Supporting Information

Exciton Kinetics, Quantum Efficiency, and Efficiency Droop of Monolayer MoS_2 Light Emitting Devices

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S1. Variation of peak energy and valence band splitting with temperature

The peak shifts of both modes, shown in Fig. S1(a), can be well described using the Varshni's semi-empirical equation[1], $E_g(T) = E_g(0) - \frac{\alpha T^2}{T+\beta}$ (α and β are the characteristics of the given material), with fitting parameters of E_0 = 2.053 ± 0.003 eV, α = (5 ± 1)×10^{-4} eV/k, β = 460 ± 200 k for mode B and E_0 = 1.868 ± 0.003 eV, α = (2.2 ± 0.7)×10^{-4} eV/k, β = 250 ± 100 k for mode A. Mode B shows a larger shift than mode A with increasing temperature indicated by a larger value of α for mode B compared to that for mode A. The observed unequal shift of modes A and B is accompanied by a reduction of the valence band splitting from 182 meV to 137 meV with increasing temperature from 83 K to 423 K, shown in Fig. S1(b). Our observed reduction of valence band-splitting resembles the well-known modulation of the conduction band-splitting in quantum well (QW) structures. In QWs the conduction band-splitting could be reduced by reducing the population difference of the splitted sub-bands via electrical gating under a constant magnetic field.[2] In our case, the population modulation is the result of phonon-mediated optical transitions, as described in the manuscript.

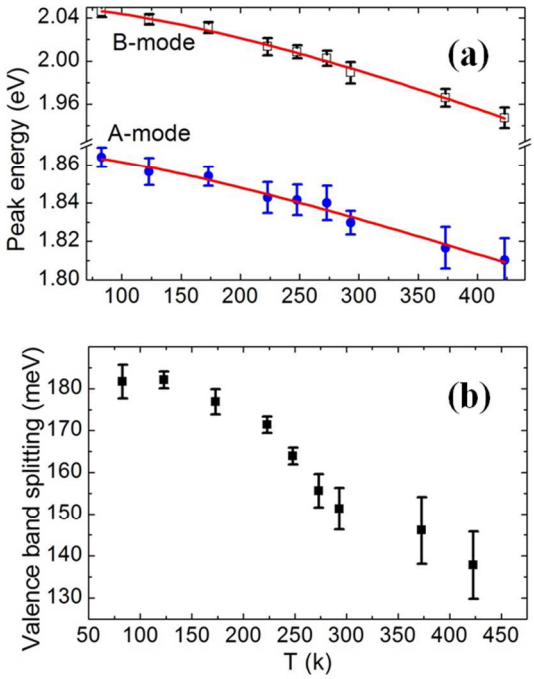

Figure 1. Plot of the (a) variation of peak energy and (b) valence band splitting as a function of measurement temperature.

S2. Origin of inhomogeneous broadening

Inhomogeneous broadening is related to non-phonon scattering processes such as exciton-exciton, exciton-carrier and exciton-defect scattering. We did not observe a significant change of FWHM with modulating the excitation power by four orders of magnitude, as shown in Fig. S2. Therefore, we rule out the exciton-exciton scattering as the possible origin of such a large inhomogeneous broadening. Also, exciton-free carrier scattering should be negligible due to the large exciton binding energy of 1L MoS_2 (80 meV, see the manuscript). Thus, we attribute the observed inhomogeneous broadening to the exciton-defect scattering. These defects may originate from the free surface and the MoS_2/substrate interface.

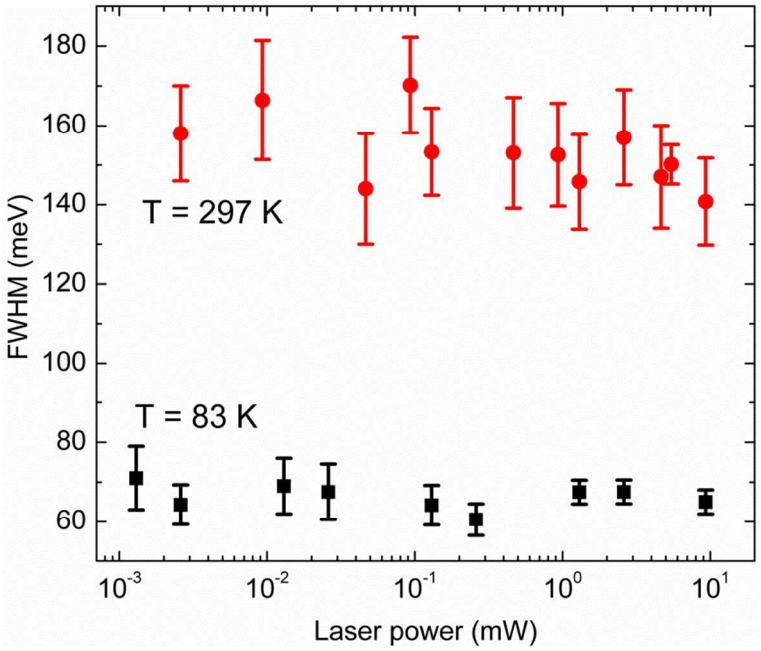

Figure 2. Plot of the FWHM of mode A as a function of laser power.

S3. Exciton binding energy

The integrated PL intensity of mode A decreases with increasing temperature, common to other bulk semiconductors, with an activation energy of E_0 = 80 ± 10 meV. Since the value of E_0 does not change by modulating the excitation power in the range of 10 μW to 10 mW, the observed quenching could not be due to the activation of non-radiative recombinations. In addition, Auger recombination has an activation energy of ~ 22 meV (see the manuscript), much lower than the value of E_0 = 80 ± 10 meV. Therefore, the observed quenching is likely due to thermal dissociation of the excitons and the obtained value of E_0 = 80 ± 10 meV is directly related to the exciton binding energy.

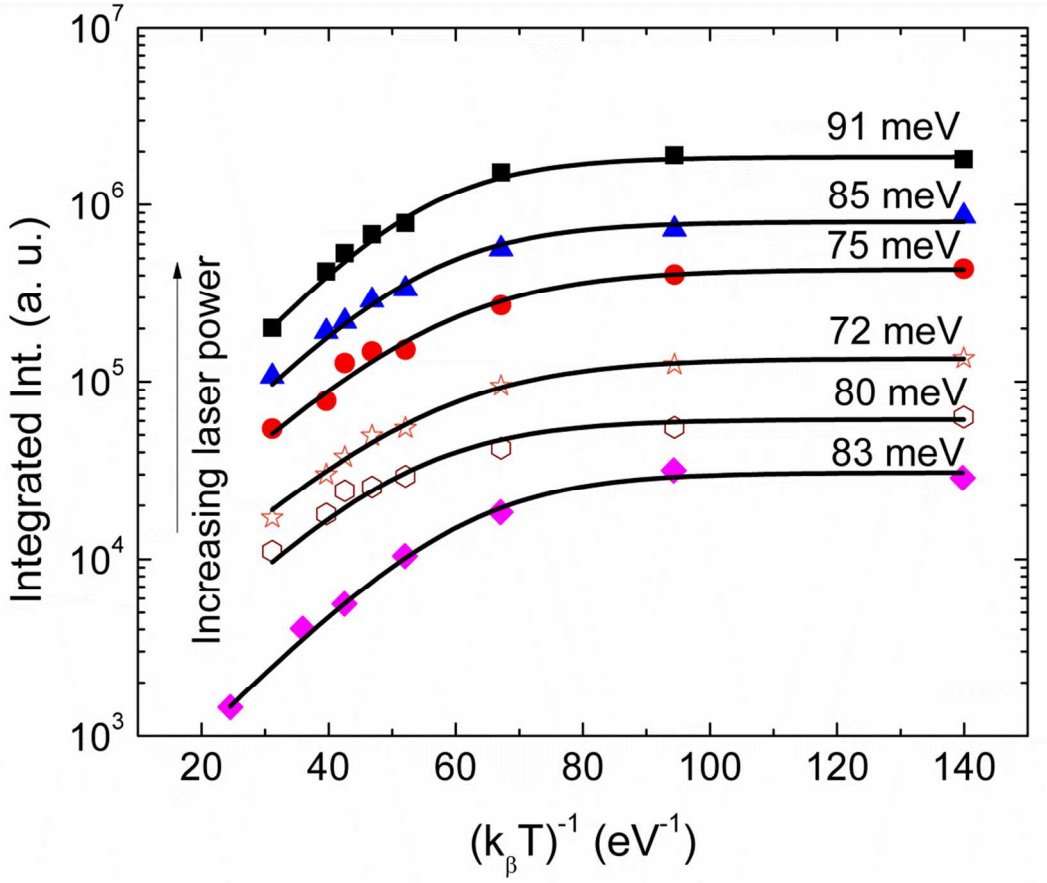

Figure S3. Plot of the integrated PL intensity of mode A as a function of $(k_\beta T)^{-1}$ for different excitation powers with the corresponding derived binding energy.

S4. Temperature dependence of recombination lifetime

The overall recombination lifetime (τ) of mode A is shown in Fig. S4 for temperatures of 83 K, 223 K and 373 K using $A = 10^{10}$ s^{-1}. In the low generation rate regime, the lifetime is constant and determined by Shockley-Read-Hall (SRH) process (τ_{SRH} ~ 100 ps). In intermediate generation regime, the lifetime is determined by both SRH and Auger processes ($\tau^{-1}=\tau_{SRH}^{-1}+\tau_r^{-1}$) and for high generation rates the lifetime is determined by Auger

recombination. It is clear that the overall lifetime is not sensitive to temperature due to the very low activation energy of Auger process and the temperature-independent SRH coefficient used in this work.

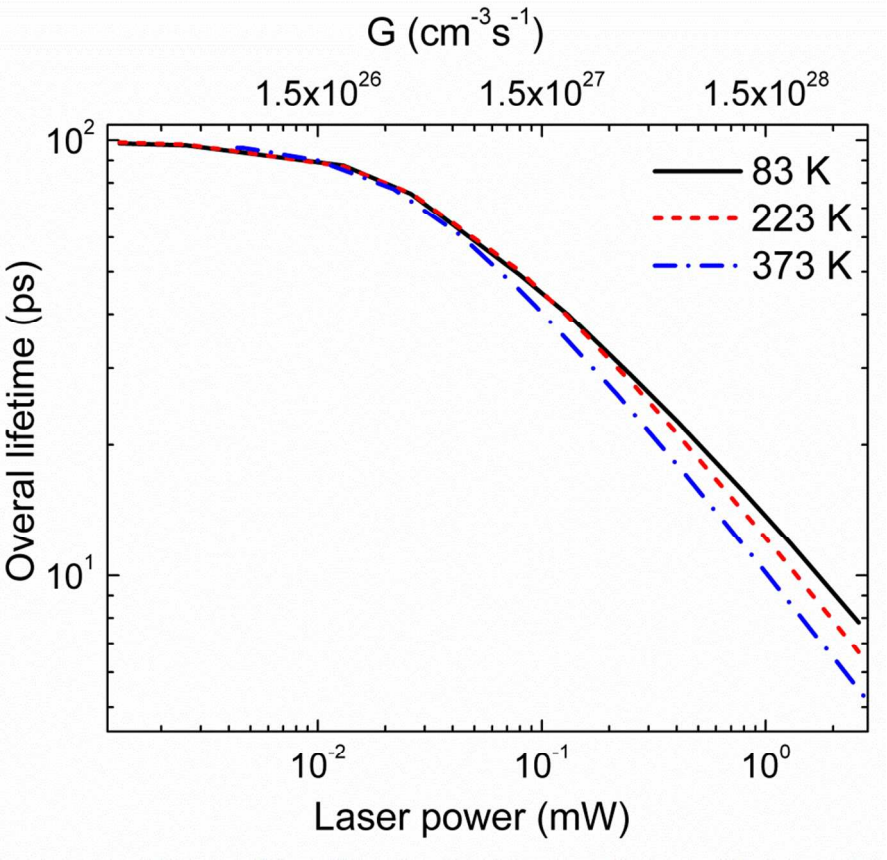

Figure S4. Plot of the overall lifetime of mode A as a function of excitation power for a 1L MoS_2 for temperatures of 83 K, 223 K and 373 K.

References:

(1) Varshni, Y. Temperature Dependence of the Energy Gap in Semiconductors. Physica (Amsterdam) **1967**, 34, 149.

(2) Engels, G.; Lange, J.; Schäpers, Th.; Lüth, H. Experimental and Theoretical Approach to Spin Splitting in Modulation-Doped InGaAs/InP Quantum Wells for B→0. Phys. Rev. B. **1997**, 55, R1958.