Experimental observation of a negative grey trion in an electron-rich WSe$_2$ monolayer

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Abstract
We measure the evolution of low temperature photoluminescence in a WSe$_2$ monolayer with increasing electron concentration level. By comparing non-resonant and resonant laser excitation, we find that the formation of negative trions is facilitated by very efficient phonon emission. The most prominent line in photoluminescence spectra in the intermediate range of carrier concentrations (below $5 \cdot 10^{12}$ cm$^{-2}$) is found to be 66 meV below the bright negative trion. Its measured properties, including low oscillator strength and the temperature dependence point to an interacting bright intervalley and dark intervalley trion state as the origin of the line.

Keywords: grey trion, transition metal dichalcogenides, intervalley interaction, photoluminescence, reflectance, resonant excitation

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

Introduction

Since the first observation of photoluminescence from mono-layers (MLs) of MoS$_2$, [1, 2] the optical properties of monolayer transition metal dichalcogenides (TMDs) with the formula (W, Mo)(S, Se)$_2$ have been the subject of intense studies [3–6]. Their photoluminescence (PL) spectra contain a number of excitonic features [7, 8], as the screening of electrostatic interactions remains weak even for monolayers that are embedded in a higher dielectric constant cladding [9, 10]. Strong spin-orbit interactions lift the spin degeneracy of the valence and conduction bands at the K and K$'$ valleys, which are the locations of the direct bandgap [11, 12]. A lack of inversion symmetry results in coupling of the valley and spin indices at these symmetry points. The optical selection rules are such that each of the two valleys can be addressed individually using circularly polarized light [13]. For WSe$_2$ and WS$_2$ monolayers, the lowest energy optical transitions are forbidden under normal light incidence; they are either spin forbidden for intravalley transitions or momentum forbidden for intervalley transitions [4]. This situation is in contrast to MoSe$_2$, for which the lowest energy direct optical transition is spin conserving. The spin subbands ordering in the conduction band of MoS$_2$ is still under debate [14–16].

Even though the exciton ground state for WSe$_2$ MLs is dark [17, 18], radiative recombination from free neutral (X) and charged (trions, X$^{-/+/+}$) excitons is observed even at low temperatures [7, 17]. In addition, in contrast to MoSe$_2$ MLs, typical photoluminescence spectra in WSe$_2$ MLs contain features at energies below those of free excitons and trions. This signal has been interpreted as originating from the radiative recombination of excitons that are localized on impurities [3, 19–22] or in strain-induced potential fluctuations [23, 24]. More recently, phonon assisted PL of intervalley dark excitons, with electrons scattered from the K(K$'$) valley into lower-lying energy states in the K'(K) and the Q(Q$'$) valleys, has successfully explained PL spectra recorded from charge-neutral WSe$_2$
MLs on SiO₂ [25] and hBN [26]. Direct access to intravalley spin forbidden excitons have been gained either by mixing these states with bright excitons using external magnetic fields [27] or directly by collecting light with an electric field vector that has a component perpendicular to the ML plane [28, 29].

However, several lines in PL spectra recorded from doped WSe₂ MLs do not have clearly identified origins. Various interactions of excitons with collective states for the free electron gas have been proposed to explain the PL lines at high electron concentrations [30–32]. Lines with intensities that scale as the square of the excitation power have been assigned to the recombination of either neutral biexcitons or five-particle negatively charged biexcitons [33–35]. Although a comprehensive theoretical analysis of possible complexes in negatively charged WSe₂ MLs has identified the spectral positions of complexes in the photoluminescence, some of them still need to be verified experimentally [36].

Here, we analyze sub-bandgap PL spectra in a negatively charged WSe₂ monolayer. We observe a qualitative change in the spectra as free carriers are introduced by electrostatic gating. We show that the fast onset of a trion signal may be caused by double resonance in phonon scattering. The strongest spectral feature at intermediate electron doping levels is consistent with the presence of interacting bright intervalley and dark intervalley trions [37].

Methods

A WSe₂ ML was exfoliated from a bulk WSe₂ crystal onto a polydimethylsiloxane (PDMS) stamp and transferred onto a Si/SiO₂ substrate. The WSe₂ ML was then contacted to predefined metal contacts with a few-layer-thick graphene flake that had been transferred onto the WSe₂ using another PDMS stamp. The two flakes were offset in such a way that most of the WSe₂ surface was uncovered. Another contact was made to the p-doped Si substrate, which was separated from the WSe₂ by a 308 nm thick layer of SiO₂. The device geometry is shown schematically in figure 1.

The sample was placed in a liquid-helium-cooled cold finger cryostat with electrical and optical access. The sample temperature was varied between 12 and 60 K. The carrier concentration in the ML was controlled by the application of a bias voltage, $V_g$. The leakage current remained below 1 nA over the whole range of applied voltages, $V_g = −30$ to 100V. This voltage range corresponds to a change of the carrier concentration from a hole concentration of $p = 2.45 \cdot 10^{12} \text{ cm}^{-2}$ to an electron concentration of $n = 6.65 \cdot 10^{12} \text{ cm}^{-2}$. These values have been calculated for a parallel plate capacitor model with 308 nm thick SiO₂ layer as dielectric, on the assumption that the monolayer is depleted from free charge carriers at $V_{g,b} = 5.0 \text{ V}$, a voltage at which trion emission is weakest. This situation corresponds to a value for the background hole concentration in the monolayer of $p \approx 3.5 \cdot 10^{11} \text{ cm}^{-2}$.

For PL measurements, the WSe₂ ML was excited using a continuous wave laser with a photon energy of 1.88 eV, which was focused to a spot of 1.6 µm diameter on the ML using an objective lens with a NA of 0.47. The excitation power was kept at a low level (<3 µW μm⁻²) to ensure that photo-generated carriers had a negligible effect on gate-induced carrier concentration changes. For resonant PL excitation, we used a continuous wave Ti: sapphire laser emitting at 1.75 eV, i.e. at the energy of the neutral exciton. The PL signal, which was collected using the same objective lens as that used for the excitation, was detected using a Si charge-coupled device at the output of a spectrometer.

Results and discussion

The evolution of PL the signal from a WSe₂ ML with varying charge carrier type and concentration is shown in the form of a colour map in figure 2(a). Representative spectra are shown in figure 2(b). PL of the monolayer with a low carrier concentration is dominated by radiative recombination of excitons. It is accompanied by a band of emission at lower energies (labelled I in the figure). An example of spectrum from this doping range is shown in figure 2(b) for $V_g = 7 \text{ V}$. The intensity and spectral shape of I-band depends on the position on the monolayer (see figure S1 in the supplementary information (stacks.iop.org/JPhysCM/31/415701/mmedia)) and is strongly suppressed in the monolayer encapsulated in hBN as shown in figure S12 in the supplementary information. The application of a voltage, $V_{g}$, to the gate rapidly changes the PL spectra. Both the exciton and the I-band emission decay with applied voltage and are replaced by new lines, which are specific to doping type and concentration and uniform across the monolayer (figure S11) and between the samples (figure S12).

The exciton line, X, is gradually replaced by $X^-$ as the electron concentration increases up to about $< 3 \cdot 10^{12} \text{ cm}^{-2}$. The $X^-$ line is red-shifted by 31 meV from X and it red-shifts further with increasing electron concentration as electrostatic screening by the free electrons becomes stronger [10, 39, 40]. When the electron concentration exceeds $n \approx 5.0 \cdot 10^{12} \text{ cm}^{-2}$, the $X^-$ line is replaced by a much brighter line, $X^{2-}$, which is located 56 meV below X. It has been suggested that this line originates from the fine structure of the trion [3], the presence of double charged trion $X^{3-}$ [34] or an exciton interacting with short-range intervalley plasmons [30].
Over the entire range of carrier concentrations in which the X$^-$ line is present, it is accompanied by another line at approximately 1.66 eV (labelled X$^-$ g). No such replica is visible for the positive trion, X$^+$, as one can see in figure SI3 of the supplementary information. The correlation between the X$^-$ g and X$^-$ lines can be seen in the intensity ratio of the two lines as the carrier concentration and excitation power are varied (figures 2(c) and (f), respectively). The X$^-$ g line is more intense than the X$^-$ line and is the brightest line in the photoluminescence spectra over the range of electron concentrations between $0.5 \times 10^{12}$ cm$^{-2}$ and $5.0 \times 10^{12}$ cm$^{-2}$, as can be seen in figures 2(a) and (b). A signal with this energy has been interpreted as originating from the recombination of dopant-bound excitons [22, 41], although the presence of a fixed but unknown carrier concentration in the experiments then renders such an assignment difficult.

Upon excitation with photons whose energy is at resonance with the exciton energy, as shown in figure 2(d), Raman signal lines are superimposed on the PL signal from the sample. The strongest line, which appears at the position of the X$^-$ line, does not shift in energy with carrier concentration indicating that it is dominated by unresolved A′ and E′ Raman lines [42]. This double resonance between excitation at the energy of the X line and scattered photons at the energy of the X$^-$ line indicates that one can expect efficient trion formation in this system [43]. Whereas the intensity of the X$^-$ line is dominated by the Raman signal, upon resonant excitation the X$^-$ g line becomes the brightest PL line over the entire probed carrier concentration range, further confirming the correlation between the X$^-$ and X$^-$ g lines.

Although X$^-$ g is more pronounced in the PL spectra than X$^-$, it is absent in reflectance spectra, even though the X$^-$ signal is clearly visible, as shown in figure 2(e). This result indicates that the X$^-$ g line originates from a state that has low oscillator strength. Its relatively high PL intensity must therefore result from high occupancy of this state. At the same time, the shelving of excitons in this long lived state leads to the reduction of the total PL signal compared with undoped

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Figure 2. (a) Colour map of PL plotted as a function of gate-channel voltage (carrier concentration level). The PL was excited with a 1.88 eV laser. A positive (negative) voltage introduces excess electrons (holes) in the WSe$_2$ ML. The neutral exciton emission line is labelled X, while the positive (negative) bright trion is labelled X$^+$ (X$^-$). X$^-$ and X$^-$ g are present at moderate electron concentrations, while X$^-$ dominates the spectra at high electron concentrations. (b) Representative PL spectra recorded for different electron concentration levels with all lines labelled. (c) Gate voltage dependence of the integrated intensities of the exciton and trion lines. (d) Colour map of PL plotted as a function of gate voltage (carrier concentration level) during excitation using a 1.75 eV laser (resonant with the X line). The brightest line is at the energy of the X$^-$ line; its intensity results from PL signal overlap with a strong Raman line, indicating a double resonance [38]. The Raman line is detuned from X$^-$, which now appears very weak. The X$^-$ g line is stronger than in (a). (e) Reflectance spectra acquired from the electron-doped ML. The neutral exciton signal has decreased as the electron doping increased while the negative trion signal increased in strength. X$^-$ g is absent from the spectra. (f) Normalised integrated intensities of the X$^-$ and X$^-$ g lines determined from spectra acquired at $V_g = 20$ V, plotted as a function of the normalised integrated intensity of the X line (acquired at different laser excitation intensities) following a power law dependence with exponent $\alpha$, as shown in the figure. The intensities of the X, X$^-$ and X$^-$ g lines are normalised to unity at the lowest excitation power.
Figure 3. Maps of gate-voltage-dependent PL measured at (a) 40 K and (b) 60 K. Positive and negative trion emission lines near the neutrality point are brighter when compared with the X line while $X^-_u$ is suppressed.

Figure 4. Photoluminescence spectra acquired from an electron-doped ML ($V_g = 45$ V, $n \approx 2.55 \cdot 10^{11}$ cm$^{-2}$) upon excitation using (a) right-hand circularly polarized light and (b) horizontally polarized light. Only the X line shows valley coherence.

Figure 5. A photogenerated bright exciton, upon binding an electron in the same valley, forms an intravalley negative trion (left panel). The intravalley bright trion can be scattered into the lower energy momentum dark trion by electron scattering from the spin up (higher energy) subband in the conduction band at the K valley to the spin up (lower energy) subband in the conduction band subband at the K’ valley (middle upper panel). Interactions between this dark trion and a bright trion with both electrons in the higher energy subbands of the conduction band at the K and K’ valleys (middle lower panel) lead to a formation of a new ground state of the trion (grey trion). Radiative recombination of the grey trion leaves an electron in the higher energy subband of the conduction band (right panel).
measured to be 32 meV and has been used to estimate \( \Delta_{CB} \) as being equal to 26 meV \[27\]. These values for \( \Delta_{CB,T} \) and \( \Delta_{CB} \) indicate that the energy separation between \( X^+ \) and \( X^- \) of approximately 58 meV, which is very close to the value of 55.3 \( \pm \) 0.3 meV measured at a voltage bias of 20V \((n \approx 8.75 \cdot 10^{11} \text{ cm}^{-2})\) as an average across the entire sample area.

**Conclusions**

We have shown that photoluminescence spectra obtained from a moderately \( n \)-doped WSe\(_2\) monolayer are dominated by a negative trion related signal. Very low doping levels are sufficient to observe negative trions, indicating that trion formation and recombination are very efficient. Trion formation may be facilitated by efficient phonon emission by the exciton. This scattering process manifests itself as a double resonance in Raman scattering seen when the incident photons are resonant with the exciton states and the scattered photons with the trion states. At an intermediate electron concentration, the most intense photoluminescence is measured from the radiative recombination of a grey trion, which is the ground state of the interacting bright intervalley and dark intertrionally. This state is yet another multi-particle complex identified in WSe\(_2\) monolayer alongside others, such as dopant-bound excitons and negatively charged biexcitons.

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