Alloying effect on bright–dark exciton states in ternary monolayer Mo$_x$W$_{1-x}$Se$_2$

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Abstract

Binary transition metal dichalcogenides (TMDCs) in the class MX$_2$ (M = Mo, W; X = S, Se) have been widely investigated for potential applications in optoelectronics and nanoelectronics. Recently, alloy-based monolayers of TMDCs have provided a stable and versatile technique to tune the physical properties and optimize them for potential applications. Here, we present experimental evidence for the existence of an intermediate alloy state between the MoSe$_2$-like and the WSe$_2$-like behavior of the neutral exciton (X$_0$) using temperature-dependent photoluminescence (PL) of the monolayer Mo$_x$W$_{1-x}$Se$_2$ alloy. The existence of a maximum PL intensity around 120 K can be explained by the competition between the thermally activated bright states and the non-radiative quenching of the bright states. Moreover, we also measured localized exciton (X$_0$) PL peak in the alloy and the observed behavior agrees well with a model previously proposed for the 3D case, which indicates the theory also applies to 2D systems. Our results not only shed light on bright–dark states and localized exciton physics of 2D semiconductors, but also offer a new route toward the control of the bright–dark transition and tailoring optical properties of 2D semiconductors through defect engineering.

Introduction

Due to their direct optical bandgaps and strong light–matter interaction represented by robust excitons, binary transition metal dichalcogenide (TMDC) monolayers have attracted attention both for their potential in modern devices and interesting fundamental physics [1–10]. In contrast, multi-element alloys of monolayer TMDCs provide researchers better control of their optoelectronic responses and, therefore, deeper insight into the underlying fundamental physics of this material system [11–13]. Alloy-based monolayers of TMDCs have been used to tune the optical bandgap via compositional engineering [14, 15]. In addition, TMDC alloys provide an extra-wide tuning range of the spin states in the valence band (up to a few tens of meV) and the conduction band (hundreds of meV), because of the spin–orbit (SO) coupling relative to the transition metal d-orbitals [15]. The sign of the spin-splitting in the conduction band strongly dictates the optically generated valley polarization and the dark versus bright exciton recombination of the neutral exciton (X$_0$) ground state. Hence, an understanding of the competition between the bright–dark exciton states in monolayer Mo$_x$W$_{1-x}$Se$_2$ alloys is critical for modulating the physical properties of the alloys and improving their light emission efficiency.

Here, we experimentally demonstrate bright–dark exciton state transitions in TMDC monolayers of Mo$_x$W$_{1-x}$Se$_2$ alloys. The monolayers were isolated from crystals using the mechanical exfoliation technique, and these monolayers present good chemical stability in ambient conditions along with high photoluminescence (PL) efficiency. We probe the temperature-dependence of the conduction band SO spin-splitting of the bright versus dark exciton light emission. For MoSe$_2$ and WSe$_2$ monolayers, the PL intensity of neutral excitons (X$_0$) increases and decreases by an order of magnitude, respectively, as functions of
temperature, in agreement with other reports (16–18). Interestingly, the ternary monolayer TMDC shows a transition between these two extreme behaviors. We hypothesize that the bright–dark states transition originates from scattering processes that flip the spin of the electron, which induce relaxation between dark and bright states. The bright–dark states relaxation is dominated by an equilibrium population through spin-conserving processes with phonon-assisted emission [18, 19]. Additionally, a sub-bandgap emission peak that experiences a large blue shift and increasing overall PL intensity as a consequence of the anion Se vacancy generation was observed, demonstrating a localized state exciton behavior at defect sites. We employed a localized-state model to explain the observed behavior and found that the experimental results and theory model agree well. Our results not only provide insight into the bright–dark states and localized exciton physics of 2D semiconductors, but also enable a new route toward control of the bright–dark transition and tunable optical properties of 2D semiconductors through modification of the elements in the alloy.

For this study, monolayers of an Mo0.5W0.5Se1.9 alloy were exfoliated from a bulk crystal (2D semiconductors, see supplementary methods, available online at stacks.iop.org/NJP/19/073018/mmedia). Figure 1(a) presents the Mo1–xWxSe2 crystalline structure, which resembles a honeycomb lattice. Figure 1(b) shows a typical optical image of a monolayer alloy on a 300 nm SiO2/Si substrate. To probe the alloy stoichiometry, scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX) was used, see supplementary figure S2. The SEM–EDX data was measured for different flakes and the concentration varies only by 2%. The SEM–EDX results (supplemental figure S2) indicate that the crystal contains 17.6% Tungsten, 17.2% Molybdenum, and 65.1% Selenium. No other elements were detected in such an alloy. One should note that the obtained alloy stoichiometries here are limited by the resolution of the EDX technique. Advanced techniques with better resolution may provide more precise information of alloy behavior dependence on stoichiometries. Additionally, the alloy Mo0.5W0.5Se1.9 was further characterized using high-resolution transmission electron microscopy, as shown in figure 1(c). The alloy clearly shows a periodic atomic arrangement with a honeycomb-like structure, despite the random distribution of the Mo/W atoms. Furthermore, the electron diffraction
results, as shown in figure 1(d), further demonstrate that the alloys are highly crystallized and layered in the hexagonal phase.

To better investigate the alloy optical properties, the TMDC alloy was further characterized using Raman and PL. The Raman spectra dependence on the layer number of the alloy is shown in figure 2(a). The alloy displays a prominent Raman peak around 246 cm$^{-1}$. The intensity decreases with increasing number of layers, which is caused by the screening effect of the interlayer [20, 21]. Figure 2(c) shows the Raman spectrum of the monolayer alloy compared with monolayers of MoSe$_2$, Mo$_{0.5}$W$_{0.5}$Se$_{1.9}$, and WSe$_2$. We found that the dominant Raman mode position was located between the out-of-plane A$_{1g}$ mode of MoSe$_2$ at 241 cm$^{-1}$ and the WSe$_2$ at 251 cm$^{-1}$, consistent with previously reported values [20–22].

In order to gain a deeper insight into the robust exciton behavior and SO splitting at valence bands in such alloy flakes, we investigated the thickness-dependent PL spectra at room temperature (RT). Figure 2(b) shows the PL spectra dependence on the layer number of the Mo$_{0.5}$W$_{0.5}$Se$_{1.9}$. The spectrum of the monolayer Mo$_{0.5}$W$_{0.5}$Se$_{1.9}$ shows PL peaks around 780 nm ($\sim$1.589 eV) and 652 nm ($\sim$1.90 eV), which correspond to the X$_0$ and X$_B$ direct exciton transitions of the alloy, respectively. One notes that the X$_0$ and X$_B$ exciton peak positions indicate a large SO splitting ($\sim$0.312 eV) of the valence bands. With increasing layer number, weak PL peaks are observed at 810 nm ($\sim$1.53 eV) for bilayer and 830 nm ($\sim$1.493 eV) for few layers. The low intensity and red shift of the PL peaks with an increasing layer number are attributed to the quantum confinement effect, which is consistent with the dependence of the PL peak on the layer number [2, 10]. Figure 2(d) shows the PL spectrum of the monolayer alloy compared with the monolayer MoSe$_2$ and WSe$_2$. It is clear that the dominant PL peaks at 780 nm ($\sim$1.589 eV) of the alloy monolayer are located between the 795 nm ($\sim$1.56 eV) of monolayer MoSe$_2$ and 749 nm ($\sim$1.66 eV) of WSe$_2$, consistent with previously reported values [16–18].

The experimental evidence of spin-splitting in the spin-polarized conduction band of the transition metal can be seen in the nature of the neutron exciton (X$_0$) ground state by way of optically dark (electrons in the highest valence band and the lowest conduction at K/K’ points show antiparallel spins) or bright (parallel spins) states (see figure 3(a)). One notes that the conduction bands in TMDC materials originate from the dz$_2$ orbitals
of metal atoms and, to create order, there are no spin splitting of the bands \[23, 24\]. However, with regards to the role of the less strongly coupled chalcogen orbitals and the higher-order interactions to other orbitals of the metal atoms, theory predicts that the spin-polarized conduction band will generate a spin splitting of tens of meV \[23–26\], resulting in a band splitting between bands of opposite electron spin. The sign of spin-splitting polarized in the bands is dependent on varying TMDC materials. For monolayer WX\(_2\) (X = S, Se), electrons in the highest valence band and the lowest conduction band and at K/K' points show an antiparallel spin (dark state) \[18, 27\]. In contrast, for MoX\(_2\) (X = S, Se), electrons in the upper valence band are expected to have a spin polarization that matches that in the lower conduction band (bright state) \[23–25, 28\].

For a better understanding of the competition between the bright and the dark exciton states of the neutral exciton (X\(_0\)) in such ternary monolayer alloys, we investigated the temperature dependent excitonic PL spectra. Figure 3(b) shows the temperature-dependent PL from monolayer Mo\(_{0.5}\)W\(_{0.5}\)Se\(_{1.9}\). As the temperature decreases from RT to \(T = 120\) K, the intensity of the X\(_0\) exciton emission decreases and the emission feature blue-shifts 56.7 meV due to the temperature-dependent effect on the band gap \[16\]. The ternary sample Mo\(_x\)W\(_{1-x}\)Se\(_2\) shows a behavior qualitatively similar to binary TMDC MoSe\(_2\) in the range from RT to \(T = 120\) K. Interestingly, figure 3(b) displays the significant decrease in the neutral exciton (X\(_0\)) PL intensity observed when cooling from \(T = 120\) K. For temperatures between 120 and 30 K, we can separate the PL intensity evolution of the neutral exciton (X\(_0\)) and the trion (X\(_T\)) for ternary samples, which are shown in figure 3(c). For ternary samples, we find that the neutral exciton (X\(_0\)) PL intensity decreases as the temperature drops below \(T = 120\) K, in contrast with
the increase in intensity with a decrease in temperature above $T = 120$ K. The PL behavior is qualitatively similar to binary TMDC WSe$_2$ when the temperature is decreased from $T = 120$ to $T = 15$ K (see supplemental figure S4).

These temperature-dependent PL measurements provide experimental evidence of the sign of the conduction band SO-splitting in these ternary materials. The abnormal PL emission (high temperature–like MoSe$_2$ and low temperature–like WSe$_2$) clearly shows the transition between bright and dark states in ternary monolayer Mo$_{0.5}$W$_{0.5}$Se$_{1.9}$. Such transition behavior in this ternary monolayer alloy can be explained by the theoretical predictions regarding spin flips of the electron inducing relaxations between dark and bright excitons [18, 19]. Regarding the dynamic mechanism leading to population equilibrium between these bright and dark states relaxation, theory predicts the occupation of both conduction bands was governed by equilibrium populations via spin-conserving processes (see figure 3(a)). At temperatures below 120 K, excitons mostly recombine through the hot (fast) relaxation channel. The decreasing PL intensity of the neutral exciton ($X_0$) with decreasing temperature suggests that a lower-lying dark state exists in the ternary monolayer Mo$_{0.5}$W$_{0.5}$Se$_{1.9}$ that reduces emission from the bright states (see figure 3(a)), indicating that thermal activation from the dark states was significantly suppressed. On the other hand, the decreasing PL intensity of neutral exciton ($X_0$) with increasing temperature from $T = 120$ K to RT indicates that the bright states relax directly to the valence band through non-radiative recombination processes (see figure 3(a)), which is very similar to the temperature dependence of MoSe$_2$. The competition between the thermally activated bright states and the non-radiative quenching of the bright states gives rise to the abnormal PL emission behavior in this ternary alloy. Results for similar ternary alloys with different atomic ratios and WSe$_2$ are also provided in supplementary information. We found that only the Mo$_{0.3}$W$_{0.7}$Se$_{1.9}$ composition gives a clear PL intensity transition in the measured temperature range (see supplementary S5). More Mo content leads to the monotonic decrease of PL intensity and WSe$_2$ shows a clear monotonic increase of PL intensity as the temperature goes higher. Our observation of the intermediate state, which captures the beautiful transition between more MoSe$_2$ like behavior to more WSe$_2$ like behavior, provides direct evidence of alloy composition dependence of spin-polarized conduction bands with a small gap splitting between bands of opposite electron spin, as well providing an opportunity to explore new many-body effects in 2D semiconductors. In addition, as shown in figure 3(c), the abnormal shape of the low-energy PL peak is the distribution of localized excitons, and the broadening lineshape may be explained with the localized excitons model [32, 33]. Such significant broadening of the luminescence is attributed to the random distribution of the Mo and W, known as alloy broadening [29–31].

Figure 4(a) shows schematic diagrams of different disorder potentials. Excitons below (above) the potentials are localized (delocalized) and take longer (shorter) to capture electrons. The inset shows an illustration of the PL process with $X_Y$ and $X_0$. At low temperatures, the thermal excitation energy ($k_B T$) is less than the exciton binding energy, such that the electrons may prefer to stay in the trion or localized state. This energy level is lower than that of the exciton state. The excited electrons are trapped by the defect levels just below the conduction band, which explains the PL peak position of the localized state exciton ($X_0$). This energy level is lower than that of the neutral exciton (see figure 3(a)). These trapped electrons relax by emitting phonons and then recombine with the valence band hole by emitting localized state exciton ($X_0$) emission. When the temperature increases, localized excitons can be thermally activated into the delocalized states (free electron-hole recombination) and then captured by the competing recombination as free carriers or nonradiative decay channels. The electrons escape their bound trion state due to thermal fluctuations. Therefore, it is expected that the PL intensity of trapped (localized) exciton emission decreases monotonically with increasing temperature (see figure 3(b)).

The luminescence intensity $I(T)$ of a localized exciton ($X_0$) is quenched with increasing temperature induced by the ionization of the excitons from the defects. The temperature dependence can be modeled via the formula [32]

$$\frac{I(T)}{I(T = 0)} = \frac{1}{1 + C \exp(-E_A/k_B T)},$$

(1)

$E_A$ represents the thermal activation energy and $C$ represents a pre-factor. Usually, the activation energy is found to be equal to the localization energy, $E_A = Q$. From the fitting (solid red line in figure 4(b)), we calculate the thermal activation energy to be 24.7 meV. Additionally, we found that the peak positions of the neutral exciton ($X_0$) fit well (solid line in figure 4(c)) using a standard semiconductor bandgap dependence of $E_g(T) = E_g(0) - \frac{\hbar \omega_c}{2 \pi} \left( \tanh \left( \frac{\hbar \omega_c}{2 \pi k_B T} \right) - 1 \right)$ [16], where $E_g(0)$ is the ground-state transition energy at 0 K, $\omega_c$ is a dimensionless coupling constant and $\hbar \omega_c$ is the average phonon energy. From the fitting, we extract the parameters of $X_0$: $E_g = 1.676$ eV, $S = 2.69$, and $\hbar \omega_c = 30.7$ meV.

The temperature dependence of the luminescence spectra from localized excitons ($X_0$) can be quantitatively described by a model found in [32]. Assuming all localized excitons ($X_0$) have the same radiative recombination rate, the peak position of a localized exciton ($X_0$) can be written as [32, 33]
This model takes into account the thermal activation and transfer of the localized excitons, which are used to fit the experimental results in semiconductor alloys (3D) and quantum dots (0D). We employed this model to fit the experimental results in 2D TMDC alloys (see figure 4(d)). By considering the thermal activation energy and the transfer of localized excitons, we found that the peak positions of the localized exciton \( (X_B) \) fits well (solid line in figure 4(d)) using this model. As shown in figure 4(d), the localized exciton is frozen at temperatures below \( T = 30 \) K, confirming good agreement between the theoretical model and the experiment. It is important to note that the activation energy \( (E_A = 24.7 \text{ meV}) \) obtained in figure 4(b) is less than the value of \( (E_A - E_0 = 40 \text{ meV}) \) in figure 4(d), meaning defects in the alloy are thermally activated as non-radiative centers to quench the luminescence, thus reducing the thermal activation energy. The temperature dependence of the luminescence spectra of localized excitons qualitatively agrees with our proposed model, indicating that the model can be developed for a general case (i.e., 3D, 2D, 1D, 0D) for localized excitons such that it reproduces, quantitatively, all the anomalous temperature behaviors of localized-state luminescence. The main reason this model can be generalized is that the model of such localized electronic states is assumed to be a distribution function of energy and is expected to be an ensemble with a Gaussian-type density of states. It is important to note that the main difference between 2D TMDCs and GaAs quantum wells is the much smaller size of the exciton Bohr radius (~0.5 nm) in a TMDC ML, compared to ~10 nm in GaAs quantum wells. Such a small size of the exciton Bohr radius and the correlation length of potential fluctuations most likely explains the ultrafast intrinsic radiative lifetime in TMDCs. In our case, the anion Se vacancy creates a complex spatial landscape for the electronic states and brings about the presence of localized states with energies of several hundred meV below the band gap, thereby resulting in high luminescence efficiency as well as the abnormal \( X_B \) luminescence peak position shift.

In conclusion, the temperature-dependent PL in ternary monolayer TMDCs was investigated. Experimental evidence for the existence of a composition dependence of the neutral exciton emission intensity was demonstrated and explained by the spin flips of the electron inducing relaxation between dark and bright excitons. A sub-bandgap emission peak with an increase in the overall PL intensity, and a large blue shift were found to arise from the anion (Se) vacancy acting as a trap state, indicating a localized state exciton behavior at defect sites. This work provides strong evidence of alloying tuning on bright–dark states relaxation and deeper
understanding of localized exciton physics of 2D semiconductors and paves the way towards control of the bright–dark states transition and tailoring the optical properties of 2D semiconductors by defect engineering.

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Author contributions

YPL and JY conceived the project and designed the experiment. YPL prepared the monolayer and few-layer samples and completed RAMAN and PL measurements. XZ and YL performed HRTEM measurements and the corresponding analysis, SL carried out experimental SEM–EDX measurements and analyzed the experimental data. All authors contributed to discussions and manuscript revision.

Competing for financial interests

The authors declare no competing financial interests.

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