Electrically tunable excitonic light-emitting diodes based on monolayer WSe₂ p-n junctions

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The development of light-emitting diodes with improved efficiency, spectral properties, compactness and integrability is important for lighting, display, optical interconnect, logic and sensor applications¹⁻⁸. Monolayer transition-metal dichalcogenides have recently emerged as interesting candidates for optoelectronic applications due to their unique optical properties⁹⁻¹⁶. Electroluminescence has already been observed from monolayer MoS₂ devices^{17,18}. However, the electroluminescence efficiency was low and the linewidth broad due both to the poor optical quality of the MoS₂ and to ineffective contacts. Here, we report electroluminescence from lateral p-n junctions in monolayer WSe, induced electrostatically using a thin boron nitride support as a dielectric layer with multiple metal gates beneath. This structure allows effective injection of electrons and holes, and, combined with the high optical quality of WSe2, yields bright electroluminescence with 1,000 times smaller injection current and 10 times smaller linewidth than in MoS₂ (refs 17,18). Furthermore, by increasing the injection bias we can tune the electroluminescence between regimes of impurity-bound, charged and neutral excitons. This system has the required ingredients for new types of optoelectronic device, such as spin- and valley-polarized light-emitting diodes, on-chip lasers and two-dimensional electro-optic modulators.

Few-layer group-VIB transition-metal dichalcogenides (TMDs) are a class of semiconductors in the two-dimensional limit^{9,10,19}. Because of their large carrier effective mass and reduced screening in two dimensions, electron–hole interactions are much stronger than in conventional semiconductors. This leads to large binding energies for both charged and neutral excitons, which, as a result, are spectrally sharp, robust and amenable to electrical manipulation^{16,20,21}. In addition, the large spin–orbit coupling²² and acentric structure of TMDs provides a connection between spin and valley degrees of freedom¹⁴, light polarization^{11,13,15,16} and magnetic and electric fields²³ that can be exploited for new kinds of device operation.

Although in bulk TMDs the bandgap is indirect, in the limit of a single monolayer it becomes direct^{9,10}, fulfilling the most basic requirement for efficient light emission. Indeed, electroluminescence has already been reported from monolayer MOS_2 field-effect transistors (FETs), occurring near the Schottky contact with a metal¹⁷ or with highly doped silicon¹⁸. However, the efficiency and spectral quality was much lower than has been demonstrated in other nanoscale light emitters such as carbon nanotubes⁷.

There are two reasons for this. First, efficient electroluminescence requires effective injection of both electrons and holes into the active region, which should therefore be within a p–n junction. Second, MoS_2 is known to have poorer optical quality than other group-VIB TMDs, possibly due to impurities. In contrast, it has been shown previously that monolayer WSe_2 has excellent optical properties^{16,24}. Here, we demonstrate that combining monolayer WSe_2 with a p–n junction architecture using electrostatic doping produces efficient and electrically tunable excitonic light-emitting diodes (LEDs).

Figure 1a,b presents a schematic and optical image of a device made by a combination of electron-beam lithography and the transfer of exfoliated sheets. A monolayer WSe₂ sheet sits on a sheet of hexagonal boron nitride (BN), typically 10 nm thick, which acts both as a smooth, disorder-free substrate to minimize non-radiative energy relaxation pathways and as a high-quality gate dielectric. Applying voltages to the two 7 nm palladium gate electrodes beneath the BN can create two separate electrostatically doped regions in the WSe₂ separated by a 300-nm-wide undoped strip. Gold/vanadium (60/6 nm) source and drain contacts were evaporated on top. Importantly, they overlap the gates to reduce the Schottky barriers at the contacts. For electrical transport measurements, a d.c. bias V is applied to one contact (the source) and the current I from the other (the drain) is measured by a virtual-earth current preamplifier. The silicon substrate is grounded.

We start by showing that a p-n junction can be created electrostatically. First, we set the gate voltages $V_{\rm g1}$ and $V_{\rm g2}$ to the same value. Figure 1c shows the current produced with a bias of V=0.5 V as the gate voltage $V_{\rm g1}=V_{\rm g2}$ is swept at 60 K (roomtemperature measurements are shown in Supplementary Fig. 1). The current increases rapidly for gate voltages >+ 6.5 V (electron doping) and <- 6.5 V (hole doping), demonstrating ambipolar operation. In the inset, the red *I-V* curve, taken at $V_{\rm g1}=V_{\rm g2}=+8.0$ V, is almost symmetric, as expected for both gated regions being equally electron-doped. The nonlinearity near zero bias can be associated with the undoped gap between the gates and residual Schottky barriers at the contacts. In contrast, the blue *I-V* curve, taken with $V_{\rm g1}=+8.0$ V and $V_{\rm g2}=-8.0$ V, shows the strong rectification behaviour expected for a p-n junction.

The p–n junction can be investigated in detail using scanning optical measurements^{25,26}. Figure 2a presents a microscope image of a device and Fig. 2b a corresponding scanning photocurrent image, measured with zero bias at 100 K using a 10 μ W

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LETTERS



Figure 1 | Monolayer WSe₂ p-n junctions. a,b, Cartoon (a) and optical micrograph (b) of multiple monolayer WSe₂ p-n junction devices with palladium backgates (V_{g1} and V_{g2}) and source (S) and drain (D) contacts. The source-drain voltage (V_{sd}) is applied to one contact and the current (A) is read out of the other. During electroluminescence in the WSe₂, electrons (blue) and holes (yellow) move towards each other (arrows) and recombine. The backgates are separated from the WSe₂ by hexagonal BN. The device sits on a layer of silicon dioxide on a silicon substrate. **c**, Main panel: Variation of current with both bottom gate voltages set equal ($V_{g1} = V_{g2} = V_{g2}$) for one junction at bias $V_{sd} = 500$ mV, showing ambipolar behaviour. Inset: $I-V_{sd}$ characteristics when the two gate voltages are set to be equal ($V_{g1} = V_{g2} = 8$ V, red) and opposite ($V_{g1} = -8$ V, $V_{g2} = 8$ V, blue) values above the injection threshold.



Figure 2 | Photoresponse of monolayer p-n junction at 100 K. a, Microscope image of a monolayer p-n junction device. The source and drain contacts are white, the two bottom gates are red, and the BN is blue. **b**, Corresponding scanning photocurrent image showing pronounced photocurrent generation localized to the junction. The orange dashed lines outline the source and drain contacts whereas the blue dashed lines outline the backgates. **c**, Integrated photoluminescence map. **d**, Peak photoluminescence energy map showing p and n regions as a result of the different energies of oppositely charged excitons. X⁻ (X⁺) represents the negatively (positively) charged exciton found in the n (p) region **e**, Top to bottom: Selected spectra from n-doped region (blue), junction (black) and p-doped region (red) with negative, neutral (X^o), and positive exciton features indicated. All maps taken with $V_{g1} = +8$ V, $V_{g2} = -8$ V. Scale bars, 4 µm.

diffraction-limited 660 nm laser spot scanned over the sample. We see a large photocurrent signal localized between the gates, with a peak magnitude of 5 nA. Taking into account the 1% absorption

of WSe₂ monolayers at 660 nm (ref. 27), the internal quantum efficiency reaches a maximum of \sim 5%. Such a photocurrent is the natural result of the junction functioning as a photodiode, with



Figure 3 | Photoluminescence and electroluminescence. a, At 300 K, the electroluminescence spectrum (blue) generated by a current of 5 nA closely resembles the photoluminescence spectrum (red). **b**, Electroluminescence image (red) superimposed on device image (greyscale). The dashed lines outline the WSe₂ monolayer. Scale bar, 2 μ m.

photogenerated carriers separated by a strong depletion field concentrated in the undoped gap. The sensitivity of the photodiode can be tuned over a wide range by varying the gate voltages and bias (Supplementary Fig. 2).

Figure 2c presents a corresponding map of the integrated photoluminescence intensity, which indicates the high optical quality of the whole WSe₂ sheet and shows that the luminescence is not substantially quenched by the underlying gates. More revealingly, Fig. 2d shows a colour map of the peak photoluminescence photon energy, exhibiting two distinct regions clearly correlated with the expected n-doped (blue) and p-doped (red) parts of the WSe₂ above the gates. The reason for this is made clear in Fig. 2e, which shows photoluminescence spectra taken at different positions. The detailed origin of these spectral features has been established previously¹⁶. Above the gate held at $V_{g1} = +8.0$ V (blue trace) the negatively charged X⁻ trion (two electrons and one hole) dominates, implying an excess of electrons. Above the other gate, held at $V_{g2} = -8.0$ V (red trace), the higher-energy positively charged X⁺ trion (two holes and one electron) dominates, implying an excess of holes. In the gap between the gates (black trace) the neutral exciton X^o peak can also be seen, consistent with no doping in that region. Here, the superimposed X⁺ and X⁻ peaks may come from the gated regions, because the laser spot is larger than the gap.

When the device is configured as a p-n junction ($V_{g1} = -V_{g2} = 8$ V), but not otherwise, we observe bright electroluminescence. Good spectra can be obtained even at room temperature with a current of 5 nA, as illustrated (blue) in Fig. 3a. This current is three orders of magnitude smaller than in MoS₂ FETs^{17,18}. In fact, in our best device we observed electroluminescence at an injection current as low as 200 pA (Supplementary Fig. 3). To understand the nature of the electroluminescence, we superimpose a normalized photoluminescence spectrum of undoped monolayer WSe₂ (red). It is known that the photoluminescence of WSe₂ arises from the recombination of direct-gap excitons; thus, the similarity between the electroluminescence and photoluminescence spectra implies that the injected electrons and holes form excitons before recombining radiatively. This is a natural consequence of the large exciton binding energy due to the strong Coulomb interaction in monolayer TMDs. Figure 3b presents an image of the total electroluminescence intensity (coloured) superimposed on a simple white-light reflection image (greyscale). It is clear that the electroluminescence emanates from the entire length of the monolayer junction between the two gates.

At low temperatures, the electroluminescence spectrum develops an interesting structure. Figure 4a shows a plot of electroluminescence intensity as a function of current and photon energy. There are three main spectral features: a narrow higher-energy peak (green arrow), a broad central peak (brown arrow) and a lower-energy



Figure 4 | Tuning valley-exciton electroluminescence at 60 K. a, Electroluminescence intensity plot as a function of bias current and photon energy. From left to right, the arrows indicate the impurity-bound exciton (X¹), the charged excitons (X⁻ then X⁺) and the neutral exciton (X⁰). **b**, Plot of photoluminescence intensity as a function of photon energy and gate voltage $V_{g} = V_{g1} = V_{g2}$. **c**, Selected electroluminescence spectra at different bias currents. As the current increases, we observe electroluminescence tuning from X¹ through X⁻ and X⁺ and finally X⁰. The bottom spectrum is fit by four Gaussian lineshapes, one for each exciton species. **d**, Band diagram and device schematic showing electroluminescence generation from valley excitons. Wavy red arrows indicate electroluminescence. Dashed red (blue) arrow indicates the direction of hole (electron) flow. Filled and empty circles indicate carriers in the +K and -K valleys. Both valleys are shown to be populated, leading to electroluminescence that has both right (σ^-) circular polarization.

LETTERS

peak (black arrow). The shapes and relative intensities of these features change with current. Their origins can be deduced from a comparison with the photoluminescence, the intensity of which is plotted in Fig. 4b as a function of photon energy and common gate voltage $V_g = V_{g1} = V_{g2}$. Here we see the tuning of the dominant exciton species as the carrier density is changed by gating¹⁶. The photoluminescence feature that is strongest at $V_{g} = 0$ is due to X^o recombination. It has a similar width to, and is at the same position (1.69 eV) as, the narrow electroluminescence peak, which we therefore identify as the X^o emission. The dominant photoluminescence feature at $V_g > 0$, which shifts from 1.663 eV to 1.625 eV as V_g increases from 0 to +8 V, is due to X^- (of which there are multiple species¹⁶). The broad electroluminescence feature occurs in the same range of energies, implying that it is dominated by X⁻. The dominant feature in the photoluminescence at $V_g < 0$ is due to X⁺. This aligns with the high-energy shoulder (grey arrow) on the broad electroluminescence feature at \sim 1.670 eV. There is also a band of emission from impurity-bound excitons (X¹) in the photoluminescence, which matches the lower-energy electroluminescence feature centred at 1.59 eV.

The finding that X^- dominates the electroluminescence in Fig. 4a is consistent with the observation that X^- has much stronger photoluminescence than the other exciton species (Fig. 4b). The shifts of the trion peaks in the photoluminescence with V_g imply that the trion binding energy depends on the perpendicular electric field. Hence, the fact that the width of the broad peak in the electroluminescence is explained by the variation of the perpendicular electric field across the junction. On the other hand, the X^o peak shifts very little with V_g in the photoluminescence and is therefore insensitive to the field; thus, the X^o electroluminescence peak is also sharp. The X^o electroluminescence linewidth is found to be as narrow as 5 meV, which is an order of magnitude smaller than for electroluminescence from MoS₂ (refs 1,7).

Figure 4c presents the electroluminescence spectra at selected current values, illustrating sequential population of the excitonic states, which could be due to current pumping or to changes in the electric field at the junction under different source-drain biases. At the lowest current (24 nA), only the excitons with lowest energy (X^I and X⁻) are seen. At a higher current (27 nA) the X⁺ shoulder appears and at 31 nA an X^o peak is also present. At the highest current (33 nA) we illustrate how the spectrum can be decomposed into four Gaussian peaks. It is also apparent that the relative strength of the X^I peak decreases as the current increases.

The above observations reflect complex exciton dynamics, which are not yet fully understood. Time-resolved photoluminescence measurements have shown that the lifetimes (for radiative and non-radiative processes combined) of the free excitons and the impurity-bound excitons are ${\sim}5~\text{ps}$ and 100 ps respectively^{28-31} in monolayer MoS₂, which we expect to be similar to WSe₂. The electron-hole pair injection rate is $\frac{1}{e}$ (e is electron charge), which is one pair per 5 ps at 32 nA, comparable to the lifetime of a free exciton but much shorter than that of X^I. Therefore, there could be only of order one free exciton but many impurity-bound excitons present in the junction. We speculate that that the presence of multiple X¹ combined with the strong Coulomb interactions enhances non-radiative recombination, which limits the X¹ emission at higher currents. Alternatively, the saturation of the X¹ peak could also be due to the filling of impurity states, as observed in standard photoluminescence and photocurrent experiments.

We measured the total photon emission rate at the largest applied current of 35 nA to be $\sim 16 \text{ million s}^{-1}$ (Supplementary Note 1). This is 10 times larger, for 1,000 times smaller current, than reported for MoS₂ devices^{17,18}. It corresponds to one photon per 10⁴ injected electron–hole pairs. We expect that the overall device efficiency could be improved by increasing the injection

current for a given voltage by reducing the contact resistance, by improving the WSe_2 crystal quality, and by employing improved membrane transfer techniques.

Finally, we mention an important implication of these results. It has been conclusively demonstrated using polarization-resolved photoluminescence that the excitons in monolayer WSe_2 are formed in the $\pm K$ valleys¹⁶. The excellent match of the electroluminescence with the photoluminescence thus proves that the electroluminescence also comes from such valley excitons. In the experiments described here, the injected electrons and holes populate both valleys equally, as shown in Fig. 4d, forming excitons in both valleys and thus producing unpolarized light, as we have verified (Supplementary Fig. 4). As a result of the spin-valley locking in monolayer TMDs, where the +K and -K band edges have opposite spin¹⁴, we expect that using ferromagnetic contacts to obtain spin-polarized injection will allow the creation of spin- and valley-LEDs with controllably polarized emission³².

Note added in proof: During the preparation of this Letter we became aware of two similar studies^{33,34}.

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Author contributions

X.X. conceived the experiments. J.S.R. fabricated the devices and performed the measurements, assisted by P.K. and A.M.J. J.S.R. and X.X. performed data analysis, with input from D.C. and W.Y. N.G., J.Y. and D.G.M. synthesized and performed bulk characterization measurements on the WSe₂ crystals. T.T., K.W. and K.K. provided boron nitride crystals. X.X, D.C., J.S.R and W.Y. wrote the paper. All authors discussed the results.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to X.X.

Competing financial interests

The authors declare no competing financial interests.