Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Nanoscale Mapping of Excitonic Processes in Single-layer MoS_2 using Tip-enhanced Photoluminescence Microscopy

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§S1 Enhancement factor calculation of Raman and PL bands

The Enhancement factor (ρ) of Raman and PL bands in the near-field of a metal-coated tip is commonly estimated using the relation[1]

$$\rho = \left(\frac{I_{NF}^{R}}{I_{FF}^{R}} - 1\right)\left(\frac{d_{FF}}{d_{NF}}\right)^{2}$$

…(S1)

where, I_{NF}^{R} and I_{FF}^{R} are fitted Raman and PL peak intensities in near-field and far-field spectra respectively; d_{FF} is the size of the far-field laser probe, which is measured to be 370 nm for our microscope; d_{NF} is the effective size of near-field probe, which is estimated to be 21 nm from the resolution obtained in the TEPL image presented in Figure 3e in the manuscript.

Using these values the enhancement factor of A_{1g} Raman and A-exciton PL bands for single-layer MoS_2 in the presence of an Ag-coated tip (from the tip-in and tip-out spectra shown in Figure 4(a) are calculated to be 622 and 448 , respectively using Equation (S1).

§S2 Mathematical formulation for measuring the effect of metal-coated tips on local electron population in single-layer MoS_2

The exciton population can be modelled based on the rate of generation (G), rate of recombination (R) and rate of transformation from excitons to trions (T):

$$\frac{dn_{A^0}}{dt} = G - R - T$$

…(S2)

$$R = n_{A^0} \times \Gamma_{A^0}$$

…(S3)

$$T = n_{A^0} \times k_{A^-}$$

…(S4)

n_{A^0} , Γ_{A^0} , k_{A^-} are population of excitons, decay rate of exciton and transformation of excitons to trions, respectively. It can be derived from the rate equation that[2]

$$\frac{I_{A^0}}{I_{total}} = \frac{n_{A^0} \cdot \gamma_{A^0}}{n_{A^-} \cdot \gamma_{A^-}} = \frac{\frac{G}{\Gamma_{A^0} + k_{A^-}} \cdot \gamma_{A^0}}{\frac{k_{A^-}}{\Gamma_{A^-}} \frac{G}{\Gamma_{A^0} + k_{A^-}} \cdot \gamma_{A^0}}$$

...(S5)

I_{A^0} and I_{A^-} denote PL intensities originating from excitons and trions respectively, and γ_{A^0} and γ_{A^-} denote radiative decay rate of excitons and trions, respectively.

Considering mass action model[53] the rate equation can be expressed as

$$\frac{n_{A^0} n_e}{n_{A^-}} = CK_B T e^{-\frac{E_{A^-}}{K_B T}}$$

...(S6)

K_B and E_{A-} denotes Boltzmann's constant and activation energy for transformation from an exciton to a trion, respectively.

For MoS_2 the constant *C* can be calculated from the effective mass of excitons and trions[3]:

$$C = \frac{4m_{A^0} m_e}{\pi \hbar^2 m_{A^-}} = 4.076 \times 10^{11}\ meV^{-1} cm^{-2}$$

...(S7)

The electron population can be calculated as

$$n_e = 1.05 \times 10^{13} . \frac{n_{A^-}}{n_{A^0}} = 1.05 \times 10^{13} \cdot \frac{\gamma_{A^0}}{\gamma_{A^-}} \cdot \frac{I_{A^-}}{I_{A^0}}$$

...(S8)

The following values were used to calculate C:

Parameter	Description	Value	Unit
m_0	Mass of free electron	9.11E-31	Kg
mA^0	Effective mass of neutral exciton	$0.8m_0$	Kg
mA^-	Effective mass of negatively charged trions	$1.15m_0$	Kg
m_e	Effective mass of electron in single layer MoS2	$0.35m_0$	Kg
ħ	Planck's constant	6.58E-13	meV.s
K_B	Boltzmann constant	8.62E-02	meV/K
T	Room temperature	300	K
E_{A-}	Exciton to trion activation energy	2.00E-02	meV

The calculated values for Figure 2d was reproduced from the work reported by Mouri[2] *et al.* based on the equation given below:

$$\frac{I_{A^-}}{I_{A^0}} \approx \frac{4\times 10^{-14} n_{el}}{1+4\times 10^{-14} n_{el}} \quad \text{...(S9)}$$

§S3 Stacked deconvoluted PL curves

Figure S1 shows the stacked PL curves measured with the tip in contact (tip-in) (black curves) and retracted from (tip-out) (red curves) the sample. The deconvoluted PL spectra of different excitons are also shown.

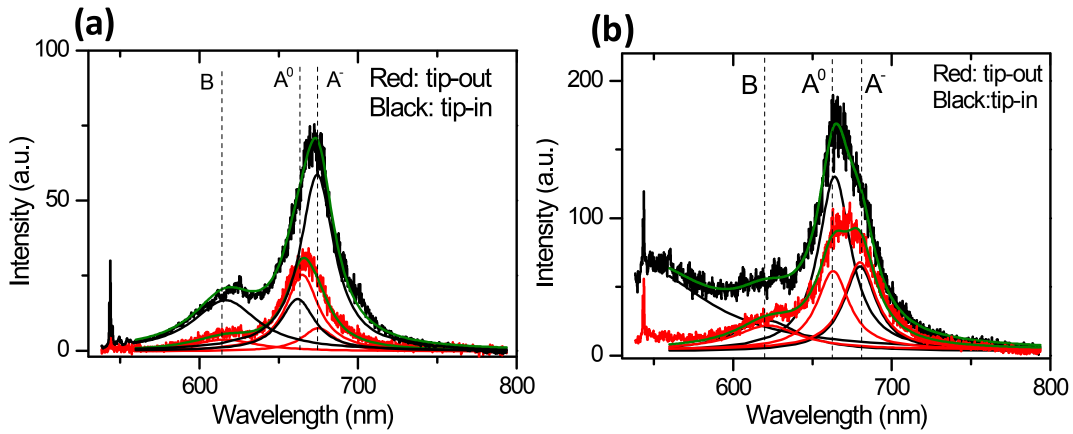

Figure S1 Deconvoluted PL spectra measured with the tip in contact (tip-in) and retracted from (tip-out) the sample using (a) Ag-coated tip and (b) Au-coated tip.

§ S4 PL emission bands from different tips

A PL spectrum on the area of glass recorded whilst TEPL mapping using Ag-coated tip is shown in Figure S2(a). It can be seen that the PL emission band from Ag-coated tip is too weak to affect the PL band of MoS_2.

Au-coated tip shows a broad emission band at the left side of PL band, which is shown in Figure S2 (b). In the deconvolution a Gaussian peak had been set at the high energy side of the PL band to get right deconvoluted PL spectra of different excitons.

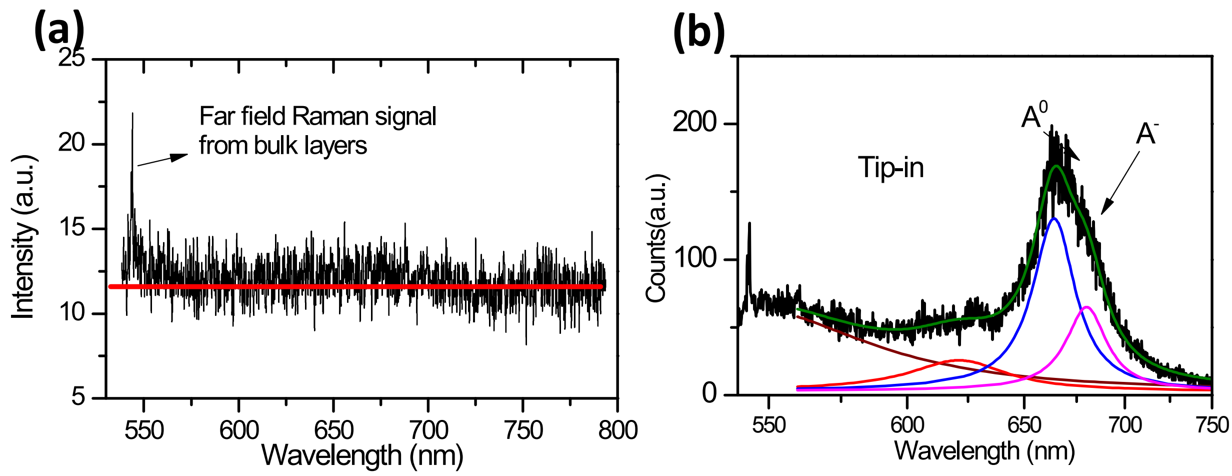

Figure S2 (a) Recorded PL and Raman spectrum in TEPL mapping using an Ag-coated tip; (b) deconvolution of PL and Raman spectrum using an Au-coated tip.

§ S5 Average tip-in PL spectrum

An average tip-in PL spectra from monolayer area of Figure 5a is shown in Figure S3. An average PL spectrum measured with tip-out is also shown for comparison. It can be found that the tip-in spectrum shows dominant intensity of trion(A^-), while the tip-out spectrum shows dominant intensity of exciton(A^0).

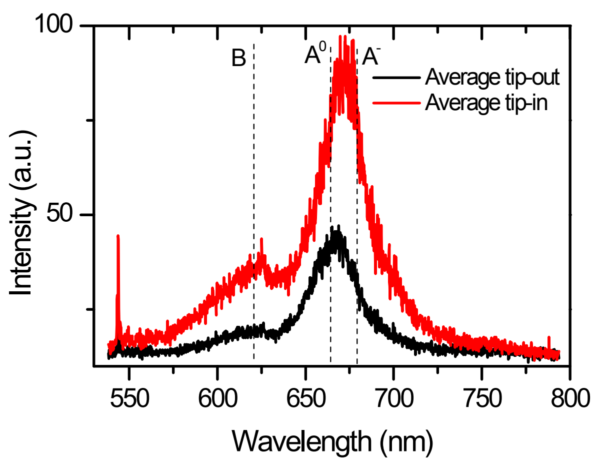

Figure S3 Average tip-in PL spectrum from single-layer area in Figure 5. Average PL spectrum from this single-layer measured with tip-out is also shown for comparison.

References

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2. S. Mouri, Y. Miyauchi and K. Matsuda, *Nano Lett.*, 2013, **13**, 5944-5948.

3. T. Cheiwchanchamnangij and W. R. L. Lambrecht, *Phys. Rev. B.*, 2012, **85**.