) and 57 meV (Figure S2), respectively, which are considered to be the biexciton binding energies of MoSe$_2$. These values match very well with the calculated binding energy (58 meV) of an excited state biexciton in MoSe$_2$ (see Table 1). Freestanding 2L MoSe$_2$ has a biexciton binding energy slightly smaller than that of 1L MoSe$_2$, which might be due to the relatively larger screening in 2L MoSe$_2$. According to the theoretical model, an excited state biexciton consists of a charge attached to a trion. The formation of an excited state biexciton state (TC) can be denoted as $T + C \rightarrow TC$, where T is a trion and C is a charge. In great contrast, the calculated binding energy of a ground state biexciton (spatially symmetric exciton pairs, denoted as A + A $\rightarrow$ AA) in MoSe$_2$ is only 18 meV (Table 1), which is much smaller than the observed biexciton binding energy.

In addition to the binding energy difference, another way to differentiate the excited state and ground state biexcitons is to probe the dynamic relationship between the densities of biexcitons and trions. Based on the different formation mechanisms of these biexcitons, the density of excited state biexcitons should increase with the increase of trion density, whereas the density of ground state biexcitons should decrease because the formation of trions can reduce the density of excitons. Here, we successfully used an electrostatic doping technique to control the trion density in a 2L MoSe$_2$ metal-oxide-semiconductor (MOS) device (Figure S5) at 83 K, which leads to the dynamic modulation of biexciton emission (Figure 3).

First, we carried out the PL intensity mapping as a function of photon energy and gate voltage, using a relatively low excitation power of 264 $\mu$W (Figure 3a). Under a back gate voltage of 50 V, the negative trion (T) emission peak was dominant in the PL spectrum. At the same time, a new PL peak (labeled as X) at the low energy side appeared. When a negative back gate voltage of $\sim$50 V was applied, the exciton (A) emission peak became dominant and the new PL peak X disappeared (Figure 3a,c). To obtain a better insight, we generated the PL intensity mapping again using a relatively high excitation power of 602 $\mu$W (Figure 3b). The intensity of this new PL peak X increased much faster than the intensities of the exciton and trion peaks. Based on the superlinear increasing manner, this new PL peak X is assigned to the emission of biexcitons. From Figure 3b,d, we can clearly see that the density of biexcitons increases with increasing density of negative trions and decreases with increasing density of excitons. This further confirms that biexcitons observed here are excited state biexcitons (Figure 3e), instead of ground state biexcitons (Figure 3f). According to the calculation results by Varga et al., the binding energy of ground state biexcitons is only 18 meV, very close to the binding energy of trions. Therefore, it might not be possible to distinguish the ground state biexcitons and trions in experiments. Also, excited state biexcitons are more likely to be observed in experiments than ground state biexcitons because excited state biexcitons are energetically favorable and are spatially extended. In addition, we only observed the emissions of excitons and trions but no emission of biexcitons in 1L MoSe$_2$ MOS devices at 83 K (Figure S6), which is consistent with a previous report. The different PL behaviors in 2L and 1L MoSe$_2$ MOS devices are likely caused by the different trion densities in 2L and 1L MoSe$_2$ samples (as will be discussed later).

Due to thermally activated dissociation, biexcitons in both the freestanding MoSe$_2$ samples (Figure 1) and the 2L MoSe$_2$ MOS device (Figure 3) could only be observed at cryogenic temperatures (T $< 100$ K), which is similar to previously reported biexcitons in other TMD semiconductors. The requirement of cryogenic temperature would significantly limit the potential applications of biexcitons. Fortunately, our experimental data (Figures 1–3) have shown that the probability of biexciton emissions in atomically thin MoSe$_2$ can be enhanced under the following three conditions (Figure 4a): (1) reduced dielectric screening, (2) enhanced density of trion states, and (3) high excitation laser power.

Here, we successfully demonstrated the emission of excited state biexcitons at room temperature in freestanding 2L MoSe$_2$ samples, in which those three parameters were all well-optimized (Figure 4). To achieve a clear comparison, we measured PL intensity mapping plots at room temperature as a function of photon energy and excitation power for four types of MoSe$_2$ systems (Figure 4b–e): freestanding 2L freestanding 1L, SiO$_2$-supported 2L, and SiO$_2$-supported 1L. A biexciton emission feature at $\sim$1.490 eV was observed only in the freestanding 2L MoSe$_2$ sample under relatively high excitation power at room temperature. To confirm the assignment of the biexciton peak in Figure 4b, we fitted the PL spectra and plotted the integrated intensities of the biexciton and exciton peaks as a function of excitation power, as shown in Figure S7. At low excitation power, the trion peak (T) was dominant in the PL spectrum. With the growth of excitation power,

| Table 1. Measured and Theoretically Calculated Binding Energies of Biexcitons in TMDs (meV) |
|------------------------------------------|-----|-----|-----|-----|
| theory (A + A)$^{25}$                       | 22  | 18  | 24  | 20  |
| theory (T + C)$^{25}$                       | 69  | 58  | 67  | 59  |
| experiments $^{14}$                         | 70$^{1}$ | 60$^{9}$ | 65$^{13}$ | 52$^{11}$ |

Note: T is a trion; C is a charge, and A is an exciton. $^{a}$This work.
however, the intensity of the X peak increased much faster than that of the trion peak. Particularly, when the excitation power was lower than 50 μW, the integrated intensity of the trion and biexciton peaks increased as a function of power with exponent (α) values of ∼0.85 and ∼1.01, respectively. When the excitation power was higher than 50 μW, the X peak became dominant in the PL spectrum, and the α values of the trion and biexciton peaks became ∼0.55 and ∼1.41, respectively. The superlinear power dependence of this X peak further confirms its biexciton assignment. At high excitation power, the α value of the trion peak decreases, whereas that of the biexciton peak increases, which suggests the conversion of the trions to excited state biexcitons. In addition, the α value of the trion peak at room temperature was slightly less than 1, similar to the situation observed in other TMD semiconductors due to the lack of full equilibrium. On the other hand, the ratio of α values between biexciton and trion (1.41/0.55) increases dramatically when the excitation power is higher than 50 μW, suggesting that there might be a threshold value of trion density. Before the threshold, the transformation from trion to biexciton is restrained to some extent; beyond the threshold, the transformation from trion to biexciton start to dominate. In the power-dependent PL measurements, we used relatively low pumping power, and the power-induced spectral shifts of the exciton peaks in all freestanding and SiO2-supported samples were less than 2.9 meV (Figures 4c,e and 3c,d), similar to the situation in a previous report. This suggests that our pump laser has negligible heating effect on all the samples. The band gap renormalization effect can be ignored in Figure 4b, owing to the relatively low photodoping level (Supporting Information).

The reason why biexciton is observed in freestanding 2L instead of 1L MoSe2 at room temperature could be explained as follows. The 1L MoSe2 gives only one PL peak at ∼1.562 eV from the emission of excitons at room temperature, whereas 2L MoSe2 gives only one PL peak at ∼1.520 eV from the emission of trions, which can be clearly observed from their temperature-dependent PL measurements (Figure S8a,b). This difference might be caused by the relatively low initial doping levels in MoSe2 crystals and the different band gap nature in 1L and 2L MoSe2.
2L MoSe₂ samples. The 1L MoSe₂ possesses a direct band gap and thus a relatively balanced distribution of thermal charges in the K−K valleys of the band structure, where the PL transitions occur. In contrast, 2L MoSe₂ possesses an indirect band gap and thus an unbalanced thermal charge distribution in the K−K valleys, which leads to a higher trion density (Figure S8c,d). Therefore, at room temperature, a freestanding 2L MoSe₂ sample possesses low dielectric screening and high trion density, which leads to the emission of excited state biexcitons under a relatively high excitation power. The demonstrated capability of biexciton engineering at room temperature in MoSe₂ will allow us to explore fundamental many-body interactions in a simplified room-temperature 2D platform, which will enable a class of quantum devices such as bright entangled and correlated photon sources operating at room temperature.21 In addition, based on theoretical calculations, biexcitons have a radius larger than that of excitons and trions in 2D TMDs (Supporting Information). Because of the larger separation between charges in biexcitons, the Coulomb interactions of biexcitons are more likely to be influenced by dielectric screening of the external media than those of trions in TMDs.11

CONCLUSIONS

In conclusion, we observed tightly bound excited state biexcitons with a binding energy of ~60 meV in atomically thin MoSe₂, which was confirmed by both the agreement of experimental and theoretical values of the binding energy and the observed formation dynamics of these excited state biexcitons. We also found that the emission from these excited state biexcitons in atomically thin MoSe₂ strongly relies on three important conditions: reduced dielectric screening, high density of trions, and high excitation power. By optimizing those three conditions, we successfully triggered the emission of excited state biexcitons in freestanding 2L MoSe₂ samples at room temperature. Our findings will provide a platform to explore fundamental many-body interactions in atomically thin semiconductors. We envisage that such a 2D platform can form the basis of bright quantum sources of entangled and correlated photons, thus enabling a class of ultrafast optoelectronics and
quantum devices with applications in quantum communications and cryptography.

**METHODS**

**Device Fabrication and Characterization.** Mechanical exfoliation was used to dry transfer 1L and 2L MoSe$_2$ flakes onto the SiO$_2$/Si substrate (a 275 nm layer of thermal oxide on n$^-$-doped silicon), near the prepatterned Au electrode for those MOS devices. The Au electrodes were patterned using standard photolithography, metal deposition, and lift-off processes. Another thick graphite flake was similarly transferred to electrically bridge the MoSe$_2$ flake and the Au electrode, forming a MOS device. For the suspended samples, 1L and 2L MoSe$_2$ samples were dry transferred onto a 275 nm SiO$_2$/Si substrate with pre-etched 3 μm deep holes.

**Optical Characterizations.** PL measurements at room temperature and 83 K were conducted using a Horiba JobinYvon T64000 micro-Raman system equipped with charge-coupled device (CCD) and InGaAs detectors, along with a 532 nm Nd:YAG laser as the excitation source. For low-temperature (down to 83 K) measurements, the sample was placed into a microscope-compatible chamber with a low-temperature controller (using liquid nitrogen as the coolant). The power-dependent PL measurements at 6 K and TRPL bias was applied using a Keithley 4200 semiconductor analyzer. Detecting the PL intensity decay by a Si single photon avalanche diode signal was collected by a grating spectrometer, thereby either recording the alpha300S system in the scanning confocal microscope configuration. Micro-PL spatial mapping was performed using a commercial WiTec confocal microscope with a pulsed laser (frequency doubled to 522 nm, with a 300 fs (TCSPC) system and uses liquid helium as the coolant. A linearly polarized laser was used for low-temperature (down to 83 K) measurements, where the sample was placed into a microscope-compatible chamber with a low-temperature controller (using liquid nitrogen as the coolant).

**ACKNOWLEDGMENTS**

We would like to acknowledge the facility support from the ACT node of the Australian National Fabrication Facility (ANFF). We also acknowledge financial support from ANU Ph.D. student scholarship, China Scholarship Council, ANU Major Equipment Committee fund (No. 14MEC34), Australian Research Council (ARC) Discovery Early Career Researcher Award (DECRA) DE140100805, ARC Discovery Project (DP150103733), the Natural Science Foundation of Fujian Province, China (Grant No. 2015J01029), and Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (the second phase).

**REFERENCES**


**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b03909.

Details of additional experimental PL measurement results and data analysis (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: yuerui.lu@anu.edu.au.*

**ORCID**

Qinghua Qin: 0000-0003-0948-784X

Dragomir Neshev: 0000-0002-4508-8646

Yuerui Lu: 0000-0001-6131-3906

**Author Contributions**

Y.L. designed the project; J.P. carried out sample mechanical exfoliation and microscopy imaging; J.Y. and J.P. carried out the PL measurements; F.W., S.M., H.T., and C.J. built the setup for PL measurements; D.N. built the setup for micro-PL mapping; T.L. and J.-C.Z. conducted the DFT calculations; J.P., Y.L., and J.Y. analyzed the data and prepared the manuscript; all authors contributed to the manuscript. J.P. and J.Y. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.
(22) Klingshirn, C. F. Semiconductor Optics; Springer: Berlin, 2007; Vol. 3.