Electrical control of neutral and charged excitons in a monolayer semiconductor

Jason S. Ross1,*, Sanfeng Wu2,*, Hongyi Yu3, Nirmal J. Ghimire4,5, Aaron M. Jones2, Grant Aivazian2, Jiaqiang Yan5,6, David G. Mandrus4,5,6, Di Xiao7, Wang Yao3 & Xiaodong Xu1,2

Monolayer group-VI transition metal dichalcogenides have recently emerged as semiconducting alternatives to graphene in which the true two-dimensionality is expected to illuminate new semiconducting physics. Here we investigate excitons and trions (their singly charged counterparts), which have thus far been challenging to generate and control in the ultimate two-dimensional limit. Utilizing high-quality monolayer molybdenum diselenide, we report the unambiguous observation and electrostatic tunability of charging effects in positively charged ($X^+$), neutral ($X^0$) and negatively charged ($X^-$) excitons in field-effect transistors via photoluminescence. The trion charging energy is large (30 meV), enhanced by strong confinement and heavy effective masses, whereas the linewidth is narrow (5 meV) at temperatures $<$55 K. This is greater spectral contrast than in any known quasi-two-dimensional system. We also find the charging energies for $X^+$ and $X^-$ to be nearly identical implying the same effective mass for electrons and holes.
Above bandgap photo-excitation creates electrons and holes in the conduction and valence bands, respectively. If the screening is weak enough, the attractive Coulomb interaction between one electron and one hole creates a bound quasi-particle known as a neutral exciton ($X^0$), which has an energy structure similar to a neutral hydrogen atom. Excitons can further become charged by binding an additional electron ($X^-$) or hole ($X^+$) to form charged three-body excitons analogous to $H^-$ or $H_2^+$ respectively\[^{1-3}\]. These exciton species are elementary quasi-particles describing the electronic response to optical excitation in solids and are integral to many optoelectronic applications from solar cells and light-emitting diodes\[^4\] to optical excitation in solids and are integral to many optoelectronic circuits\[^{5-7}\].

The main arena for the exploration of excitonic physics has been three-dimensional semiconductors and their heterostructures that form quasi-2D quantum wells where the carrier wavefunction typically occupies a few tens to thousands of atomic layers. Observation and control of excitons in truly 2D systems has been a long pursued goal, largely motivated by the enhancement in exciton- and trion-binding energies in the strict 2D limit\[^8\]. In addition, unlike semiconductor heterostructures, the close proximity of external stimuli to the exciton wavefunction can offer unprecedented tunability and diversifies the applications possible in devices made with 2D semiconductors.

Here we report the experimental observation and control of the fascinating excitonic physics in a 2D semiconductor by utilizing high-quality monolayer molybdenum diselenide (MoSe\(_2\)). MoSe\(_2\) belongs to the group-VI transition metal dichalcogenides, which form in layers weakly bound to each other by Van der Waals forces. The monolayers have received much attention recently as they make up a new class of 2D semiconductors with a narrow, well-separated features have temperature dependence of typical 2D excitons and exist at high temperature suggesting remarkable stability. Interestingly, the binding energies of X\(^+\) and X\(^-\) are similar implying that low-energy electrons and holes in MoSe\(_2\) have the same effective mass. Our work demonstrates that monolayer MoSe\(_2\) is a true 2D semiconductor opening the door for the investigation of phenomena such as exciton condensation\[^{17-19}\] and the Fermi-edge singularity\[^{20,21}\], as well as for a new generation of optoelectronic devices such as light-emitting diodes and excitonic circuits\[^5\].

**Results**

**Crystal structure and spectral features of monolayer MoSe\(_2\).** In monolayer MoSe\(_2\), Mo and Se atoms form a 2D hexagonal lattice with trigonal prismatic coordination (Fig. 1a). First-principles calculations show that it has a direct bandgap at the corners (K points) of the first Brillouin zone (Fig. 1b). The curvature of the bands suggests comparable effective mass for low-energy electrons and holes and holes at K points (Fig. 1c)\[^9\]. These band-edge electrons and holes near K points are predominantly from the d-orbitals of Mo atoms. Their wavefunctions are calculated to be strongly confined in the Mo layer within a length scale of \(\sim 0.2\) nm in the out-of-plane direction. Monolayer MoSe\(_2\) is thus an ideal nanomaterial for exploring excitonic physics in the ultimate 2D limit.

We use mechanical exfoliation to obtain monolayer MoSe\(_2\) on 300 nm SiO\(_2\) on n\(^+\)-doped Si and atomic force microscope to

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**Figure 1 | MoSe\(_2\) characteristics and devices.** (a) Coordination structure and top view of monolayer MoSe\(_2\). (b) Density function theory calculated band structure. (c) Band structure at K point shows 180 meV valence band splitting due to spin-orbit coupling. (d) Optical micrograph of exfoliated MoSe\(_2\) flake on 300 nm SiO\(_2\). Scale bar, 5 \(\mu\)m. (e) atomic force microscope (AFM) image of area highlighted in (d). Scale bar, 1 \(\mu\)m. (f) AFM line scan along dashed line in e. (g) Optical micrograph of MoSe\(_2\) device. Scale bar, 5 \(\mu\)m. (h) Schematic of back-gated MoSe\(_2\) device.
identify the layer thickness. Figure 1d,e show the optical micrograph and the corresponding atomic force microscope image of a representative sample, in which the monolayer thickness of ~0.7 nm is identified (Fig. 1f). Standard electron beam lithography (EBL) is used to fabricate monolayer FETs (Fig. 1g). With the contacts simply grounded, the n-doped characteristics (Supplementary Fig. S2). All FETs (Fig. 1g). With the contacts simply grounded, the n-doped characteristics (Supplementary Fig. S2). All FETs show n-doped characteristics (Supplementary Fig. S2).

The excitonic features of MoSe\(_2\) are investigated by differential reflectance and micro photoluminescence (PL) measurements (Methods). Figure 2 shows the results from an unpatterned MoSe\(_2\) sample, S1. At 20 K, we observe two main features associated with the A and B excitons in the differential reflectance spectrum. The presence of A and B excitons has been attributed to spin–orbit coupling-induced valence band splitting in bulk. The observed energy difference of ~200 meV agrees well with the calculated splitting (180 meV) in monolayers (Fig. 1c).

With the same sample and temperature under 2.33 eV laser excitation, the PL spectrum does not show a measurable feature that can be attributed to the B exciton, likely because it is not the lowest energy transition. Instead, we observe two pronounced peaks at 1.659 and 1.627 eV in the vicinity of the A exciton (Fig. 2b). Note that the PL spectrum lacks the broad low-energy peak observed in MoSe\(_2\), which has been attributed to defect-related, trapped exciton states.

The striking spectral features demonstrate the high quality of our MoSe\(_2\) samples (Methods) and provide strong evidence for monolayer MoSe\(_2\) being a direct bandgap semiconductor (Supplementary Fig. S1) where the two distinct transitions are excitons. The higher-energy emission at 1.659 eV is the neutral exciton, X\(_0\), and the lower-energy peak is a trion. In unpatterned samples, we assume the trion to be X\(^-\) because all measured devices show n-doped characteristics (Supplementary Fig. S2). All measured unpatterned samples show a binding energy, which is the energy difference between trion and X\(_{\text{h}}\), of ~30 meV (Fig. 2b, inset). This is more than twice the typical numbers reported in GaAs quantum wells and similar to a recent mention in MoSe\(_2\).

**Gate dependence of MoSe\(_2\) PL.** To confirm the above assignment and control the exciton charging effects, we performed gate-dependent PL measurements using monolayer MoSe\(_2\) FETs. Here the excitation laser is at 1.73 eV for better resonance with the luminescent states. Figure 3a shows a colour map of the PL spectrum of device D1 at 30 K as a function of back-gate voltage, \(V_g\), in which we clearly observe four spectral features whose intensities strongly depend on \(V_g\). Near zero \(V_g\), the spectrum shows a broad low-energy feature around 1.57 eV and a narrow high-energy peak at 1.647 eV. With large \(V_g\) of either sign, these peaks disappear and a single-emission peak dominates the spectrum. Both peaks (at negative or positive \(V_g\)) have similar energies and intensities with the latter increasing with the magnitude of \(V_g\).

This observed gate dependence confirms the assignment of states as labelled in Fig. 3a. Because the broad low-energy peak does not show up in unpatterned samples before FET fabrication, we attribute it to exciton states trapped to impurities (X\(^1\)), which are likely introduced during EBL processing and are not the focus of this paper. The sharp peak at 1.647 eV is the X\(^0\), slightly red-shifted compared with unpatterned samples. From the gate dependence, we identify the peaks near 1.627 eV as the X\(^-\) and X\(^+\) trions when \(V_g\) is largely positive and negative, respectively. Remarkably, these two distinct quasi-particles (X\(^+\) and X\(^-\)) exhibit a nearly identical binding energy. The difference is within 1.5 meV over the whole applied \(V_g\) range. Because the binding energy of a trion is dependent on its effective mass, this observation implies that the electron and hole have approximately the same effective mass.

The gate-dependent measurements unambiguously demonstrate the electrical control of exciton species in a truly 2D semiconductor, as illustrated in Fig. 3b. The conversion from X\(^0\) to trion can be represented as \(e(h)+X^0\rightarrow X^-\) (X\(^+\)), where \(e\) and \(h\) represent an electron or a hole, respectively. By setting \(V_g\) to be negative, the sample is p-doped, favouring excitons to form lower-energy-bound complexes with free holes. As \(V_g\) decreases, more holes are injected into the sample, and all X\(^0\) turn into X\(^+\) to form a positively charged hole-trion gas. With positive \(V_g\), a similar situation occurs with free electrons to form an electron-trion gas. In the following, we show that a standard mass action model can be used to describe the conversion dynamics.

Figure 3c shows the extracted X\(^0\) (black) and trion (red) peak intensity as a function of \(V_g\) where we have adjusted the negative \(V_g\) data due to background signal. The plot shows that the maximum X\(^0\) intensity is about equal to the saturated trion PL when X\(^0\) vanishes. This observation indicates conservation of the total number of X\(^0\) and trion in the applied voltage range and similar radiative decay rates for both quasi-particles. Thus, the PL intensity represents the amount of the corresponding exciton species. Because the dynamic equilibrium of free electrons, holes and excitons are governed by the rate equation and law of mass action, we calculate the gate-dependent X\(^0\) and trion abundance (Supplementary Fig. S3), shown by the solid lines in Fig. 3c, which agrees with the data.

In the simulation, we first fit the X\(^0\) curve to obtain our two free parameters: the maximum background electron concentration \(n_{\text{B}}\), which agrees with the data.

![Figure 2](https://example.com/figure2.png)  
**Figure 2 | Differential reflectance and PL spectra of monolayer MoSe\(_2\) at 20 K.** (a) Differential reflectance shows A and B excitons. (b) PL excited by 2.33 eV laser shows neutral exciton (X\(^0\)) and the lower-energy charged exciton (X\(^-\)). PL from the B exciton has not been observed. Inset, PL of the exciton peaks. The X\(^-\) shows a binding energy of about 30 meV.
Temperature dependence of MoSe$_2$ PL. The observed exciton states also show fine features consistent with 2D excitons, such as temperature-dependent line shape, peak energy and relative weight of X$^0$ and trion, which further supports the excitonic nature of this monolayer system (Fig. 4). Figure 4a shows the evolution of X$^-$ and X$^0$ (normalized PL) as a function of temperature in an unpatterned sample, S2, under 1.96 eV laser excitation. At low temperatures, we again observe a binding energy of 30 meV. As the temperature rises, we see the X$^-$ signal drop significantly at about 55 K, which we attribute to electrons escaping their bound trion state due to thermal fluctuations (Supplementary Note 1).

Figure 4b is the zoom-in plot at 15 K where we observe slightly different line shapes for X$^-$ and X$^0$. The X$^0$ peak is symmetric showing homogenous thermal broadening effects and is well fit by a hyperbolic secant function that yields a full-width-half-maximum of 5 meV$^{27,28}$. However, the X$^-$ peak shows a slightly asymmetric profile with a long low-energy tail consistent with electron-recoil effects$^{27}$. The recombination of a X$^-$ with momentum $k$ will emit a photon and leave a free electron with the same momentum $k$ due to momentum conservation. From energy conservation, the emitted photon has an energy $\hbar \omega = \hbar \omega_0 - \hbar^2 k^2 c / 2 M_{X^0}$, where $\hbar \omega_0$ is the energy of trions with $k=0$, and $M_{X^+}$ and $M_{X^-}$ are the X$^0$ and X$^-$ effective masses, respectively. The line shape of trion PL will thus be the convolution of a symmetric peak function (hyperbolic secant) and an exponential low-energy tail function (Supplementary Fig. S5 and Supplementary Note 2). When the temperature is >70 K,
we find that homogenous broadening dominates over electron recoil and the PL spectrum is fit well by two hyperbolic secant functions (Fig. 4c).

From the fits, we extract the X- and X' peak position (Fig. 4d) and the ratio of the integrated intensity of the X- to the X' (Fig. 4e) where we do not present trion data >150 K because it becomes negligible. We find that the peak positions are fit well (solid line in Fig. 4d) using a standard semiconductor bandgap dependence of $E_g(T) = E_g(0) - rac{S}{k_B T}$, where $E_g(0)$ is the ground-state transition energy at 0 K, S is a dimensionless coupling constant and $k_B T$ is an average phonon energy. From the fits, we extract for X- ($E_g$) the $E_g = 1.657$ (1.625) eV, S = 1.96 (2.24) and $k_B T = 15$ meV for both. Applying our mass action model (Supplementary Fig. S3 and Supplementary Note 1) with a trion-binding energy of 30 meV results in a good fit to the X- X' intensity ratio (solid line in Fig. 4e).

Discussion
In summary, we have shown that monolayer MoSe2 is a true 2D excitonic system, which exhibits strong electrostatic tuning of exciton charging via a standard back-gated FET. The observed narrow, well-separated spectral features are within the titanium (Tl)-Sapphire laser spectral range and thus provide remarkable opportunities to selectively probe and control specific excitons using current continuous wave and ultrafast Ti-Sapphire laser technologies. Our results further demonstrate that high-quality monolayer dichalcogenides can serve as a platform for investigating excitonic physics and photonic applications in the truly 2D limit with the potential to outperform quasi-2D systems. The results represent unique prospects for this burgeoning class of 2D materials, in particular to the X- X' peak position (Fig. 4d) and investigation of PL intensity of diverse fundamental studies and technical applications.

Note: During the review process, we became aware of the main supported by the US DoE, BES, Materials Sciences and Engineering Division (DE-SC0008145). H.Y. and W.Y. were supported by Research Grant Council of Hong Kong (HKU706412P). N.J.G., I.Y., D.G.M. and D.X. were supported by the US DoE, BES, Materials Sciences and Engineering Division. Device fabrication was

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performed at the University of Washington Microfabrication Facility and NSF-funded Nanotech User Facility.

**Author contribution**
X.X. conceived the experiments. J.S.R. fabricated the devices and performed the measurements, assisted by S.W., A.M.J. and G.A. S.W., J.S.R. and X.X. performed data analysis. H.Y., W.Y., and D.X. contributed to the theoretical explanation. N.G., J.Y. and D.G.M. synthesized and performed bulk characterization measurements on the MoSe$_2$ crystals. All authors discussed the results and contributed to writing the manuscript.

**Additional information**
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Ross, J.S. et al. Electrical control of neutral and charged excitons in a monolayer semiconductor. Nat. Commun. 4:1474 doi: 10.1038/ncomms2498 (2013).