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Exploration of exciton behavior in atomically thin WS₂ layers by ionic gating

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The photoluminescence spectra of mono- and bilayer WS₂, gated by the ionic liquid, were systematically studied at 77 K. Interesting phenomena, such as a redshift of the exciton peaks and a change in the spectral weight of the exciton, trion, and biexciton peaks, were observed at intermediate doping levels. By increasing the doping level, all the exciton, trion, and biexciton peaks vanished, which is attributed to the phase-space filling effect and the Coulomb screening effect. The variation in the band structure, which was induced by the quantum-confined Stark effect in both the mono- and bilayer WS₂, was also studied using first-principle calculations. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5022327>

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) are drawing increasing attention for not only their layer-stacking structure and characteristics that resemble those of graphene,^{1,2} but also their unique properties, which include thickness-dependent energy band gaps,^{3,4} a tightly bound exciton,^{5–7} an efficiently coupled spin-valley,^{8,9} and prominent many-body effects.^{10–16} Thus, 2D TMDs are excellent material candidates for applications in nanoelectronics, optoelectronics, and valleyelectronics, and are also ideal platforms for exploring the physics of 2D materials.

The many-body effects in 2D TMDs have been explored previously by tuning the applied laser power or external electric fields to obtain various exciton or carrier densities that change the interactions among carriers.^{7,11,17–21} At a relatively low-level carrier doping obtained by conventional gating at equilibrium, the transitions among exciton, trion, and biexciton,^{7,11} a decrease in the exciton binding energy, and the renormalization of a quasiparticle energy bandgap caused by screening the Coulomb interactions were studied.²¹ Bandgap renormalization, carrier population inversion, and the absence of exciton peaks were observed in a non-equilibrium state in highly doped mono- and bilayer WS₂ excited by intense optical pump pulses,²² indicating the emergence of a Mott transition (MT). However, the many-body effects in highly doped 2D TMDs have been rarely studied in an equilibrium state.²³

In this letter, we study the many-body effects via photoluminescence (PL) spectra in mono- and bilayer WS₂ flakes gated by ionic liquid (IL) in equilibrium states at 77 K. The exciton, trion, and biexciton peaks redshifted when the carrier density was relatively low and then, with increasing electron density, vanished at the high carrier density of $\sim 10^{14} \text{ cm}^{-2}$. We attribute this phenomenon to the high carrier density

induced Coulomb screening effect (CSE) and phase-space filling effect (PSFE) in both the mono- and bilayer WS₂, and to the quantum-confined Stark effect (QCSE) induced by an external electric field in the bilayer WS₂.

The mono- and bilayer WS₂ flakes were exfoliated from a single crystal WS₂ onto the SiO₂/Si substrate. Their thicknesses were measured using an atomic force microscope (AFM) as shown in Figs. 1(a) and 1(b), confirming that they were indeed mono- and bilayer WS₂. As shown in Figs. 1(c) and 1(d), the device used in the experiment consisted of two gold electrodes, one in contact with the WS₂ sample and the other acting as an IL gate, and was covered by a droplet of IL (see the [supplementary material](#) for the experimental methods). The width of the Schottky barrier between the WS₂ and gold was reduced to 1–2 nm by the IL-induced electrostatic screening, thus facilitating the carrier injection by tunneling.²⁴ Therefore, the Schottky contact would evolve to Ohmic contact if the IL gate created a high enough carrier density.

When a positive gate voltage was applied to the device, negative ions were drawn to the IL gate electrode, while positive ions were pushed to the surfaces of both the sample and the electrode in contact with the sample, as shown in Fig. 1(c), leading to an accumulation of electrons below these positive ions.²⁵ When a negative voltage was applied, the electrons were depleted, and then holes accumulated in the sample.²⁵ A capacitor model was used to estimate the carrier density under the IL gate application as $n = CV/eA$, where C is the IL capacitance, V is the effective voltage applied to the sample, e is the charge of an electron, and A is the effective area of the capacitance.²⁶ Note that the area of the gate electrode covered by the ionic liquid was approximately equal to that of the electrode in contact with WS₂ in our experiment [Fig. 1(d)], thus the effective voltage applied to the samples was roughly half of the gate voltage (V_G) that we applied to the device [Fig. 1(c)]. In the following

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FIG. 1. (a) AFM image of a monolayer WS_2 sample. (b) AFM image of a bilayer WS_2 sample. (c) Diagram of the metal-oxide-semiconductor device during the experiment. (d) Optical image of a typical metal-oxide-semiconductor device in our experiment. The scale bar is $200\ \mu\text{m}$.

paragraphs, the gate voltage (V_g) refers to the effective voltage applied to the samples. The capacitance per unit area (C/A) for the electron was estimated to be $7.2\ \mu\text{F cm}^{-2}$,²⁷ and the highest electron carrier density in this work ($V_g \sim 2\ \text{V}$) was calculated as $9.0 \times 10^{13}\text{ cm}^{-2}$.

Figure 2 shows the PL spectra obtained from a monolayer WS_2 flake under different gating voltages. Without gating, we observed several peaks in the spectra. The peaks at 2.075 eV and 2.044 eV correspond to exciton (X) and trion (X^-), respectively. We attribute the peak at 2.022 eV to a superposition of the defect-bound exciton (L_1) and biexciton (XX), labeled L_1/XX , while the peaks below 2 eV correspond to the defect-bound excitons.⁷ The presence of these

peaks is consistent with previous reports, and the determination of the exciton (X), trion (X^-), biexciton (XX), and defect-bound excitons (BX) was confirmed by gate-dependent, excitation-intensity-dependent, and helicity-resolved PL measurements.⁷ To rule out the effects from IL, the PL spectra of both IL and monolayer WS_2 with and without IL have been obtained (see the [supplementary material](#)). In this letter, we focus on the exciton, trion, and biexciton. As shown in Fig. 2(a), when positive IL gate voltages were applied and increased, we observed several characteristics in the PL spectra of the monolayer WS_2 : (a) the peaks red-shifted; (b) the spectral weight and number of the peaks changed with the gate voltage; and (c) all the peaks vanished

FIG. 2. (a) PL spectra of a typical monolayer WS_2 device measured at 77 K when applying various IL gate voltages. (b) Normalized PL spectra with fittings obtained from (a); the spectrum in which the peaks disappeared is not normalized. (c) Exciton (X), trion (X^-), and biexciton (L_1/XX) peak positions as functions of the IL gate voltage extracted from (a).

when the voltage increased to 2 V. The phenomena can be attributed to the many-body effects (see the [supplementary material](#)). After turning off the gate voltage, we found that all the peaks recovered. Therefore, the disappearance of the peaks at the gating voltage of 2 V was not caused by damage to the sample. When a negative gate voltage was applied and increased to -1.5 V, only the spectral weight changed with the gating voltage. The reason why the peak positions were not sensitive to the negative gate voltage can be found in the [supplementary material](#).

To clearly illustrate the evolution of the spectra from the monolayer WS_2 , the PL spectra obtained under different gate voltages are shown in Fig. 2(b), respectively. Under relatively low voltages (0 V to 1 V), the spectral weight of the peaks changed with the voltage, i.e., the relative weight of the exciton peak decreased while that of both the trion and the biexciton peaks increased. This spectral weight change can be ascribed to the fact that the formation of trions and biexcitons was energetically favorable when the electron density increased.²⁸ Note that the spectral weight is sensitive even to a slight change of carrier density, while the peak position is not sensitive to it at low gate voltages.^{18,29} By fitting the data to Gaussian functions, we obtained the exciton, trion, and biexciton peak positions, as shown in Fig. 2(c). The peak positions do not show a significant dependence on the voltage, indicating that the carrier injection through the interface between the electrode and WS_2 was still relatively low due to the Schottky barrier. As the IL gate increased from 1 V to 1.5 V, the exciton peak vanished because of the complete transition of the excitons to trions and biexcitons, as well as the redshift of the trion and biexciton peaks, which is consistent with the previous report.⁷ Interestingly, as the IL gate voltage increased to 2 V, all the peaks vanished. As stated above, both the PSFE and CSE could be responsible for the vanishment of the exciton peaks when the carrier density reached a critical point.^{20–22,30} To gain a deeper understanding of the

mechanism behind this observation, we calculated the critical carrier density for PSFE and the critical exciton density for CSE using the formulas $n_p = 2/\pi a^2$ (Refs. 20 and 31) and $n_c = 1/(2a)^2$,^{30,32} respectively, where a is the Bohr radius of the WS_2 exciton. We note that the critical carrier density is twice the critical exciton density, since an exciton is composed of one electron and one hole, both of which screen the Coulomb interaction. Therefore, the critical carrier density for CSE is $n_c = 2/(2a)^2$. Thus, we estimated the critical carrier densities for PSFE and CSE to be $n_p \sim 6.4 \times 10^{13} \text{ cm}^{-2}$ and $n_c \sim 5.0 \times 10^{13} \text{ cm}^{-2}$, respectively, using a Bohr radius of $a = 1 \text{ nm}$,^{20,22} which is in line with the values reported previously.^{20,21} Hence, the highest carrier density in our experiment at $V_g \sim 2 \text{ V}$ ($9.0 \times 10^{13} \text{ cm}^{-2}$), which was estimated using $n = CV/eA$, was higher than the critical carrier densities for both PSFE and CSE. In addition, it was previously predicted that both PSFE and CSE are responsible for the disappearance of the exciton states in 2D materials with a high carrier density, though CSE plays a more important role at low and intermediate densities.³³ Therefore, we attribute the peak vanishment to both PSFE and CSE in our experiment. When the IL gate was increased negatively from 0 V to -1.5 V , we did not observe any apparent changes in the positions of the X, X-, or L1/XX peaks, though the relative weight of the X peak increased significantly. This phenomenon was due to a gradual draining of electrons and, thus, a reduction in both the trions and biexcitons.

Figure 3 shows the PL spectra of a typical bilayer WS_2 under different IL gate voltages. At $V_g = 0$, the exciton (X) and trion (X-) peaks occurred at 2.024 eV and 1.999 eV, respectively. Interestingly, we did not observe a biexciton peak at $V_g = 0$, which is in contrast to the PL spectra of the monolayer WS_2 (Fig. 2), because the indirect band structure of the bilayer WS_2 reduced the quantum yield of the direct excitons needed to form biexcitons.¹² Similar to our observations in monolayer WS_2 , we recorded the following

FIG. 3. (a) PL spectra of a typical bilayer WS_2 device measured at 77 K when applying various IL gate voltages. (b) Normalized PL spectra with fittings obtained from (a); the spectrum in which the peaks disappeared are not normalized. (c) Exciton (X) and trion (X-) peak positions as functions of the IL gate voltage extracted from (a).

phenomena when the IL gating voltage was increased positively: a redshift of the exciton peaks, variation in the relative weight of the peaks, and the disappearance of all the exciton peaks at high carrier density, as shown in Figs. 3(a)–3(c). As observed in monolayer WS₂, the relative weight of the peaks from bilayer WS₂ varied with the applied voltage when negative voltages were applied, but the peak positions remained nearly unchanged. Unlike monolayer WS₂, the excitons survived at low and intermediate densities because the transition from exciton to biexciton did not occur, and the exciton peak redshifted even at low positive voltages due to the CSE effect. We attribute the relatively large redshift (124 meV at $V_g \sim 1.75$ V) of the exciton peak at intermediate positive voltages to the combined QCSE and CSE. The band structure evolutions of both mono- and bilayer WS₂ induced by QCSE was also studied by first-principle calculations (see the [supplementary material](#)). Both the direct and indirect gaps of bilayer WS₂ were found to continuously shrink under an external electric field, while the band gap of monolayer WS₂ was much less sensitive to the electric field.

In conclusion, we explored the evolution of the PL spectra from mono- and bilayer WS₂ samples at equilibrium under IL gating. We observed changes in the spectral weight and redshift of the exciton peaks at intermediate doping in both the mono- and bilayer WS₂ samples. Combining the first-principle calculations and experimental results, we found that both a quantum-confined Stark effect and a Coulomb screening effect contributed to the large redshift of the exciton peak in bilayer WS₂, while the quantum-confined Stark effect can be neglected in monolayer WS₂. As the carrier density increased with the increasing positive gating field, all the exciton, trion, and biexciton peaks vanished, which we attribute to the joint influences of the phase-space filling effect and the Coulomb screening effect from an excitonic state to the electron-hole plasma regime.

See [supplementary material](#) for the experimental methods, PL spectra of the ionic liquid, PL spectra of monolayer WS₂ with and without the ionic liquid, introduction of the many-body effects observed in our experiment, the reason why the peak positions are not sensitive to negative gate voltage, and first-principle calculations for the band structure evolutions of both mono- and bilayer WS₂.

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