

Creation of Single-Photon Emitters in hBN-Encapsulated Monolayer WS₂ via Controlled Thermal Annealing

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Abstract

Single-photon emitters (SPEs) in solid-state materials enable scalable quantum communication and information processing. In two-dimensional semiconductors, however, controlled generation of optically active point defects remains challenging. Here, we use *in situ* high-temperature annealing of hBN-encapsulated monolayer WS₂ on a suspended micro-heater to produce a reproducible localized exciton emitter. Annealing to \sim 1000–1100 K leads to the emergence of a spectrally isolated line, X_L , located 70–90 meV below the neutral exciton. X_L displays a resolution-limited linewidth below 0.2 meV, a radiative lifetime of \sim 0.9 ns, and clear antibunching with $g^{(2)}(0) \approx 0.4$. Photoluminescence excitation spectroscopy shows that X_L originates from intrinsic excitons trapped at vacancy-like defects generated during annealing. This approach provides a controlled and robust pathway for engineering SPEs in monolayer WS₂ and highlights the potential of defect-based quantum light sources in 2D semiconductors.

Introduction

Atomically thin TMDs such as MoS₂, WS₂, and WSe₂ host tightly bound excitons with large oscillator strength and a direct bandgap in the monolayer limit, which makes them attractive for quantum photonics and integrated optoelectronics. Their small exciton Bohr radius and reduced dielectric screening imply that excitons are highly sensitive to the local environment, so that lattice defects, strain, and dielectric disorder can transform band-edge excitons into strongly localized states that emit single photons.[1]

Single-photon emission from defect-bound excitons was first reported in monolayer TMDs such as WSe₂ and later in vacancy-engineered MoS₂, where sulfur vacancies created by electron or ion irradiation give rise to deep, atomic-scale confinement potentials[2]. In WS₂, our previous work on non-encapsulated monolayers integrated onto SiC micro-heater chips showed that high-temperature annealing above 1000 K produces a new emission band, X_L , located \sim 220 meV below the neutral exciton with a linewidth of \sim 12 meV. This emission saturates with excitation power and was attributed to excitons trapped at thermally generated sulfur vacancies. Nevertheless, the optical quality of non-encapsulated samples was limited by broad linewidths, photo-doping, and poor reproducibility, which prevented a clear demonstration of single-photon emission.

Encapsulation in hBN is now established as a key strategy to obtain intrinsically narrow exciton and trion lines in TMD monolayers. The atomically flat and chemically inert hBN environment screens charge fluctuations, suppresses surface adsorbates, and protects the monolayer during high-temperature treatments. In encapsulated WS₂, low-temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra exhibit linewidths of only a few meV and well-resolved higher-lying excitonic resonances, providing an ideal platform to reveal weak defect-related features.

In this work we exploit this high optical quality to revisit vacancy engineering in WS₂. We fabricate hBN/WS₂/hBN heterostructures on Si substrates, pick up the entire stack with a polycarbonate (PC) film, and transfer it onto the suspended SiC membrane of a commercial micro-heater chip. After release at \sim 200°C the residual PC is removed in chloroform, which preserves both the integrity of the membrane and the cleanliness of the heterostructure. The micro-heater is then integrated in a cryostat, allowing local Joule heating of the membrane up to \sim 1200 K while the surrounding environment is kept at a few kelvin.

By tracking the PL spectrum after successive annealing steps and calibrating the membrane temperature from the exciton redshift, we identify a reproducible regime around 1000–1100 K where ultra-narrow defect-bound emission emerges in encapsulated WS₂. We show that this localized exciton, X_L , is fed by intrinsic excitonic resonances, exhibits a lifetime in the nanosecond range, and displays clear photon antibunching. Compared to non-encapsulated samples, hBN encapsulation reduces the defect emission linewidth by almost two orders of magnitude while providing excellent spectral stability. These results demonstrate a controlled route to single-photon emitters in WS₂ based solely on thermal annealing.

Results and discussion

hBN-encapsulated WS₂ on micro-heater membranes

Fully encapsulated WS₂ monolayers were prepared by mechanical exfoliation of bulk crystals and assembly of hBN/WS₂/hBN heterostructures on Si/SiO₂ substrates. The stack was then picked up using a PC stamp and transferred onto the suspended SiC membrane of a Protochips micro-heater. Thermal release at $\sim 200^\circ\text{C}$ followed by chloroform rinsing removed the PC residues and yielded clean, mechanically stable heterostructures spanning the membrane.

At low temperature, the PL spectrum of the encapsulated WS₂ shows sharp excitonic resonances, including the neutral exciton X^0 , negatively charged trions, dark-exciton related features, and phonon replicas with linewidths of only a few meV. The observation of complex excitonic species and biexcitons confirms the excellent optical quality of the samples and the effectiveness of encapsulation in suppressing dielectric disorder.

Complementary PLE measurements, where the detection energy is fixed while the excitation energy is scanned, reveal pronounced absorption resonances at the A and B exciton energies as well as excited Rydberg-like states. The close correspondence between PL and PLE spectra demonstrates that the excitonic structure is preserved after transfer onto the membrane and provides a baseline for identifying new emission features that appear after annealing.

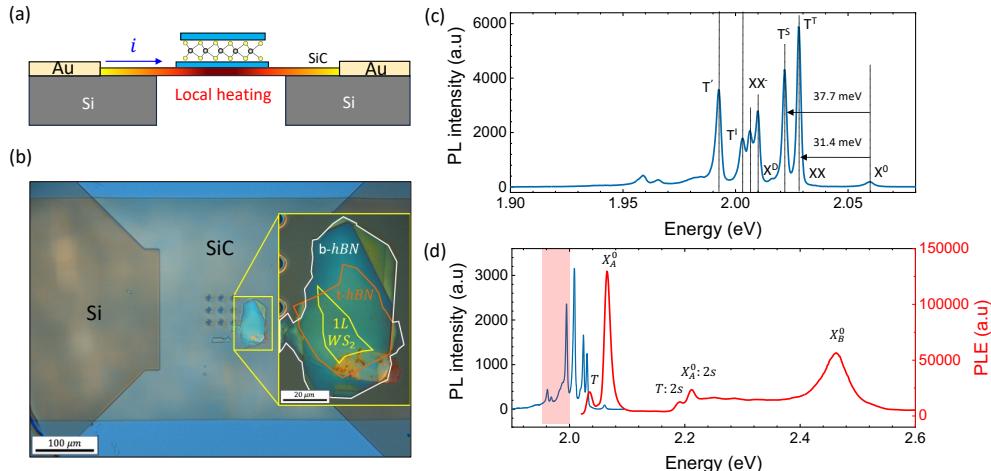


Figure 1: Optical characterization of hBN-encapsulated monolayer WS₂ on a micro-heater membrane. (a) Schematic of the micro-heater chip showing the suspended SiC membrane between metallic contacts and the hBN/WS₂/hBN stack transferred on top. (b) Optical micrograph of a representative encapsulated flake on the membrane. (c) Low-temperature PL spectrum displaying sharp neutral-exciton, trion, and dark-state related resonances with linewidths of a few meV. (d) PLE spectrum highlighting well-resolved A- and B-exciton absorption resonances and higher-lying excitonic states. Graphics are placeholders; experimental data will be inserted once figures are prepared.

Thermal annealing and emergence of the localized exciton X_L

Thermal annealing was performed *in situ* by driving a dc current through the suspended SiC membrane inside a closed-cycle cryostat. For each annealing step the current was increased to reach a target temperature, held for typically 30 min, and then turned off, after which the membrane cooled back to the base temperature of a few kelvin. The membrane temperature as a function of current was calibrated from the redshift of the neutral exciton peak using Pässler's model for the bandgap renormalization, which allowed us to extend the calibration up to ~ 900 K and extrapolate to higher temperatures.

Up to ~ 800 K the PL spectra remain dominated by the intrinsic excitonic features, apart from small reversible energy shifts and intensity changes. Above ~ 900 K a new emission shoulder appears on the low-energy side of X^0 . After annealing around 1000–1100 K this feature evolves into a spectrally isolated, ultra-narrow line X_L located about 90–100 meV below the neutral exciton. The energy separation is consistent with a deep binding potential associated with chalcogen vacancies, in analogy with sulfur-vacancy related emission observed in MoS₂.[2]

In contrast to the ~ 12 meV linewidths previously observed in non-encapsulated WS₂, X_L in encapsulated samples exhibits a linewidth below 0.2 meV at low excitation power, limited by the spectrometer resolution. This dramatic narrowing highlights the crucial role of encapsulation in suppressing environmental fluctuations and background disorder.

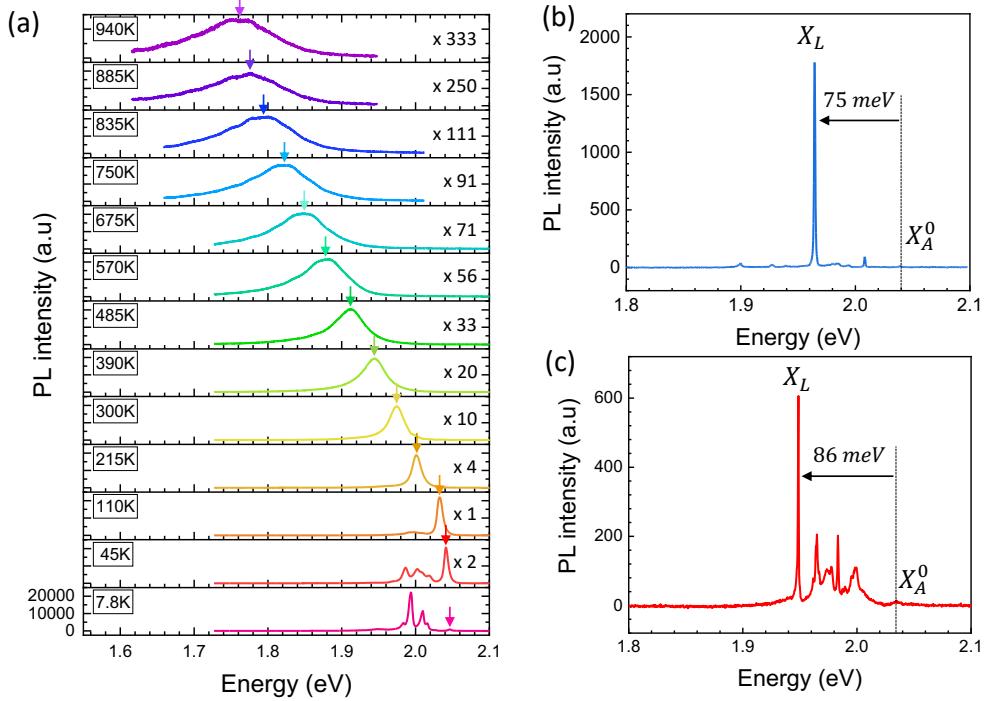


Figure 2: Thermal-annealing-induced localized exciton emission in encapsulated WS₂. (a) Low-temperature PL spectra after successive annealing steps, showing the evolution from intrinsic excitonic emission to the appearance of a narrow defect-bound line X_L below X^0 . (b) PL spectrum after annealing around 1100 K, where X_L is spectrally isolated and exhibits a resolution-limited linewidth. (c) Comparison of post-annealing spectra from multiple samples, demonstrating the reproducibility of X_L formation. (d) Power-dependent PL of X_L , showing saturation behavior characteristic of a finite density of localized defect states. Graphics are placeholders; experimental data will be inserted later.

Power-dependent PL measurements confirm the localized nature of X_L . The integrated intensity initially increases linearly with excitation power and then saturates, as expected for a small number of defect sites

that can host at most one exciton at a time. The linewidth of X_L broadens only weakly with power, which indicates that charge noise and local heating remain limited in the encapsulated structure.

Excitonic origin and radiative dynamics of X_L

To identify the excitation pathway of X_L , we perform PLE spectroscopy by monitoring the emission at the X_L energy while scanning the laser energy across the excitonic resonances. The PLE spectrum closely follows the absorption profile of the monolayer: it shows pronounced peaks at the A and B exciton energies and higher-lying states, mirroring the PLE recorded at the neutral-exciton emission energy. This one-to-one correspondence demonstrates that X_L is populated by excitons created in the WS₂ bands rather than by extrinsic states in the substrate or encapsulation layers.

Time-resolved PL (TRPL) measurements reveal that the X_L emission decays mono-exponentially with a characteristic lifetime of ~ 0.9 ns. This lifetime is significantly longer than that of trion emission in the same sample, consistent with strong spatial localization suppressing nonradiative channels. The absence of a fast nonradiative component in the decay indicates that the defect potential defines a stable and efficient radiative recombination pathway.

The quantum nature of X_L is probed through second-order photon correlation measurements using a Hanbury Brown–Twiss setup under pulsed excitation. The measured intensity correlation function $g^{(2)}(\tau)$ shows a clear antibunching dip at zero delay with $g^{(2)}(0) \approx 0.3$ without background correction, which unambiguously proves that X_L acts as a single-photon emitter. The moderate residual value of $g^{(2)}(0)$ is attributed to background emission and imperfect spectral filtering and can be further reduced by improving the collection optics and spectral selection.

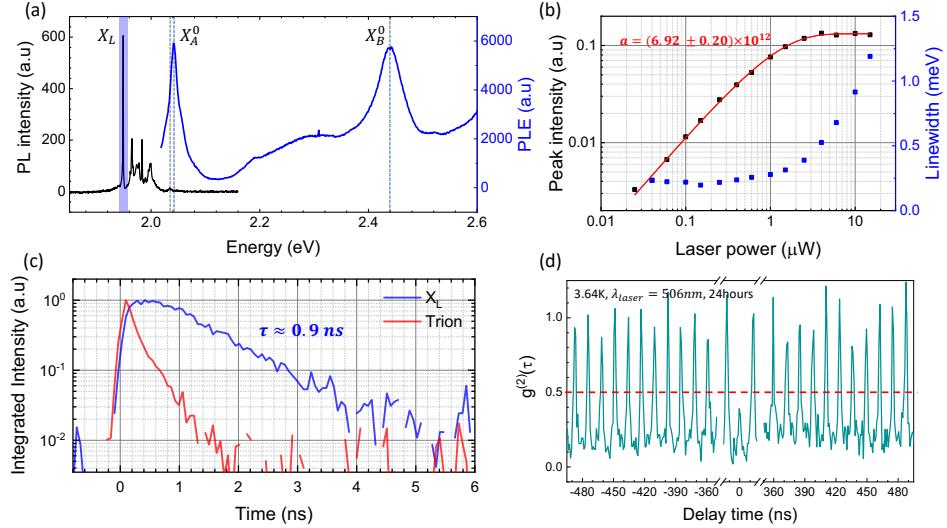


Figure 3: Optical signatures of the localized exciton X_L . (a) PLE spectrum recorded at the X_L emission energy, showing resonances at the A and B exciton absorption energies and higher-lying states. (b) Power dependence of the X_L intensity and linewidth, exhibiting saturation of the intensity and resolution-limited linewidth at low power. (c) Time-resolved PL traces of X_L and trion emission, highlighting the longer lifetime of the localized state. (d) Second-order correlation function $g^{(2)}(\tau)$ under pulsed excitation, displaying pronounced antibunching with $g^{(2)}(0) < 0.5$. Graphics are placeholders; experimental curves will be added in the final version.

Overall, the combination of spectrally isolated, ultra-narrow emission, nanosecond radiative lifetime, and antibunched photon statistics demonstrates that high-temperature annealing of encapsulated WS₂ generates robust defect-based single-photon emitters that can be probed with high spectral resolution.

Conclusion

We have demonstrated a controllable pathway to create single-photon emitters in hBN-encapsulated monolayer WS₂ by *in situ* high-temperature annealing on a micro-heater platform. The clean dielectric environment provided by hBN enables the emergence of an ultra-narrow localized exciton X_L located 90–100 meV below the neutral exciton after annealing around 1000–1100 K. X_L exhibits a resolution-limited linewidth below 0.2 meV, a radiative lifetime of \sim 0.9 ns, and clear photon antibunching with $g^{(2)}(0) \approx 0.3$, confirming its single-photon character. PLE and TRPL measurements show that X_L originates from intrinsic excitons captured by thermally generated vacancy-like defects that form deep, highly localized potentials.

Compared to non-encapsulated samples, encapsulation reduces the defect emission linewidth by almost two orders of magnitude and greatly improves spectral stability and reproducibility. Our results highlight the central role of encapsulation in defect engineering and establish encapsulated WS₂ on micro-heater chips as a versatile platform for studying exciton–defect interactions and implementing deterministic quantum light sources in 2D semiconductors.

Acknowledgements

The authors thank ... (to be completed). Funding agencies, collaborators, and technical support acknowledgments will be added here.

Supporting information

Additional experimental details, micro-heater calibration procedures, extended temperature-dependent PL maps, PLE datasets, TRPL analysis, and raw $g^{(2)}(\tau)$ histograms will be provided in the Supporting Information.

The following files are available free of charge.

- SI_WS2_annealing.pdf: Experimental methods and additional figures.
- data_WS2_XL.zip: Selected raw PL, PLE, TRPL, and HBT data.

References

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- (2) Mitterreiter, E. et al. *Nature Communications* **2021**, *12*, 3822.

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