Identifying multiexcitons in MoS$_2$ monolayers at room temperature

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One of the unique features of atomically thin two-dimensional materials is strong Coulomb interactions due to the reduced dielectric screening effect; this feature enables the study of many-body phenomena such as excitons, trions, and biexcitons. However, identification of biexcitons remains unresolved owing to their broad peak feature at room temperature. Here, we investigate multiexcitons in monolayer MoS$_2$ using both electrical and optical doping and identify the transition energies for each exciton. The binding energy of the assigned biexciton is twice that of the trion, in quantitative agreement with theoretical predictions. The biexciton population is predominant under optical doping but negligible under electrical doping. The biexciton population is quadratically proportional to the exciton population, obeying the mass-action theory. Our results illustrate the stable formation of not only trions but also biexcitons due to strong Coulomb interaction even at room temperature; therefore, these results provide a deeper understanding of the complex excitonic behaviors in two-dimensional semiconductors.

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Monolayer transition-metal dichalcogenides (TMDs) have been highlighted as a promising platform for fundamental studies of many-body interactions because the interaction emerges strongly even at room temperature because of reduced dielectric screening [1–18]. Exciton binding energies are typically large in two-dimensional (2D) systems because of the strong Coulomb interactions between charged particles; they generally range from 0.3 to 1.0 eV, and those of higher-order excitons range from 18 to 70 meV [19,20]. These binding energies are still sufficient for distinguishing higher-order excitons at room temperature, whereas they have rarely been realized in three-dimensional semiconductors or quantum wells (QWs) because of their relatively small binding energies. The tightly bound electron-hole pairs in TMDs allow negatively charged trions to be generated by electrostatic doping [4], triggering research on exciton complexes, including biexcitons, in various TMDs [5,20–25]. This unique feature of 2D semiconductors provides the opportunity to elucidate new optoelectronic phenomena involving many-body interactions that can be applied to a new class of quantum emitters for light-emitting diodes [26], optical communication devices [27], and monolayer lasers [28]; thus, it is necessary to understand these many-body interactions for practical applications realized by manipulating excitons precisely, as well as the fundamental physics of new emergent 2D systems.

However, one fundamental question is why biexcitons are not identified at room temperature, whereas trions are commonly reported [4,6,7,9,25]. In conventional semiconductors, including bulk materials, quantum dots, and QWs, biexciton formation at room temperature has been reported [29–31]. Although the biexciton binding energy (∼30 meV) of CdSe QWs is much lower than that of TMDs (which exceeds ∼60 meV) [19,20], biexcitons form stably even at room temperature, because the binding energy is higher than the thermal energy, $k_B T = 26$ meV, where $k_B$ and $T$ are the Boltzmann constant and room temperature, respectively [29]. Even though biexcitons have a stronger binding energy than trions in TMDs, biexcitons have rarely been reported at room temperature except for a report on biexciton observation at edges and grain boundaries of WS$_2$ monolayer flakes [32], while they are well studied in low-temperature experiments as well as theoretically [21,25,33].

The transition energies of the exciton and trion in monolayer MoS$_2$, a representative TMD, have been extensively investigated. Figure 1(a) summarizes the reported data from photoluminescence (PL) experiments on MoS$_2$ monolayers at room temperature [1–18]. The inset shows selected data obtained using SiO$_2$/Si substrates [2,4,5,7–9,12–15,18]. The observed A-peak positions are scattered in a wide energy range from 1.90 to 1.83 eV. The peaks assigned to the neutral exciton ($A^0$, solid circles) and trion ($A^-$, open circles) in the A exciton mode fluctuate greatly, even overlapping each other. This A peak was further obscured by the large unassigned values (A, stars), for which the fluctuation (∆E $\approx$ 70 meV) exceeds the theoretical predictions and experimental determinations of not only the trion binding energy (∼30 meV) [19,24,34], but also the biexciton binding energy (∼60 meV) [19,20,33]. This large deviation of the peak position further exemplifies the ambiguity of distinguishing exciton and trion peaks from each other owing to broad features of excitonic peaks in MoS$_2$ monolayers even at low temperature [35], while sharp and isolated peaks of multie excitons were observed in other TMDs [21,25]. Moreover, this disagreement of the peak position is more prominently affected by complex exciton generation depending on the excitation laser intensity [36], rather than by the sample conditions arising from different sampling processes. The changes in the binding energy of excitons and trions depending on the doping state, defects, growth methods, and dielectric substrates are not sufficient to cover the large deviation under the same measurement conditions, whereas the populations are noticeably affected [5,9,12,18].

In this regard, we speculate that the reported data [Fig. 1(a)] may include biexcitons, because their binding energy is within...
ΔE. The positions of excitons and trions were not clearly identified with a general consensus [Fig. 1(a)], and no effort was made to distinguish possible biexcitons from broad peaks, although the peak positions should be identified by systematic control of the doping levels of samples and the excitation laser power, because biexcitons are formed at high exciton densities [21], and neutral excitons are generated at extremely low excitation power [36], whereas trions are rarely observed at weak optical densities [2].

Here, we identify multie excitons by measuring the PL of monolayer MoS2 under systematic modulations of the electrostatic doping states and exciting optical density at room temperature. Figure 1(b) schematically depicts the binding energies (Ex, Et, and E(xx)) and transition energies (Ax, At, and A(xx)) for the neutral exciton, trion, and biexciton in the A exciton mode, respectively, where Ex = EG − Ax, Et = Ax − At, E(xx) = Ax − A(xx), and EG denotes the band gap [6,21,22,37–39]. As the photocarrier density, which is modulated by the excitation laser power (Pex) to realize optical doping (OD), and the intrinsic carrier density, which is controlled by electrical doping (ED), increase, Ax is converted to positive or negative At, depending on the excess carrier type. As the population of electron-hole pairs increases in proportion to the OD, excitons are accordingly converted into A(xx).

To investigate the multie excitons depending on ED and OD, we used monolayer MoS2 field-effect transistors (FETs), where monolayer MoS2 flakes were synthesized by chemical vapor deposition [40]. The intrinsic doping states are estimated by electrical characterization, because MoS2 reveals intrinsic n doping arising from inherent impurities, defects, and substrate effects [4,6,7,44]. Figure 2(a) shows the drain current (Ip) for VD = 0.1 V as a function of VG. The presence of a threshold VG near ~20 V clearly indicates the n doping at VG = 0 V, whereas slight p doping is observed at VG < ~40 V, where we defined the neutral doping state as VG0 = ~35 V [45]. The Fermi level shift (Δμ = μ − μ0) was calculated from the back-gate capacitance and displayed on the right-hand axis of Fig. 2(a), where μ is the Fermi level and μ0 is μ for VG = ~35 V (see Supplemental Material [46]).

The PL was measured at various Pex values for OD using a diode laser with a wavelength of 405 nm and an objective lens with a numerical aperture of 0.6 [49], where the ED density was modulated by VD in the range from ~70 to 70 V for each Pex. For Pex = ~0.5 – 500 μW, corresponding photocarrier generation rates are estimated from ~5.5 × 1018 to ~5.5 × 1021 cm−2 s−1. Figure 2(b) shows the Pex-dependent PL spectra at VG = ~40 V for the nearly neutral state. In the low-power range (0.5 – 5 μW), a sharp peak (P0 ≈ 1.9 eV) with a nearly symmetric shape is generated. A new inflection point (P1 ≈ 1.87 eV) emerges at 10 – 500 μW. At 500 μW, another new inflection point (P2 ≈ 1.84 eV) is prominent. The inset shows the full width at half maximum (FWHM) curve for the spectra, which has an S shape. As P ex increases, the FWHM slowly varies and rapidly increases to saturate at the high-power limit, which is consistent with the new emergence of the P1 and P2 peaks rather than just a simple P0 peak shift. This behavior agrees well with the biexciton emergence in QWs at room temperature [29].

Figures 2(c) and 2(d) show the measured and intensity-normalized PL spectra, respectively, for three typical Pex values as a function of VG. At Pex = 0.5 μW [Fig. 2(c), top], the P0 intensity decreases in response to VG, while the peak position is not changed [Fig. 2(d), top, black-dashed circle]. These results agree well with the previous report, in which we identify P0 = A[X [2]. Exciton saturation with increasing electron density is attributed to Pauli blocking effects resulting from the presence of excess free electrons supplied by ED [2,24]. Laser illumination with energy exceeding the exciton transition energies excites electron-hole pairs, which are further thermalized to the lowest exciton energy level. Under high electron doping, the occupied states block the injection of photoexcited electrons into the states and consequently exciton emission is reduced. Additionally, a Coulomb screening effect due to electron plasma may play a role for Eb modulation [24] but this effect is negligible because of the strong binding effects, which is confirmed by the experimental result that the peak position is not altered in this doping range [Fig. 2(d), top], in good agreement with other experimental results [2].
FIG. 2. (a) Transfer characteristics of drain current ($I_D$) for a drain voltage ($V_D$) of 0.1 V and calculated Fermi level shift as a function of $V_G$. Inset: Schematic of electrical characterization of the FET. (b) PL spectra as a function of $P_{ex}$ at $V_G = -40$ V. (c) PL spectra as a function of $V_G$ at $P_{ex} = 0.5, 50, 500 \mu W$. Orange arrows indicate the inflection points of PL spectra corresponding to dashed lines for $P_0$, $P_1$, and $P_2$. Inset: FWHM as a function of $V_G$ at $P_{ex} = 50 \mu W$. (d) Normalized PL spectra for (c). Dashed black circle: unchanged inflection. (e) Peak positions as a function of $V_G$ for $P_0$ and $P_1$ at various $P_{ex}$. At $P_{ex} = 50 \mu W$ [Fig. 2(c), middle], the $P_1$ peak is more prominent as the electron doping density increases, whereas the $P_0$ population is drastically reduced. The FWHM gradually grows and saturates at high $V_G$ (inset), implying the emergence of a new peak, not a peak shift. These behaviors are clearly visible in Fig. 2(d), middle, and agree with previous reports on trions [4,13]. Therefore, we identify $P_1$ as $A^T$. The reported $E_{Tb}^b$ agrees quantitatively with our experimental results ($P_0 - P_1 \approx 30$ meV) [19,20,24]. At $P_{ex} = 500 \mu W$ [Fig. 2(c), bottom], the emergence of the $P_2$ peak is clearly visible in heavily $n$-doped states. Furthermore, the $P_1$ intensity is modulated, but the inflection point suggests the $P_1$ position is not altered with the doping [Fig. 2(d), bottom, black-dashed circle]. Figure 2(e) shows the peak positions of $P_0$ ($A^X$) and $P_1$ ($A^T$) as a function of $V_G$ for various $P_{ex}$. The changes in the peak position depending on the doping state for $A^X$ and $A^T$ are negligible, in agreement with results for MoSe$_2$ and MoTe$_2$ [22,23]. This doping independence of $A^X$ and $A^T$ positions is contrasted to a 2D electron gas (2DEG) of QWs [50,51]. The 2DEG is easily degenerate by doping, $A^X - A^T = E^T + E_F$ and $E_F = \mu - E_C > 0$, where $E_F$, $\mu$, and $E_C$ are defined as the Fermi energy, Fermi level, and conduction band, respectively. $E^T$ is defined as the energy to dissociate one electron from two bound electrons of a trion up to $E_C$. Note that in our definition, $A^X - A^T = E_{Tb}^b$, and $E_{Tb}^b$ is an energy to dissociate a trion into one exciton and one free electron, which is slightly different from the heavily degenerated 2DEGs, where the Fermi level ($\mu$) in MoS$_2$ is located within the band gap. Thus, $E_F$ does not play a role in our definition. In our experimental conditions of $P_{ex}$ up to $\sim 500 \mu W$, no appreciable $A^T$ shift was observed. Nevertheless, at higher $P_{ex}$, strong plasma screening effects may occur, altering the exciton peak shift. Additionally, the $E_{Tb}^b$ values of TMDs have generally been studied at low temperature. At room temperature, the peaks for exciton complexes are broadened and the peak positions are redshifted by thermal effects, but the $E_{Tb}^b$ values are similar to those at low temperature, confirming our analysis [22,24].

As discussed in Fig. 2(b), the emergence of the new peak $P_2$ is obvious at high powers ($50 - 500 \mu W$). The FWHM increases gradually with the generation of $A^T$ in the intermediate power range [Fig. 2(b), inset]. The rapid increase in the FWHM and saturation at high powers is another indication of $P_2$ peak emergence. At $500 \mu W$ in Fig. 2(c), the $P_2$ intensity does not change appreciably with $V_G$ modulation, whereas the $A^T$ peak intensity is modulated significantly. The strong dependence of the $P_2$ peak on $P_{ex}$ and its position below
at various PL spectra were deconvoluted into the fixed peak positions $P_{\text{IT}}$, $P_{\text{AT}}$, and $P_{\text{AX}}$ derived from the deconvolution results in (a). Dashed line indicates $V_{\text{G}} = -35$ V.

$A^T$ are biexcitonic features [21,29]. From the observed peak position of $P_2$ ($\sim 1.84$ eV), $E_b^{XX} = P_0 - P_2 \approx 60$ meV and $P_2 = A^{XX}$. Together with the observed $E_b^T \approx 30$ meV, our result is in excellent agreement with theoretical predictions of the biexciton binding energy, $E_b^{XX}/E_b^T \approx 2$ [19,20,39].

To estimate the relative populations of multie excitons, the PL spectra were deconvoluted into the fixed peak positions at various $P_{\text{ex}}$ and $V_{\text{G}}$ on the basis of the results that the positions and binding energies of $A^X$, $A^T$, and $A^{XX}$ do not depend on $P_{\text{ex}}$ and $V_{\text{G}}$. Figure 3(a) shows typical examples of the fitted results for $n^+$ doping ($V_G = 70$ V) at various $P_{\text{ex}}$. For all of the PL spectra, the A-peak deconvolution reveals three peaks. Overall, as $P_{\text{ex}}$ increases, the $A^{XX}$ and $A^T$ peaks become more prominent, while the $A^X$ peak diminishes. Figures 3(b)–3(d) show the log-scale population contours for each exciton, $I_X$ (for $A^X$), $I_T$ (for $A^T$), and $I_{XX}$ (for $A^{XX}$), respectively, as functions of $P_{\text{ex}}$ and $V_{\text{G}}$ from the deconvolution results. For $I_X$ [Fig. 3(b)], the carrier modulation by ED is less effective at high optical densities than at low optical densities, as the optically generated electron-hole plasma under high $P_{\text{ex}}$ dominates the electrically modulated carriers, and the number of neutral excitons that are converted to multie excitons is proportional to $P_{\text{ex}}$. Figure 3(c) shows that the positive $I_T$ increases dramatically with $p$ doping ($V_G < -35$ V) at low $P_{\text{ex}}$ ($0.5$–$10 \mu$W). Similarly, the negative $I_T$ increases gradually with $n$ doping ($V_G > -35$ V) in the intermediate $P_{\text{ex}}$ range ($10$–$100 \mu$W). In Fig. 3(d), however, the $V_G$ dependence of $I_{XX}$ is almost negligible except in the heavily $n$-doped region at intermediate $P_{\text{ex}}$, but the $P_{\text{ex}}$ dependence of $I_{XX}$ is prominent [21].

To confirm the identities of the newly assigned biexciton in this study, we characterized the modulation behavior of relative populations on the basis of the mass action law for biexcitons [52]. In a chemical equilibrium state at a given temperature, the biexciton can be identified by the quadratic relation between $I_{XX}$ and $I_X$, $I_{XX} \propto I_X^2$, where in ideal biexciton generation, the exponent $\alpha$ should be 2 [21,25,29,52]. Figure 4(a) shows log-log scale $I_{XX}$-$I_X$ plots, where the linear slope corresponds to the exponent $\alpha$. Note that in a high-population region ($P_{\text{ex}} \geq 10 \mu$W), $\alpha \sim 2$ for all doping levels, which is typical evidence for identifying biexcitons [21,25,29,52]. Further, in a low-population region ($P_{\text{ex}} < 10 \mu$W), $\alpha < 2$ owing to a deficiency of states in equilibrium, as is normally observed in QW systems and WSe$_2$ [21,52]. For a given $I_{XX}$ and $I_X$ for various $V_G$, $\phi$ is determined from the $I_{XX}$ intercepts [Fig. 4(c), inset]. Because $\phi (\propto I_{XX}/I_X^2)$ is linearly proportional to $V_G$ ($\propto n$), the relationship $I_{XX}/I_X^2 \propto n$ is valid.

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[23] Monolayer MoS2 flakes were directly synthesized on a SiO2 (300 nm)/Si substrate using a vapor phase reaction method [41]. Poly(methylmethacrylate) (950 K PMMA, MicroChem Corp., 4% chlorobenzene) was spin coated onto MoS2 grown samples and dried under ambient conditions. The PMMA/MoS2 layer was detached by soaking in a 1-M KOH solution for several minutes and was washed with de-ionized water. Finally, the PMMA/MoS2 layer was transferred to the SiO2 (300 nm)/Si wafer and the PMMA was removed using acetone [11]. Two electrodes that served as electrical contacts were fabricated by using the indium microsoldering method [42,43].
[28] The electrical characteristics of the devices as a function of gate bias were measured using an electrical characterization system (Keithley 4200-SCS, Keithley Instruments) under ambient conditions.


[49] PL spectra were measured by using a laboratory-made confocal microscope. We used a diode laser with a wavelength of 405 nm (filtered by a bandpass filter) and an objective lens with a numerical aperture of 0.6. The PL signals were recorded in a spectrometer and cooled charge-coupled device camera. The PL signal acquisition times range from 5 to 60 s for $P_{\text{ex}} = 0.5 - 500 \mu\text{W}$ and the signals are normalized by the acquisition time.

