Probing exciton species in atomically thin WS$_2$–graphene heterostructures

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Abstract

We report on a detailed study of temperature-dependent photoluminescence spectroscopy of monolayer WS$_2$ grown on epitaxial graphene. The study reveals for the first time the intrinsic excitonic effects of WS$_2$ supported on one- and two-layer graphene (2LG) from room temperature to 83 K, with both excitons and trions evidenced in the entire temperature range and temperature-independent trion dissociation. All emission peaks exhibit a shift towards higher energy with decreasing temperature due to band gap renormalisation induced by electron–phonon interaction. A highly linear dependence of the photoluminescence with the excitation power is found for both WS$_2$ on one- and 2LG, confirming the excitonic nature of associated transitions and the high crystal quality of the WS$_2$–graphene heterostructure.

1. Introduction

Single-layered transition metal dichalcogenides (TMDC) have been observed to exhibit enhanced light-matter interactions granted by their two-dimensional nature which results in strong Coulomb interaction and reduced dielectric screening compared to bulk semiconductors [1, 2]. The reduced dimensionality makes it possible for excitons to bind even at room temperature, with binding energy of hundreds of meV [2], and to modulate their emission using several methods, such as light [3, 4], electric field [4, 5], magnetic field [6], and strain [7]. The ease of emission tunability offers unique advantages in optoelectronics and photonics, such as flexible, ultra-thin LEDs [8], lasers [9, 10], as well as valleytronic applications [11]. Combining single-layered materials in vertically stacked heterostructures provides an additional platform for manipulating the excitons in two dimensions, not achievable with conventional semiconductors. As such, heterostructures of MoS$_2$/WSe$_2$ [12] and MoSe$_2$/WSe$_2$ [13] give rise to indirect excitons with long lifetimes due to photoexcited electrons and holes accumulated in different layers. P–n junctions with high quantum efficiency (>60%) were demonstrated in GaTe/MoS$_2$ heterostructures [14] and interfacing TMDC with graphene achieved very efficient photocarrier extraction [15, 16]. A recent study evidenced that the excitonic properties of monolayer WS$_2$ can be effectively tuned with the number of supporting graphene layers [17], leading to enhancement of the photoluminescence (PL) response for WS$_2$ supported on two-layer graphene (2LG) compared to WS$_2$ on one-layer graphene (1LG). The excitonic effects in TMDC heterostructures exhibit rich features, such as neutral and charged excitons (trions), biexcitons, localised excitons [18], which become more evident at low temperature, and with properties and behaviour that are far from understood. For WS$_2$–graphene heterostructures there are no reports for PL temperature dependence of the excitons and trions. Clearly, knowledge of exciton behaviour is key to manipulating and controlling optical properties of these materials for their successful integration in useful...
devices. Therefore, in this work we study temperature-dependent excitonic effects in monolayer WS₂, grown by chemical vapour deposition on epitaxial graphene, in order to provide insight into their fundamental nature.

2. Methods

2.1. Synthesis of WS₂ on epitaxial graphene

The synthesis of WS₂ on epitaxial graphene was carried out by ambient pressure chemical vapour deposition. 10 mg of WO₃ powder (Source Alfa Aesar, purity 99.998%) deposited on the graphene on SiC substrate was loaded into the centre of a quartz tube and heated at 900 °C under atmospheric pressure. Sulphur vapour generated by heating sulphur powder up to 250 °C were transported by an Ar flow to react with the oxide powder, resulting in WS₂ islands growth on graphene (deposition time 60 min).

Epitaxial graphene was synthesised via Si sublimation from SiC using semi-insulating (0001) 6H-SiC (resistivity >10¹⁵ Ω cm, II–VI, Inc.). The SiC substrates were etched in H₂ at 200 mbar using a ramp from room temperature to 1580 °C to remove polishing damage. At the end of the ramp, the H₂ was evacuated and Ar added to a pressure of 100 mbar. The graphene was then synthesized at 1580 °C for 25 min in the Ar and the sample cooled in Ar to 800 °C. The graphene samples made this way are naturally n-type [19]. To avoid defect creation and sample instability when left out in air (oxygen rich environment), WS₂/graphene samples were stored in a vacuum desiccator and measured within one month following the growth. The interaction with the ambient was limited to PL and scanning Kelvin probe microscopy (SKPM) measurement time (days), which is below the month threshold noticed for the sample degradation to impact the measurements [20].

2.2. Scanning Kelvin probe microscopy

Experiments were conducted in ambient, using a Bruker Icon AFM, using Bruker highly doped Si probes (PFQNE-AL) with a force constant ~ 0.9 N m⁻¹. Frequency-modulated SKPM (FM-SKPM) operated in a single pass mode has been used in all measurements.

2.3. PL spectroscopy

Temperature-dependent PL spectroscopy was carried out using a THMS 600 heating/cooling stage (Linkam Scientific Instruments) in the temperature range from RT to 83 K coupled to a Renishaw inVia system. A 532 nm laser excitation wavelength was used for PL intensity mapping. The laser beam was focused through a long-working distance 50× microscope objective and recorded in back-scattering geometry.

3. Results and discussion

3.1. Evolution of photoluminescence in relation to graphene thickness at room temperature

The WS₂ was synthesised by chemical vapour deposition on epitaxial graphene substrates grown on SiC, as detailed in Methods. The samples were characterised by SKPM and reveal various morphologies (star-, triangular- and trapezoidal-shaped) for WS₂, with the surface potential increasing for both WS₂ and graphene with the number of layers, as illustrated in figure 1 (a). In accordance with DFT calculations [17], the SKPM shows that the WS₂ layer is largely transparent to the underlying graphene in the surface potential measurements (figure 1 (a)). The optical properties of monolayer WS₂ deposited on 1LG (WS₂/1LG) change when an additional graphene layer is introduced, going from a quenched PL signal for WS₂/1LG to a less quenched one for WS₂ on 2LG (WS₂/2LG) (figure 1(b)), as evidenced by a previous study [17]. This is due to the difference in electronic structure between 1LG and 2LG. 1LG is a semimetal without a band gap, whereas 2LG presents a small band gap due to a small asymmetry between the layers. This means that for WS₂/1LG, the photoexcited carriers, instead of recombining in WS₂, transfer very fast to graphene (on a time-scale of ~1 ps [21]) and combine non-radiatively near the Dirac point of graphene via acoustic phonon scattering, quenching the photoluminescence. The presence of a small band gap in 2LG means that the relaxation of photoexcited carriers occurs via the optical phonons which limits the decay and is therefore consistent with a longer lifetime for photoexcited carriers in the WS₂/2LG system. This means increased radiative emission, or reduced quenching efficiency in WS₂/2LG, compared to WS₂/1LG. In particular, the relaxation of photoexcited charge carriers in the innermost conduction band of 2LG takes place through phonon-assisted interband transitions, whereas the charge carriers in the outermost conduction band remain trapped due to the presence of the band gap, increasing their lifetime. The longer lifetime of photoexcited carriers in 2LG compared to 1LG has been experimentally verified by time-resolved ARPES [22].

Representative PL spectra extracted from regions corresponding to monolayer WS₂ on 1LG and on 2LG, respectively are shown in figure 2(a). The PL signal involves optical transitions between the conduction band minimum and the maximum of the spin–orbit split valence band of WS₂. On 1LG, monolayer WS₂ exhibits PL...
emission at \( \sim 1.94 \text{ eV} \), with a full-width-at-half-maximum (FWHM), \( \Gamma \), of \( \sim 40 \text{ meV} \) (figure 2(b)), associated with the direct band gap at the K point in the Brillouin zone. For 2LG-supported WS\(_2\), the PL intensity is enhanced compared to WS\(_2\) on 1LG (figure 2(a)) and the spectral shape modified such that the PL peak is defined by a superposition of two individual constituents, better evidenced by PL peak deconvolution in figure 2(c). The two components are associated with the emission from neutral exciton states at 1.93 eV, with the peak FWHM of 30 meV, and from charged exciton states (trions) at 1.9 eV and peak FWHM of 50 meV. The formation of trions requires an electron- or hole-rich environment, which is provided for WS\(_2\)/graphene heterostructure, and owing to the higher carrier density in 2LG compared to 1LG, as confirmed by previous transport experiments and calculations [17, 23].

3.2. Temperature-dependent photoluminescence

The excitonic properties in 2D heterostructures include complex features, such as localised and delocalised neutral excitons [18, 24], biexcitons [25, 26], trions [4, 27]. To further explore the excitonic features in WS\(_2\)/graphene heterostructure, the temperature dependence of PL at temperatures ranging from 83 K to RT (293 K) was measured, and the spatial distribution of PL intensity recorded in figure 3. The maps illustrate a monolayer WS\(_2\) island on epitaxial graphene, with relatively homogenous PL signal for 1LG-supported WS\(_2\) as compared to WS\(_2\)/2LG regions supported by 2LG that show higher PL intensity.

The typical evolution of PL spectra associated with PL intensity maps as a function of temperature is presented in figures 4(a) and (b) for WS\(_2\)/1LG and WS\(_2\)/2LG, respectively.
Similar to RT PL, at all investigated temperatures, ranging from 83 to 293 K, the spectra are dominated by excitons and trions and do not exhibit any additional peaks in the temperature range investigated, indicating that few defects/impurities are present in the samples to contribute to the creation of bound excitons.

Both neutral exciton and trion peaks become sharper with decreasing temperature, consistent with temperature broadening of emission peaks dominated by interaction of excitons/trions with longitudinal optical phonons [28]. This is illustrated in figure 5(a), where the FWHM was obtained by Lorenzian fitting of associated exciton and trion PL peaks. All emission peaks exhibit a shift towards higher energy with decreasing temperature (figure 4) due to band gap renormalisation induced by electron–phonon interaction. This is also demonstrated in figure 5(b), which shows the temperature dependence of PL peak positions, fitted using the O’Donnell and Chen equation, which gives the temperature dependence of semiconductor band gaps taking...
into account intrinsic interactions of semiconductors, such as electron–phonon coupling and gives indication of the strength of electron–phonon coupling [29]:

\[
E_g(T) = E_g(0) - S \left( \frac{\langle \hbar \omega \rangle}{2k_B T} \right) - 1,
\]

where \( E_g(0) \) is the band gap at zero temperature, \( S \) is a dimensionless coupling constant, \( k_B \) is the Boltzmann constant and \( \hbar \omega \) is an average phonon energy, as derived from the Huang and Rhys model [30].

Temperature dependences of the exciton and trion peak positions are fitted well with the fitting parameters listed in table 1. The values for \( E_g(0) \) are comparable to those in previous studies on WS\(_2\) monolayers [31] and indicate that the observed temperature dependence originates from the change in bandgap of WS\(_2\).

The coupling constant \( S \) appears similar for all three cases (see table 1), however the extracted values are smaller than previously reported for WS\(_2\): e.g. \( S = 2.4 \) [32], perhaps due to the interaction with graphene. The average phonon energy for WS\(_2\)/1LG and WS\(_2\)/2LG exciton compares well with previously reported values, e.g. 15 meV [33] and is in good agreement with the acoustic phonons near the K point in WS\(_2\) [34].

With few deviations, the energy difference between the exciton and trion for WS\(_2\)/2LG remains constant, suggesting that the trion dissociation in monolayer WS\(_2\)/graphene is independent of temperature, consistent with observations in previous studies of WS\(_2\) on Si [5, 32, 35].

The temperature-dependence of the PL intensity for WS\(_2\)/1LG and WS\(_2\)/2LG is presented in figure 6. An initial increase in PL intensity is observed for excitonic peaks of WS\(_2\)/1LG and WS\(_2\)/2LG, in the 183–293 K temperature range, followed by a gradual decrease of PL intensity as the temperature decreases further to 83 K. A decrease of the neutral exciton intensity with the decrease in temperature was previously observed for WS\(_2\) and WSe\(_2\) and attributed to a low-lying dark state that quenches light emission with decreasing temperature [32, 36, 37]. Typical separation value between dark and bright excitonic states observed for WSe\(_2\) and WS\(_2\) is \( \sim 50 \) meV [38], whereas the separation value observed in this study is \( 8 \) meV for the decrease in intensity from 183 to 153 K. However, the separation values observed in the experiment may not accurately reflect the separation between the dark and bright states due to competing non-radiative decay channels which exhibit strong temperature-dependence or non-equilibrium population for the two states [36]. Robust evidence for the existence of a dark state can be provided by time-resolved PL or two-photon excitation spectroscopy as

\[
\left( \frac{\hbar \omega}{2k_B T} \right) = \frac{E_g(T) - E_g(0)}{S} - 1.
\]

Table 1. Numerical values obtained for \( E_g(0), S \) and \( \hbar \omega \) fitting parameters:

| Parameter | WS\(_2\)/1LG | WS\(_2\)/2LG exciton | WS\(_2\)/2LG trion |
|----------|--------------|----------------------|-------------------|
| \( E_g(0) \) (eV) | 2.03 ± 0.01 | 2.09 ± 0.03 | 2.01 ± 0.01 |
| \( S \) | 0.19 ± 0.01 | 0.21 ± 0.02 | 0.23 ± 0.03 |
| \( \hbar \omega \) (meV) | 14.8 ± 6 | 17.4 ± 6 | 27.9 ± 6 |

Figure 5. Variation of (a) FWHM and (b) PL peak energies as a function of temperature for exciton and trion peaks associated with WS\(_2\)/1LG and WS\(_2\)/2LG, respectively. Solid lines in (a) are provided for guidance only. Solid lines in (b) correspond to fitting lines using O'Donnell and Chen equation as described in the text. Inset in (b) shows the energy difference (\( \Delta E \)) between the exciton and trion for WS\(_2\)/2LG as a function of temperature.

Table 1. Numerical values obtained for \( E_g(0), S \) and \( \hbar \omega \) fitting parameters:
exemplified by previous studies [1, 36]. Another possibility for the decrease in intensity observed in this study can be the variation of the radiative rate with the temperature.

The behaviour of the trions is different, with the intensity showing an overall decrease with decreasing temperature, in line with quenched exciton emission due to dark state in WS$_2$.

### 3.3. Excitation power dependence of PL

To further understand the origin of the observed PL peaks, excitation power dependent PL was carried out at a range of laser powers, as summarised in figure 7. The behaviour of the PL intensity as a function of excitation power is generally a good indicator of the nature of underlying radiative recombination processes and the evaluation of crystal quality [39, 40]. The PL peak shape does not change and no additional peaks emerge as the excitation power varies from 0.01 to 20 mW, indicating that no new excitonic species are created under high excitation power.

Furthermore, the neutral-exciton energy stays relatively constant as a function of laser excitation power, however the Lorentzian width broadened by $\sim$7 meV for high laser excitation power (20 mW) compared to 0.01 mW laser power for both WS$_2$/1LG and WS$_2$/2LG presumably due to photo-ionisation effects of neutral donor/acceptor impurities within the WS$_2$ band gap. In contrast, the trion peak shows a red shift for high excitation power, indicating that the trion dissociation energy increases with excitation power. The trion dissociation energy, i.e. the energy difference between the exciton and trion is related to the Fermi energy by [31, 35]:

$$E_{\text{exciton}} - E_{\text{trion}} = E_{\text{binding, trion}} + E_F$$

This implies that the increase of trion dissociation energy is due to a rise in Fermi energy, consistent with ionised electrons resulted from trion dissociation being excited to unoccupied states above the Fermi energy. The trion dissociation energy increases with the excitation power suggesting that the density of carriers, and hence the Fermi energy increases, with the excitation power. Trion dissociation results in free charge that will occupy the unoccupied states above the Fermi energy, causing the change in Fermi energy. The change in the Fermi energy can also be due to photoionisation effects of neutral donor/acceptor impurities within the band gap of WS$_2$. 

![Figure 6. PL spectra in the temperature range 83–293 K for (a) WS$_2$/1LG, (b) WS$_2$/2LG. (c) Temperature-dependent PL intensity for excitons and trions, with solid lines provided as guide to the eye.](image-url)
PL line deconvolution was carried out using Lorenzian components and intensities were plotted in relation to the laser excitation power for WS2/1LG and WS2/2LG exciton and trion, as summarised in figure 8 for data recorded at room temperature (top panels) and at 83 K (bottom panels).

At RT, the excitation power dependence of PL line intensities is highly linear for all cases, with the slope $\sim 1$, which is slightly reduced at 83 K for WS2/1LG and WS2/2LG trion. A linear behaviour is the typical power dependence for excitonic ground state emission, according to a model for direct-band gap semiconductors proposed by Schmidt et al [39]. The model describes the PL intensity as a power-law dependence on the laser excitation power $L$, as:

$$I \propto L^k,$$

where $I$ is the luminescence intensity, $L$ the excitation laser intensity and $k$ a coefficient, with $1 < k < 2$ for exciton–like transitions for laser light with $h\nu$ exceeding the gap energy (our present case).

According to the same model [39], a coefficient $k < 1$ suggests a recombination path involving free-to-bound (i.e. either recombination of a free hole and a neutral donor or that of a free electron and a neutral acceptor) and donor-acceptor pair recombination. The sublinear trend for WS2/1LG and WS2/2LG trion at 83 K is an indication that some recombination processes are due to bound excitons processes—which are more pronounced at low temperature compared to RT—because defect sites, such as unintentional impurities or sulfur vacancies [24] in the lattice become saturated with trapped excitons at higher laser intensities. The sublinear trend is slightly more pronounced for WS2/2LG, suggesting that, in addition to trion generation due to doping by the graphene substrate, donor/acceptor states within the WS2 band gap can also contribute to trion formation through photoionisation and subsequent coupling to free excitons. Photoionisation effects were previously shown to lead to trion formation in WS2 [32, 41]. However, the slightly sublinear trend observed here suggests that photoionisation effects are not the dominant factor in trion formation for WS2/2LG.

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Figure 7. PL spectra of WS2 on (a) 1LG and (b) 2LG for various excitation energies at room temperature. (c) Excitation–dependent PL peak position for neutral excitons and trions in WS2/1LG and WS2/2LG.
4. Conclusions

The intrinsic excitonic properties of WS$_2$ on epitaxial graphene have been studied using temperature-dependent PL spectroscopy from RT to 83 K. Resonances related to both neutral for WS$_2$/1LG and WS$_2$/2LG and charged excitons (trions) in WS$_2$/2LG are detected in the entire temperature range. Both excitons and trions exhibit red-shift with increasing temperature due to effective electron–phonon coupling, with temperature-independent trion dissociation in the range of temperatures investigated in this study. Luminescence in both WS$_2$/1LG and WS$_2$/2LG shows a highly linear dependence on the excitation energy confirming the excitonic nature of associated transitions. Excitation intensity-dependent PL suggests that photoionisation effects, although not dominant, contribute to the trion formation in WS$_2$/2LG. Further studies are required to clarify the origin of the non-monotonic behaviour of PL intensity with the temperature. Our study presents evidence of complex excitonic properties in atomically-thin heterostructures, whose elucidation is essential to enable 2D material-based applications in optoelectronics, photonics and valleytronics.

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