TECHNISCHE UNIVERSITÄT
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Tip-enhanced spectroscopies for studying 2-dimensional semiconductors and their interfaces

Dietrich RT Zahn

Spectroscopic Characterisation of Surfaces, Interfaces, Thin Films, and Low-dimensional Structures

Current Research Areas:

- Ternary and quaternary quantum dots
- 2D semiconductors
- Plasmonics
- Wide bandgap oxide semiconductors

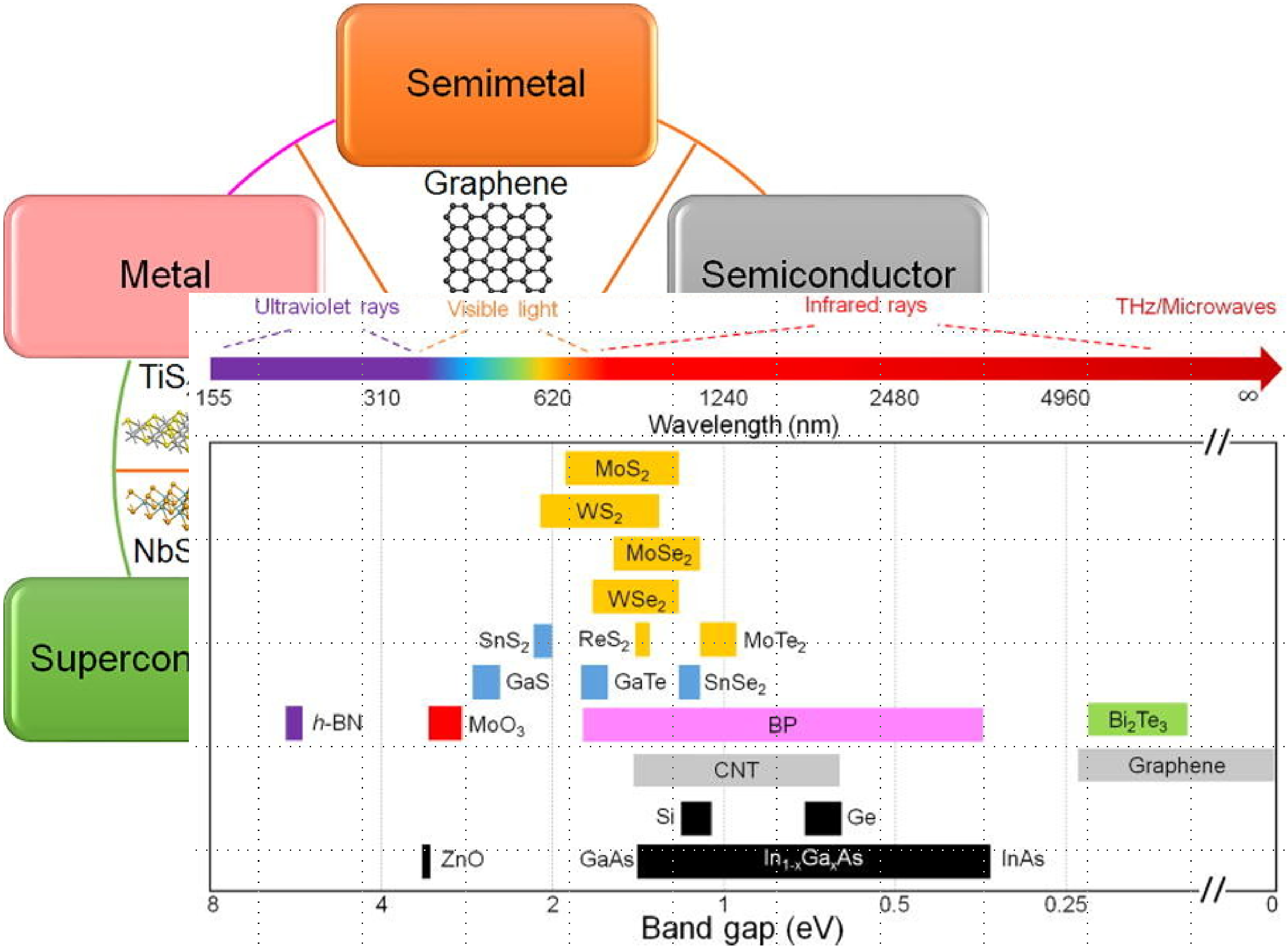
Methods

- Raman spectroscopy including surface-enhanced and tip-enhanced Raman spectroscopy
- Photoluminescence including tip-enhanced photoluminescence
- Spectroscopic ellipsometry including imaging ellipsometry
- Infrared spectroscopy including nano-IR
- Ultraviolet and X-ray photoemission spectroscopy
- Atomic force microscopy including Kelvin force microscopy and current-sensing AFM
- Electrical characterisation (IV, CV, DLTS, …)

Contents

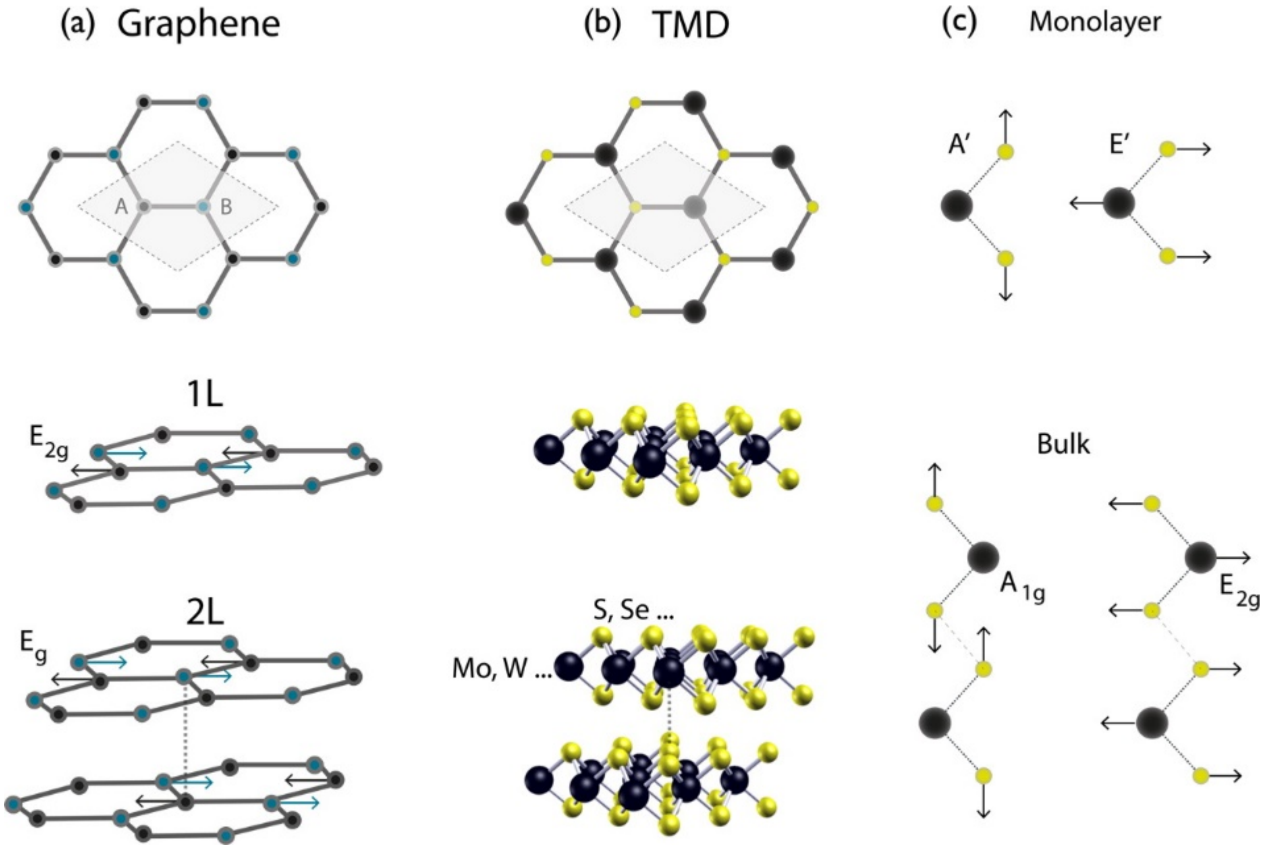
- 2-dimensional Semiconductors
- Tip-enhanced Optical Spectroscopies
- MoS_2 on Plasmonic Nanostructures
- Observation of Dark Excitons at Room Temperature

2D Material Family



Applied Physics Reviews **4,** 021306 (2017) DOI: 10.1063/1.4983646

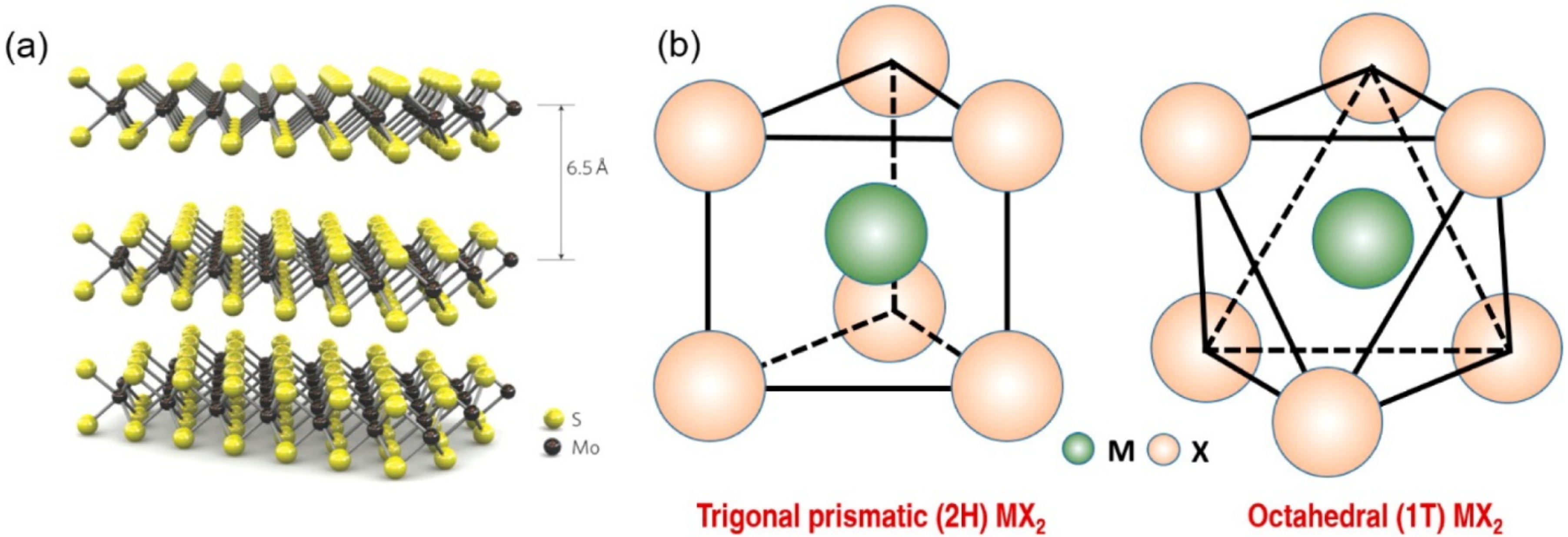
Graphene vs. TMDC: Atomic Structure



Atomic structure of (a) graphene/graphite and (b) monolayer TMDC and bulk 2H-TMDC. (c) Atomic displacements in two Raman active modes of monolayer TMDC and bulk 2H-TMDC.

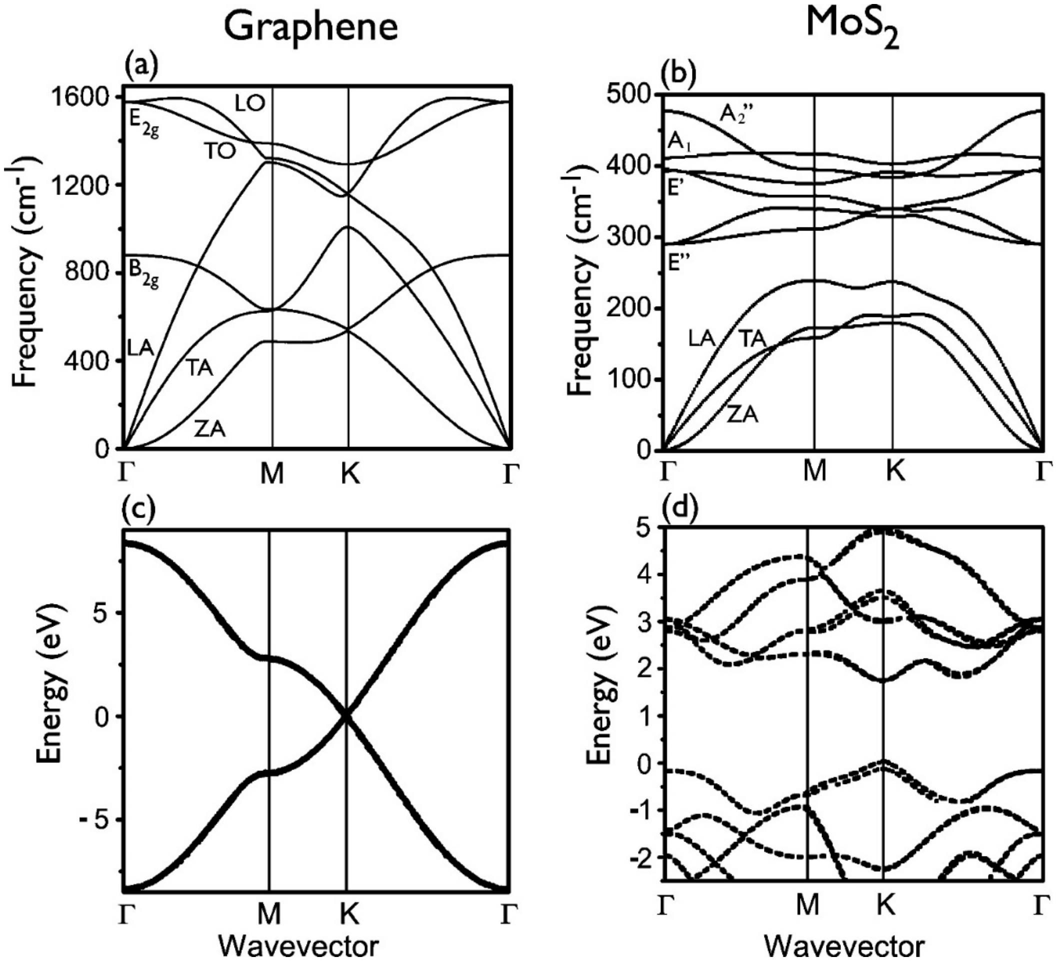
Acc. Chem. Res. **2015,** 48, 41-47. DOI: 10.1021/ar500280m

Structure of the TMDC MoS_2



Acc. Chem. Res. **2015,** 48, 56-64. DOI: 10.1021/ar5002846

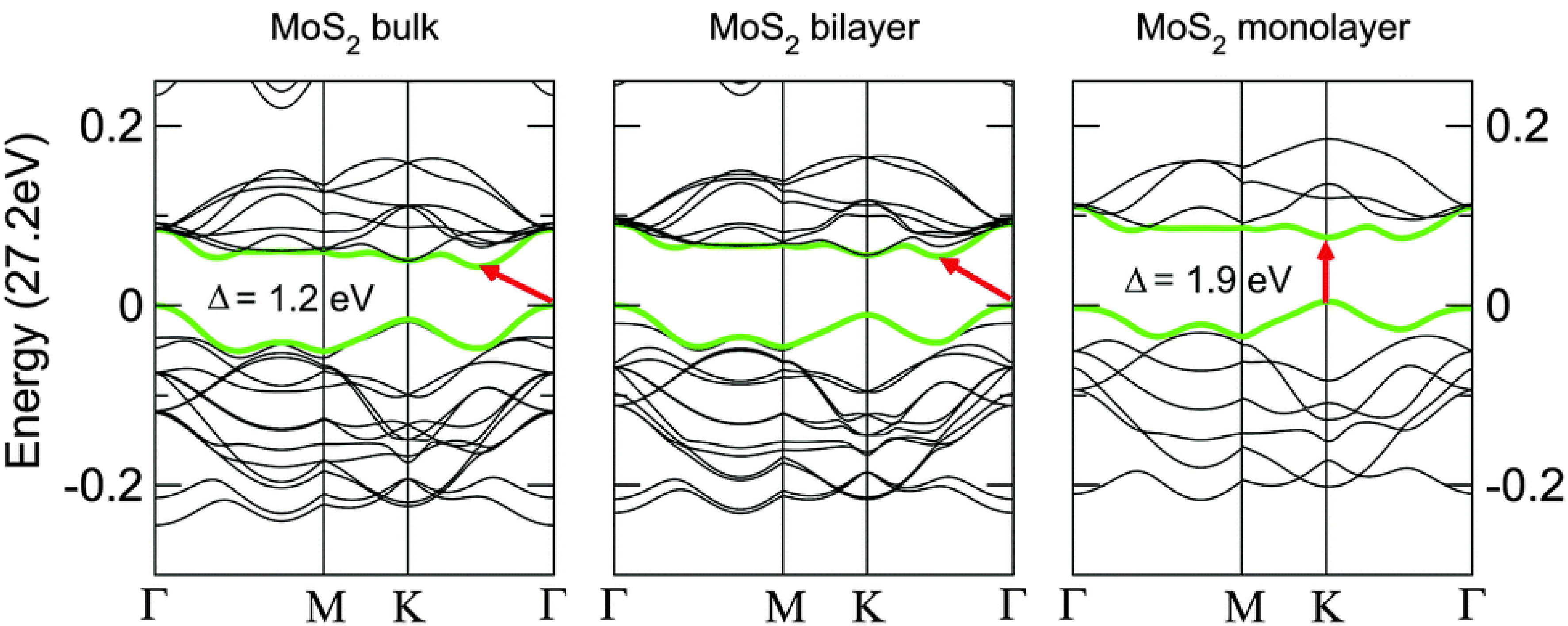
Graphene vs. TMDC: Phonon Dispersion and Electronic Structure



Phonon dispersion relations of (a) graphene and (b) MoS_2.
Electronic structure of (c) graphene and (d) MoS_2.

Acc. Chem. Res. **2015,** 48, 41-47. DOI: 10.1021/ar500280m

Band Structures of Bulk, Bilayer, and Monolayer MoS_2



The top of the valence band and the bottom of the conduction band are highlighted in green. The red arrows indicate the smallest value of the bandgap (direct or indirect) for a given thickness.

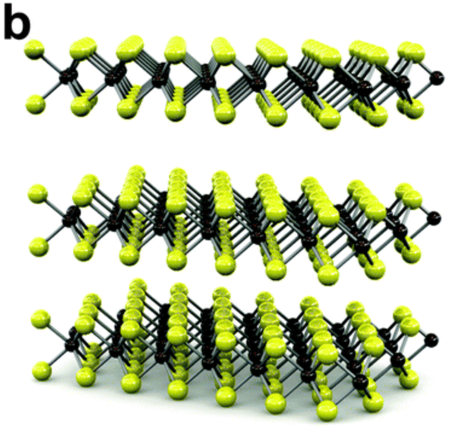
Chem. Soc. Rev., 2016,**45**, 118-151

TMDC Properties

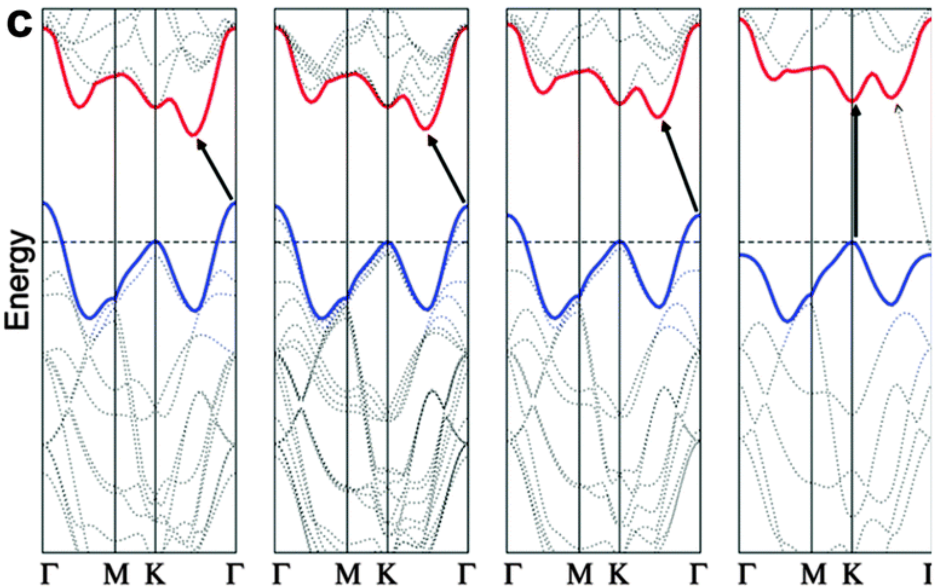
a

Bandgap (eV)		Mo	W	Ti	Zr	Hf	V	Nb	Ta	Ni	Pd	Pt
S	monolayer	1.8-2.1	1.8-2.1	~0.65	~1.2	~1.3	~1.1	metal	metal	~0.6	~1.2	~1.9
	Bulk	1.0-1.3	1.3-1.4	~0.3	~1.6	~1.6	metal	metal	metal	~0.3	~1.1	~1.8
Se	monolayer	1.4-1.7	1.5-1.7	~0.51	~0.7	~0.7	metal	metal	metal	~0.12	~1.1	~1.5
	Bulk	1.1-1.4	1.2-1.5	metal	~0.8	~0.6	metal	metal	metal	metal	~1.3	~1.4
Te	monolayer	1.1-1.3	~1.03	~0.1	~0.4	~0.3	metal	metal	metal	metal	~0.3	~0.8
	Bulk	1.0-1.2	metal	metal	metal	metal	metal	metal	metal	metal	~0.2	~0.8

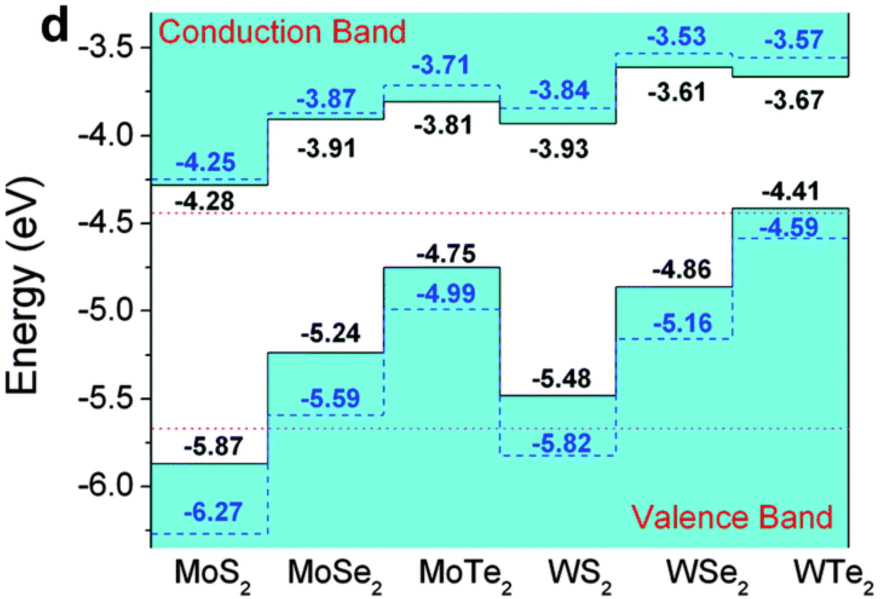
b



c

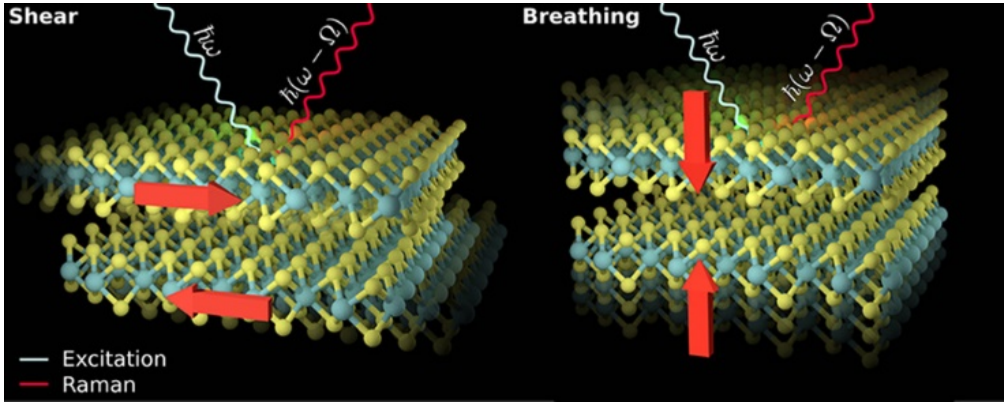


d

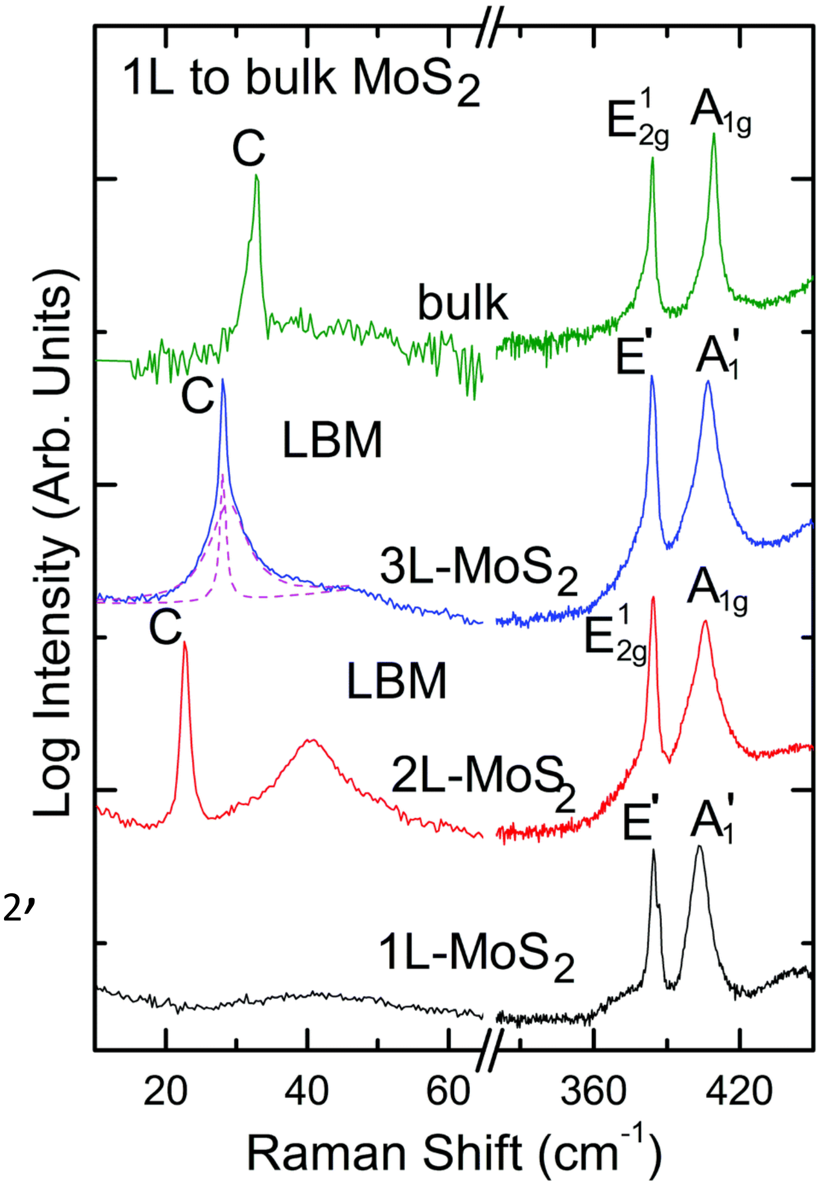


Chem. Soc. Rev., 2015,**44**, 8859-8876

MoS_2: Raman Spectra as a Function of Layer Thickness



ACS Nano 2017, 11, 12, 11777-11802



Raman spectra of 1L-MoS_2, 2L-MoS_2, 3L-MoS_2, and bulk MoS_2 measured at 532 nm.

Nanoscale, 2015,**7**, 4598-4810

Contents

- 2-dimensional Semiconductors
- Tip-enhanced Optical Spectroscopies
- MoS_2 on Plasmonic Nanostructures
- Observation of Dark Excitons at Room Temperature
- Interlayer Excitons
- Outlook

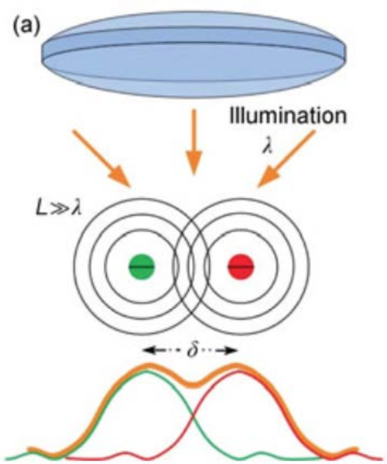
Conventional Optical Spectroscopy

Abbe diffraction limit:

$$\text{Spatial resolution} = \frac{0.61\lambda}{NA}$$

$\lambda \longrightarrow$ wavelength of the light

NA $\longrightarrow$ numerical aperture of the objective



Considering the probing lasers

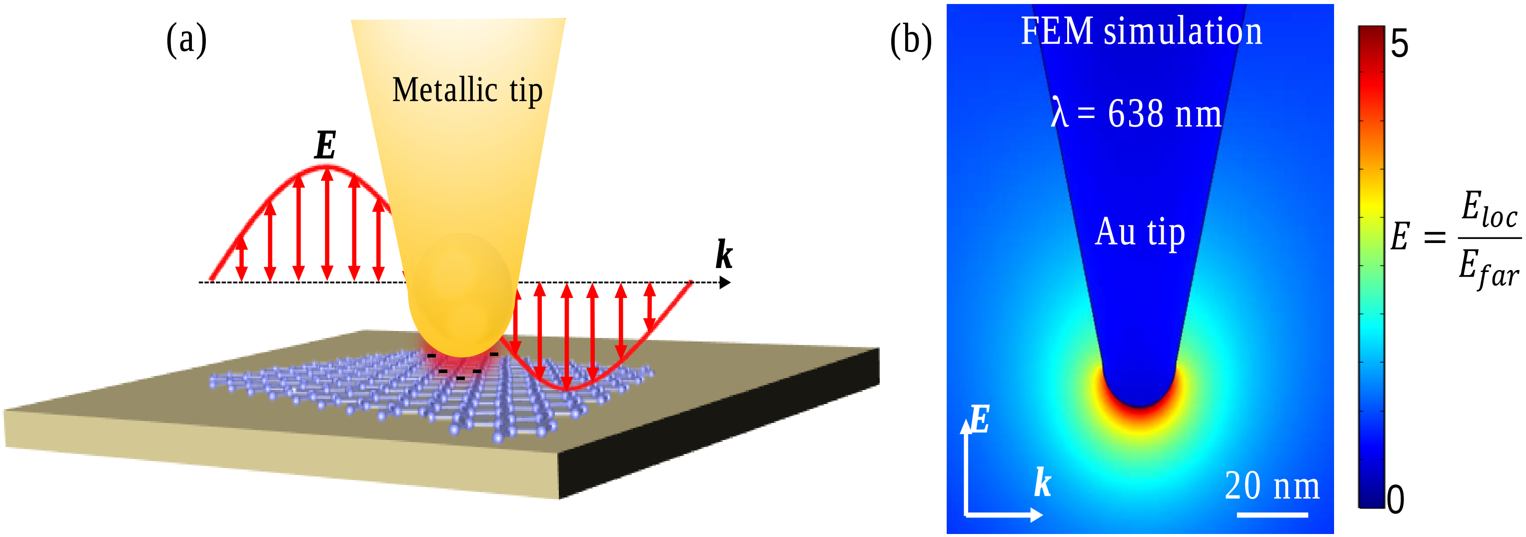
100x obj. and 0.9 NA

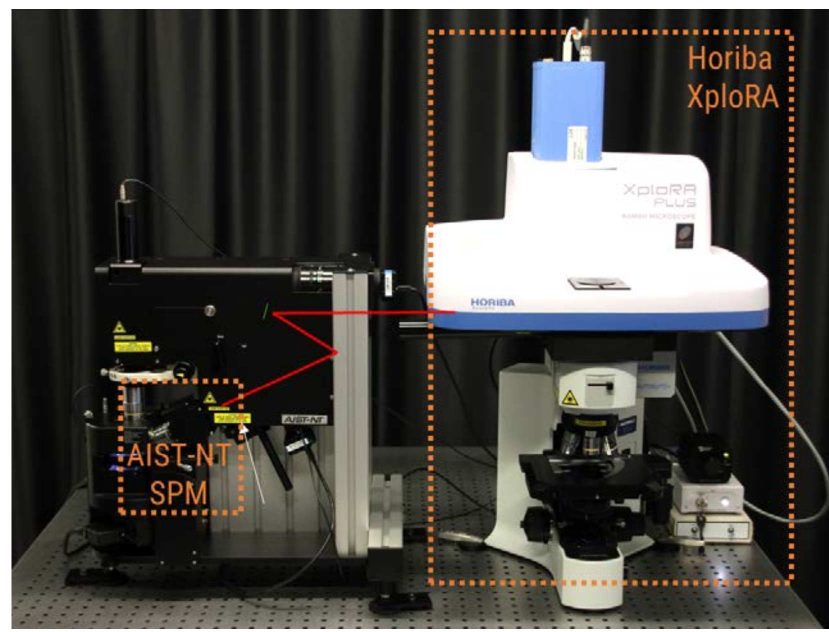
For λ = 515 nm:
Spatial resolution = 350 nm

For λ = 632 nm:
Spatial resolution = 430 nm

Zhang *et al.*; *Sci China-Phys. Mech. Astron.*, 55 1335 **2012**

Solution: Tip-enhanced Raman Spectroscopy



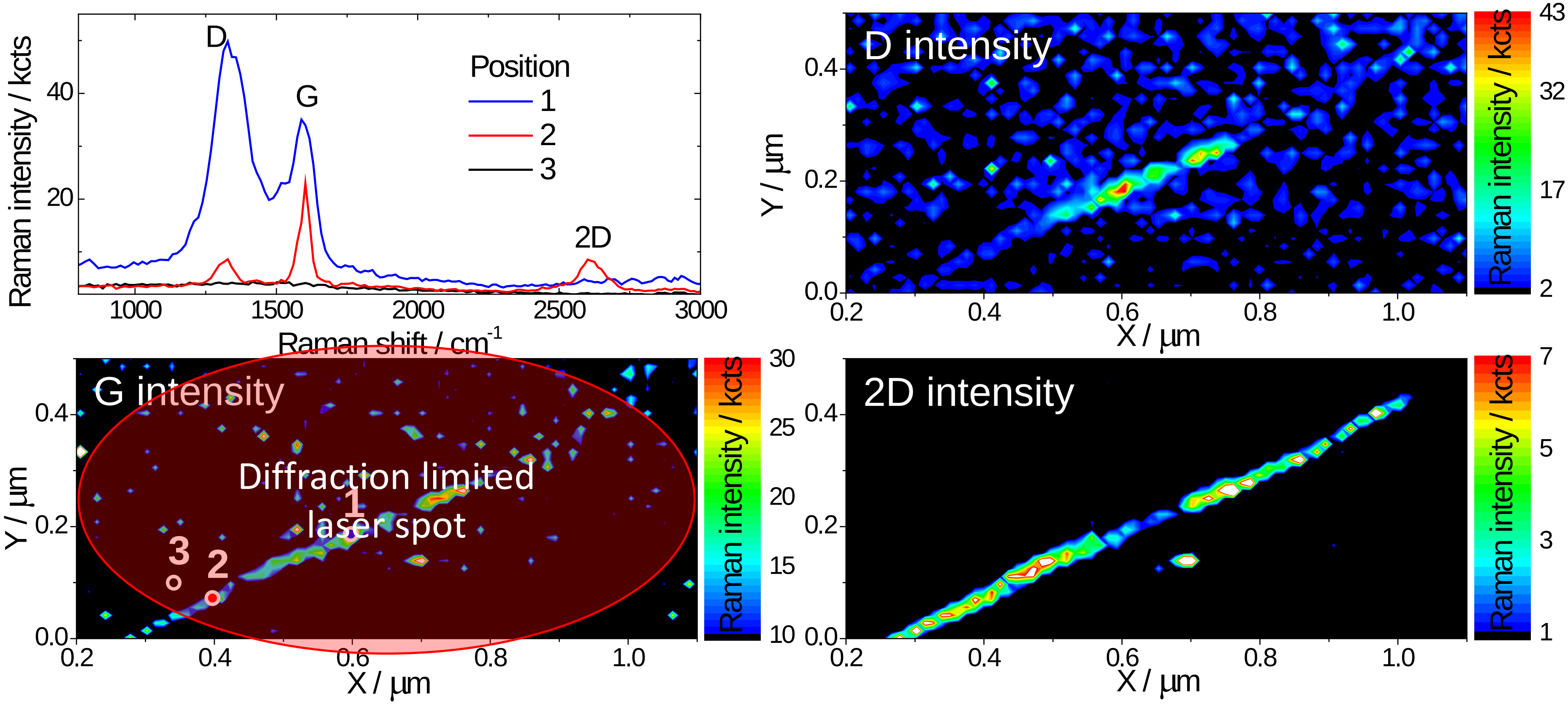


Schematic representation of TERS (a) FEM simulation of the plasmonic field enhancement at the tip apex for an Au tip (b).

Also suitable for

Tip-enhanced Photoluminescence TEPL!

TERS: Single CNT Bundle on Gold



Faraday Discussions

Cite this: *Faraday Discuss.*, 2019, **214**, 309

PAPER

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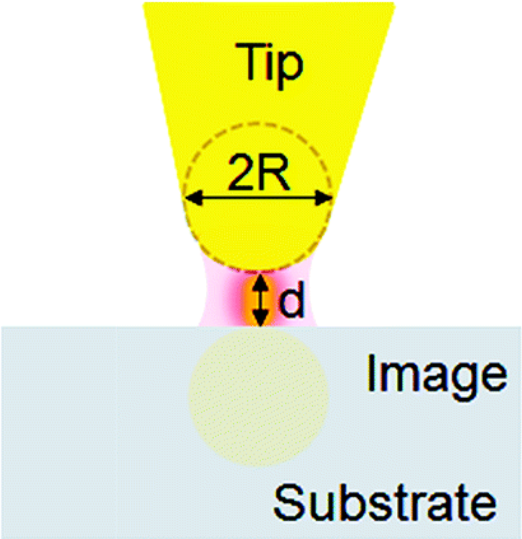
The role of a plasmonic substrate on the enhancement and spatial resolution of tip-enhanced Raman scattering†

Mahfujur Rahaman,*[a] Alexander G. Milekhin,[bc] Ashutosh Mukherjee,[a] Ekaterina E. Rodyakina,[bc] Alexander V. Latyshev,[bc] Volodymyr M. Dzhagan[ad] and Dietrich R. T. Zahn[a]



Distribution of Local Electric Field

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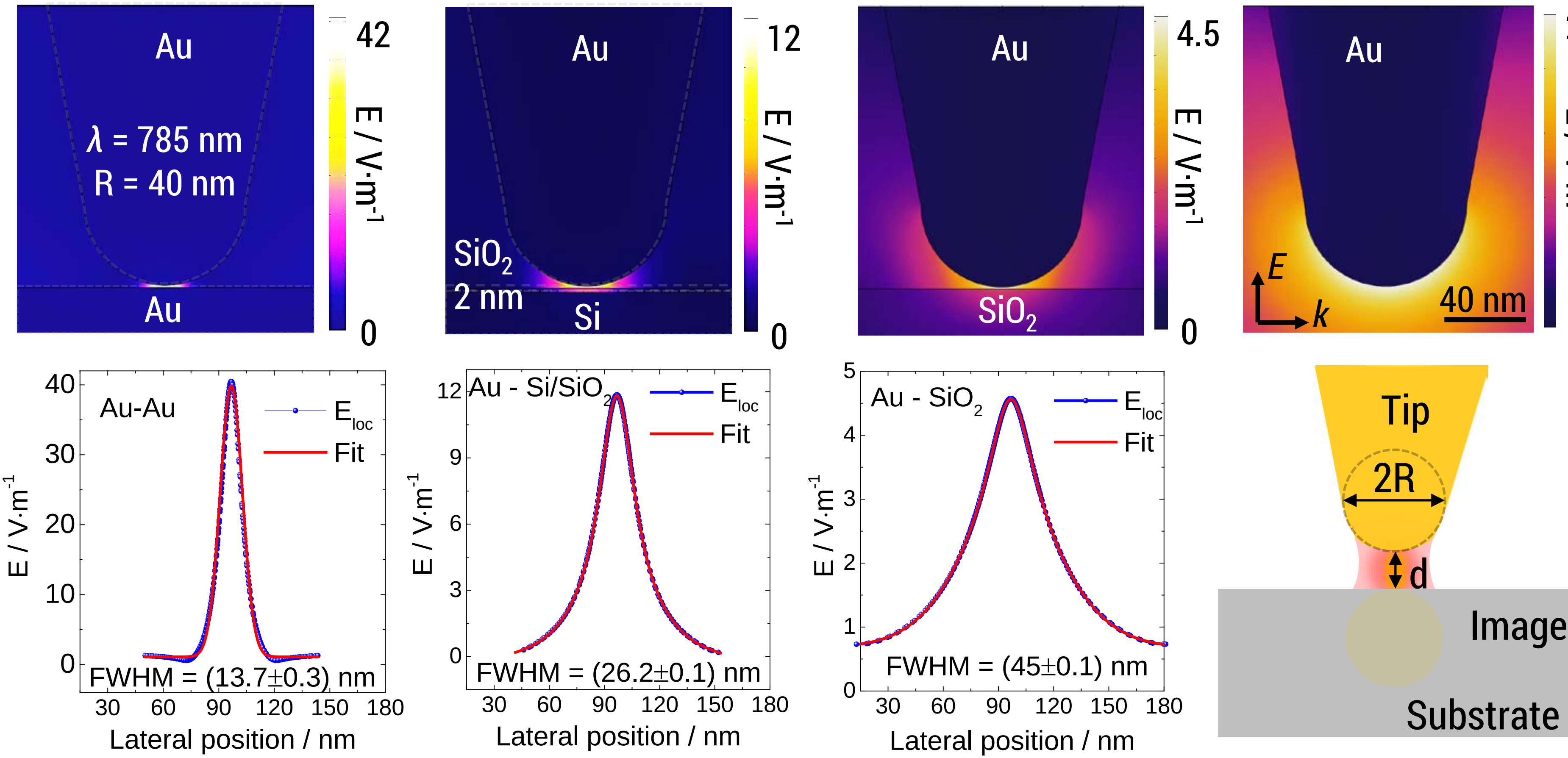
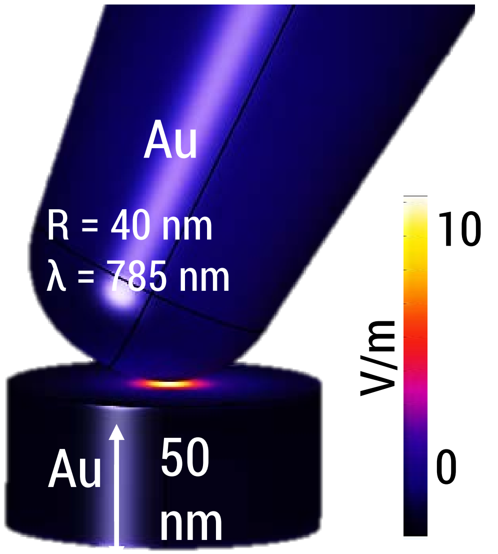
COMSOL simulations

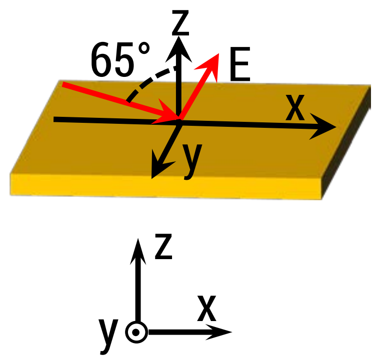


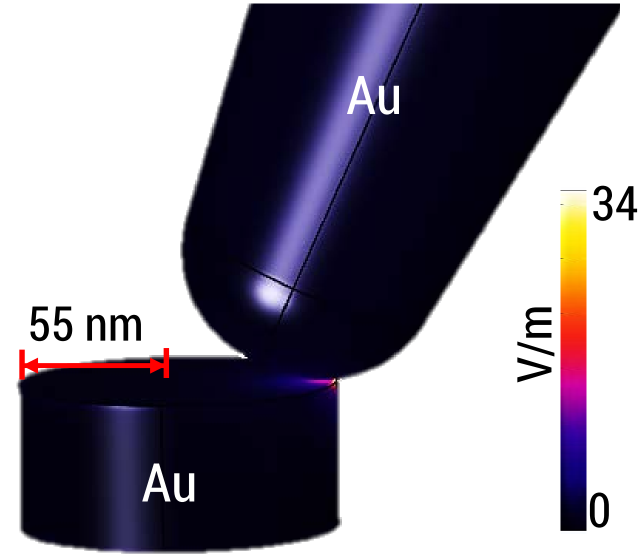
$$w \approx 2\sqrt{Rd}$$

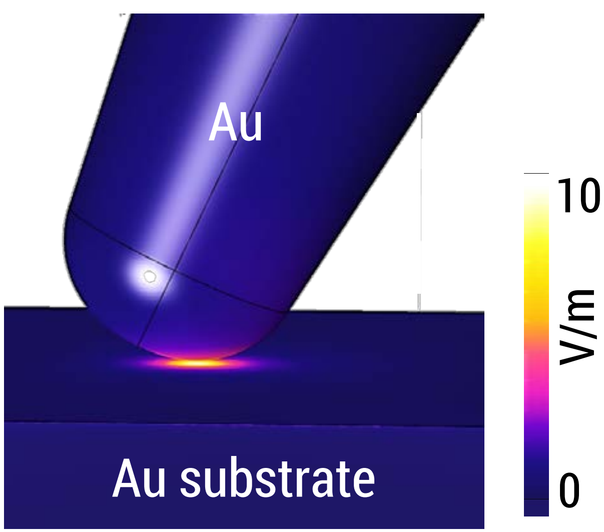
Richard-Lacroix *et al.*, Chem. Soc. Rev. 2017, 46, 3922

Simulation of Enhancement Factor and Spatial Resolution

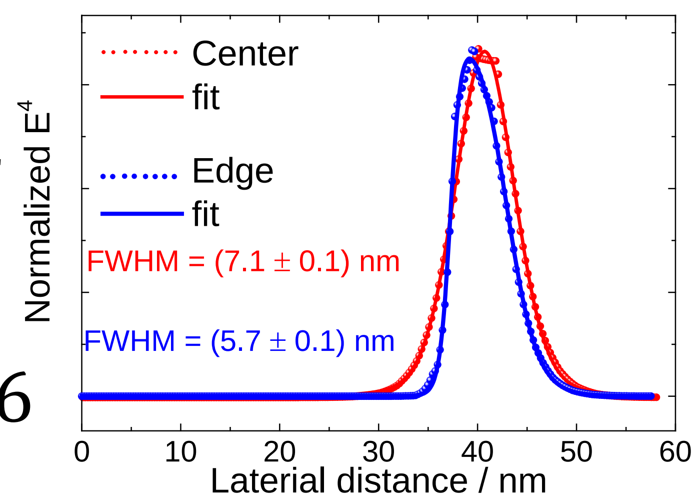








$$EF_{Rel} = \left(\frac{34}{10}\right)^4 = 133.6$$



Contents

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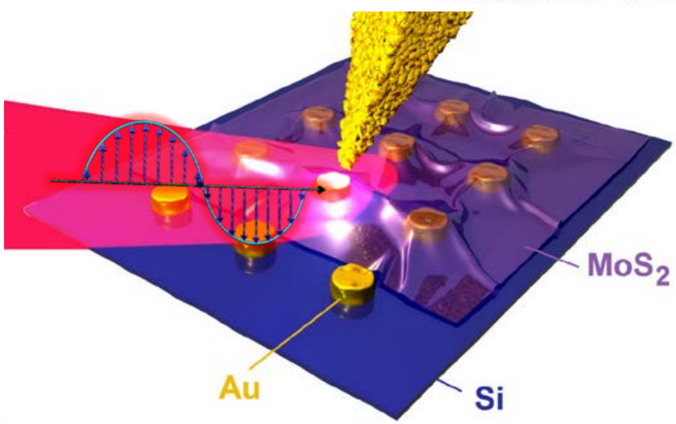
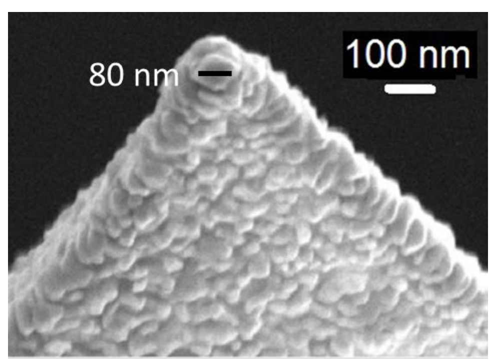
Cite this: *Nanoscale*, 2018, **10**, 2755

Giant gap-plasmon tip-enhanced Raman scattering of MoS_2 monolayers on Au nanocluster arrays†

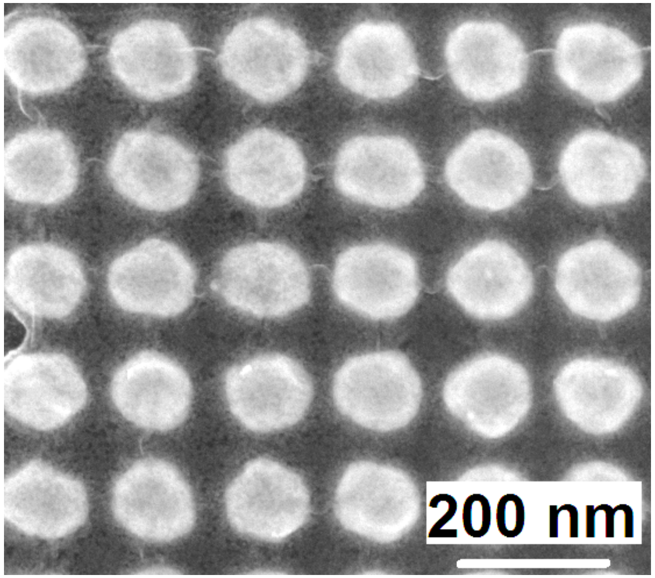
Alexander G. Milekhin, *‡[a,b] Mahfujur Rahaman, ‡[c] Ekaterina E. Rodyakina,[a,b] Alexander V. Latyshev,[a,b] Volodymyr M. Dzhagan [c] and Dietrich R. T. Zahn [c]

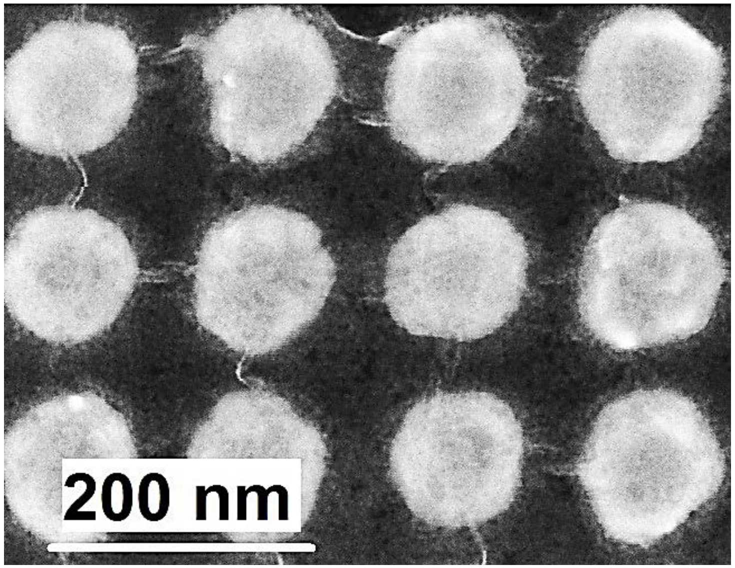


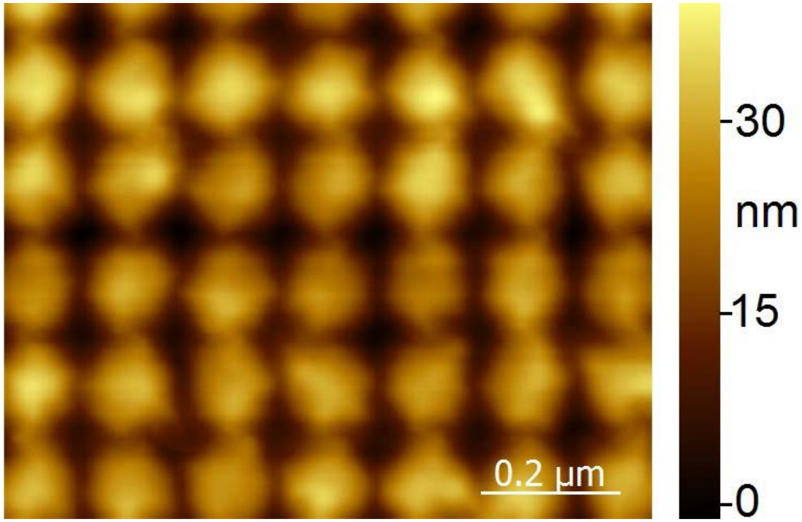


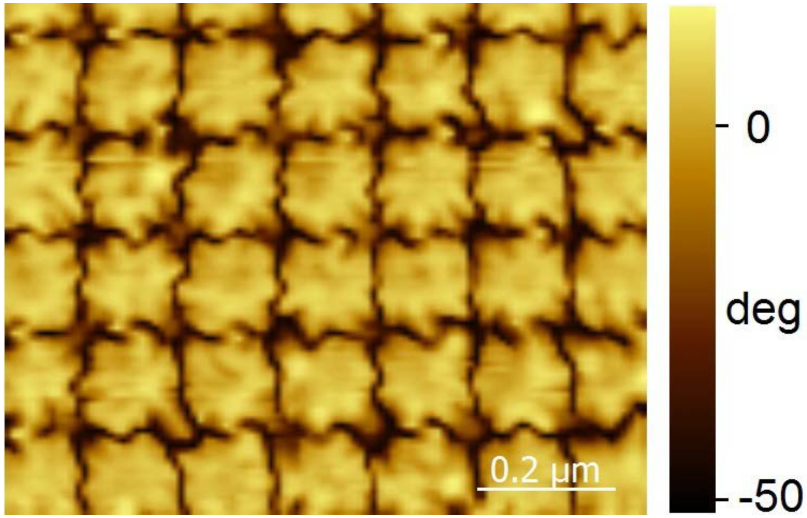
SEM image

SEM and AFM of MoS_2 on Au Disks

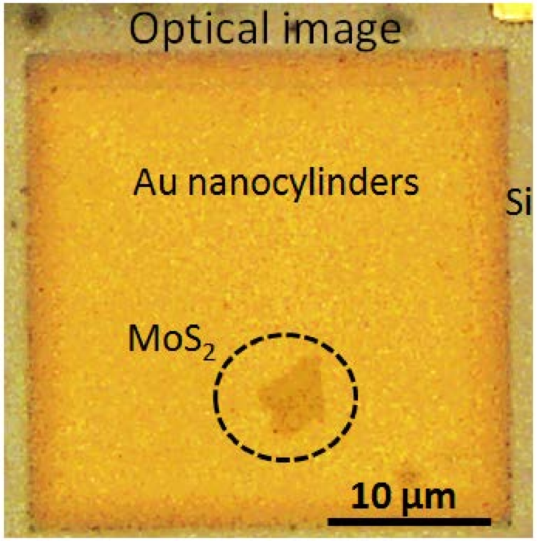


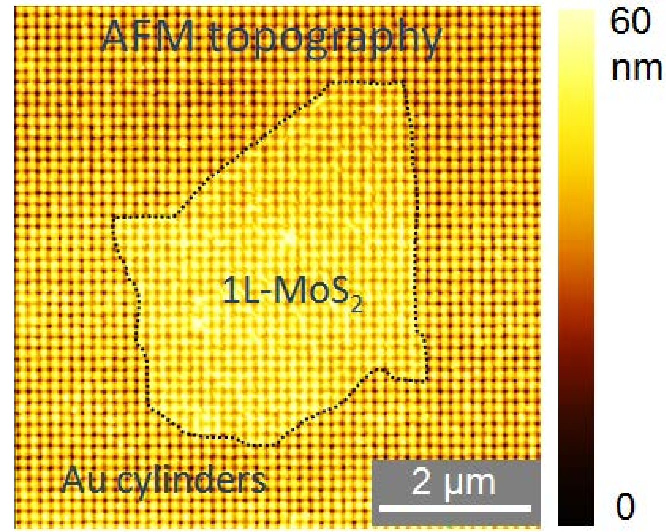




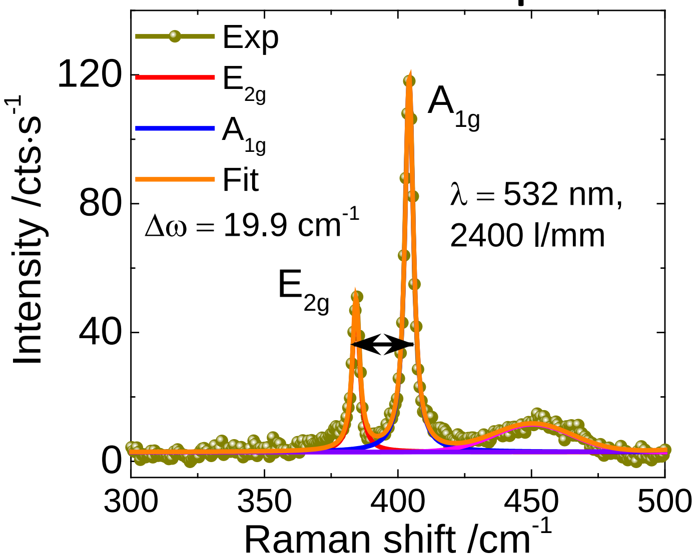


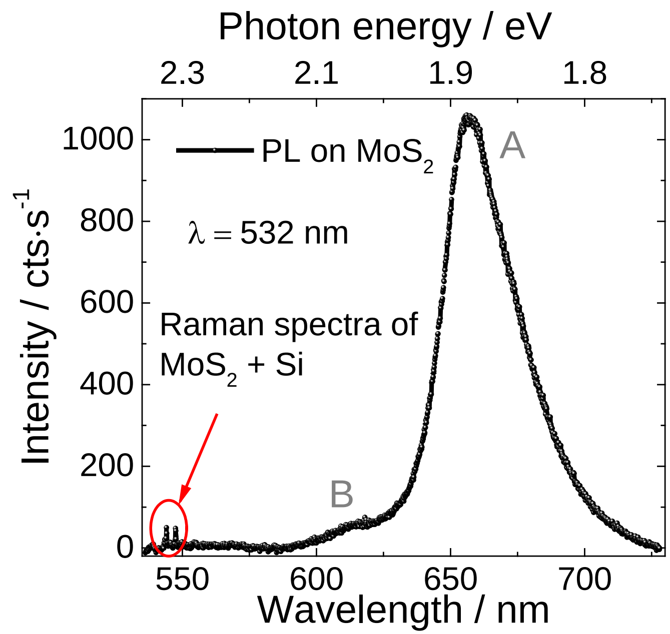
1L-MoS_2/Plasmonic Heterostructure



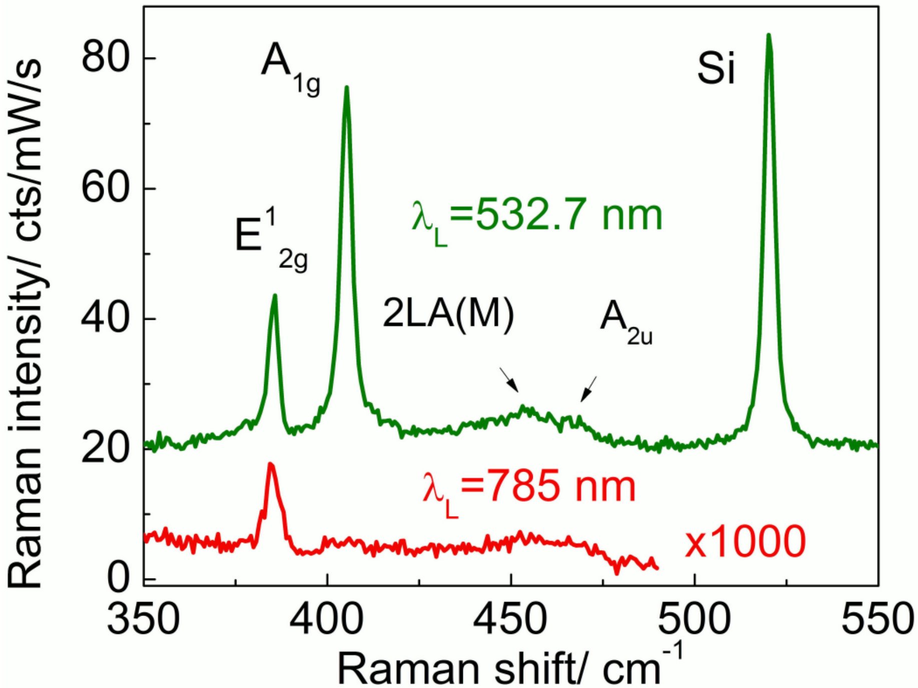


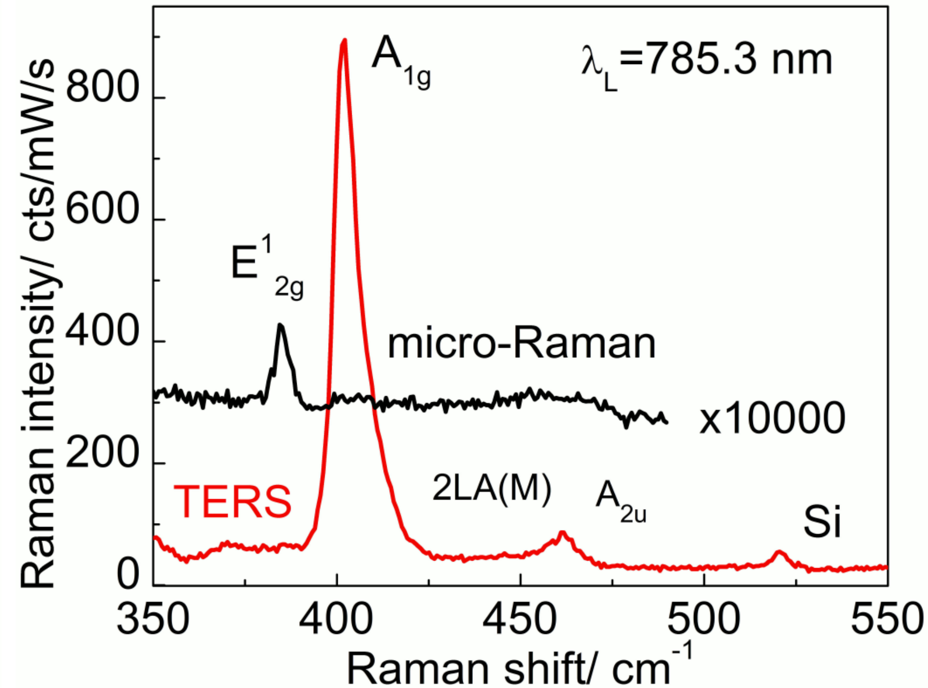
Micro-Raman spectra

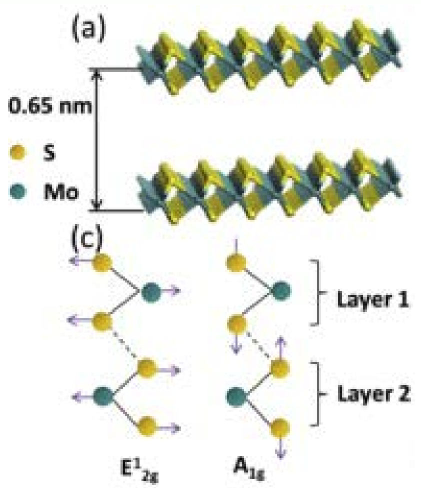




Experiment: TERS *vs* Raman







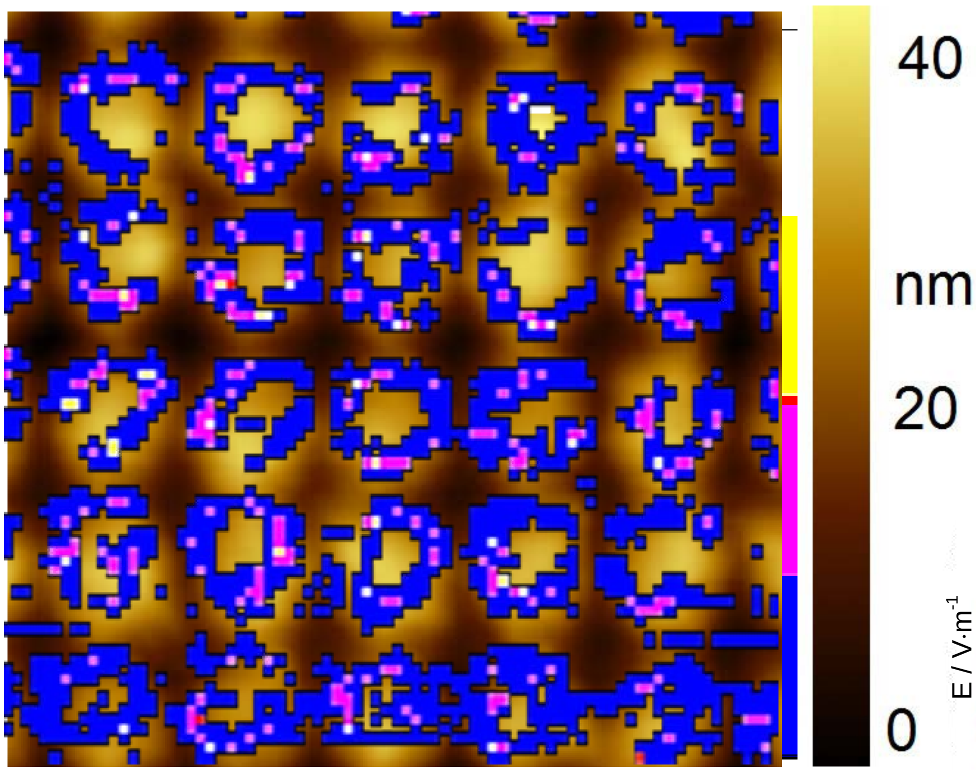
E_{exc}(785nm)=1.58eV

E_g=1.84eV

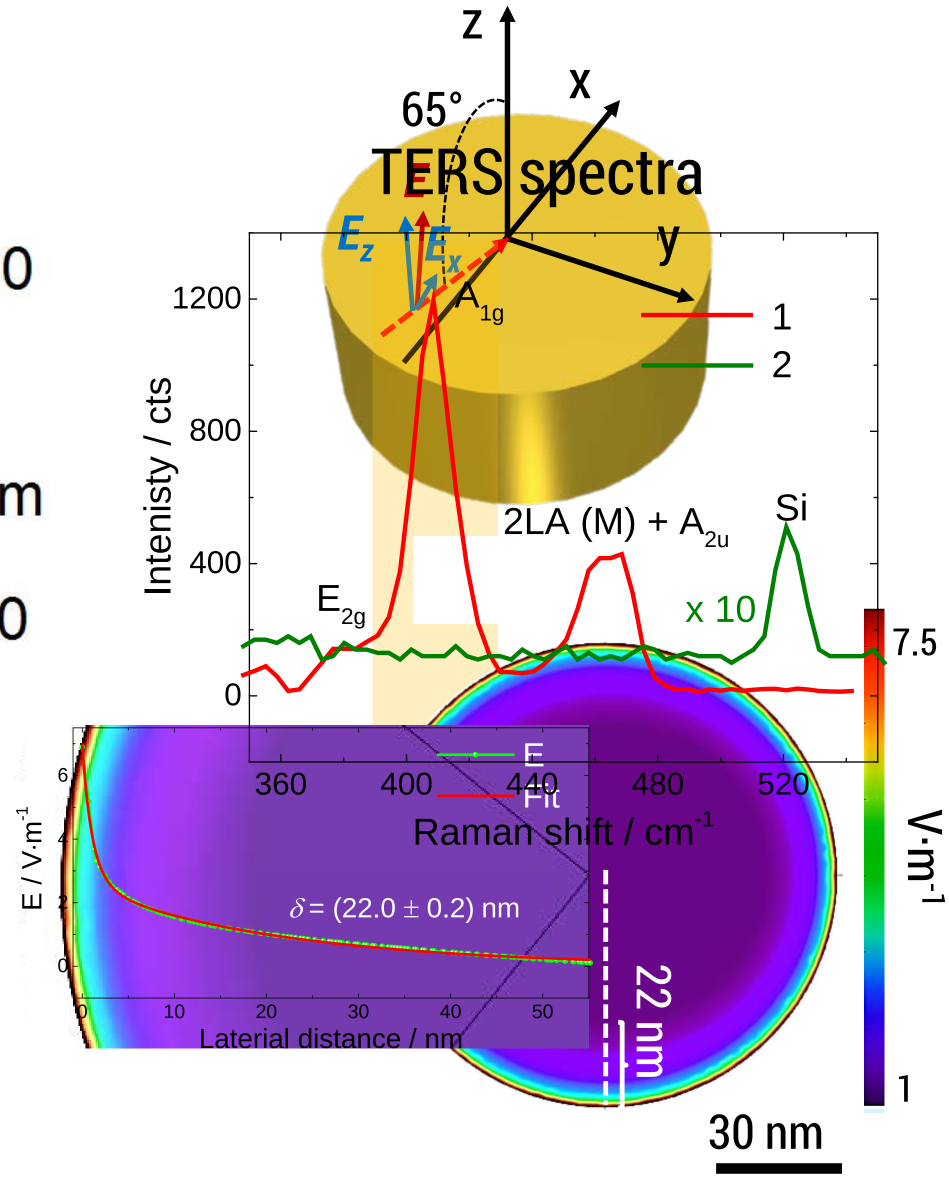
Giant TERS signal from MoS_2 monolayer is observed

TERS on 2D/Plasmonic Heterostructures

TERS map @ 410 cm^{-1}

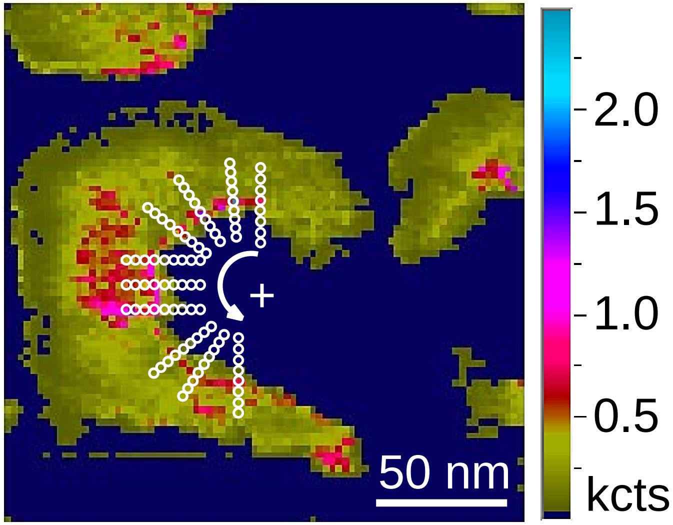


785 nm, 600 l/mm, 3 mW approx

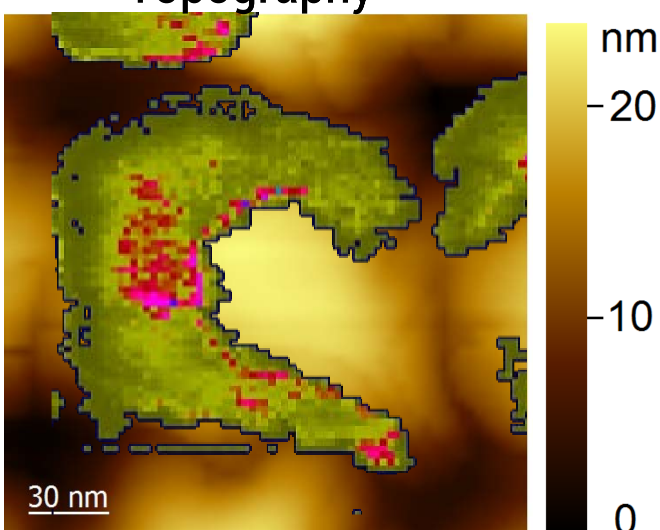


Spatial Resolution and Enhancement Factor

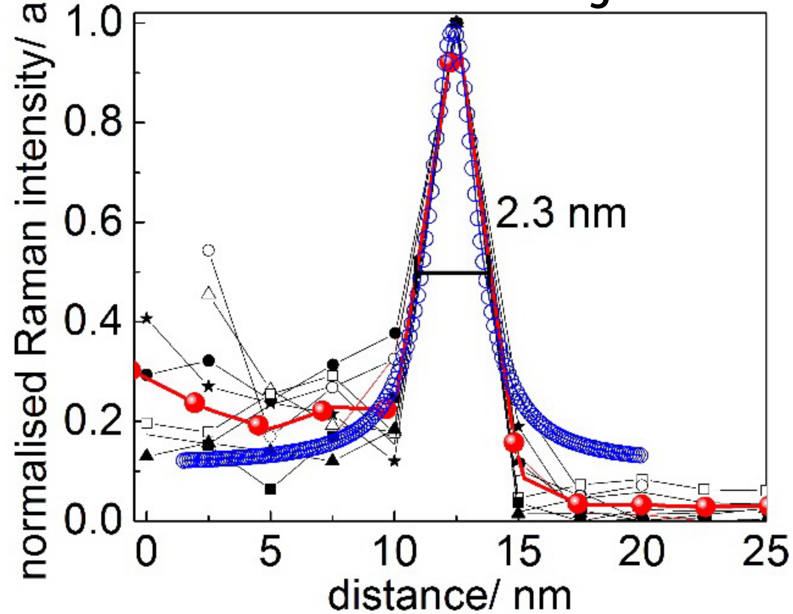
TERS map @ 410cm^{-1}



Topography



Gauss fit to the edge

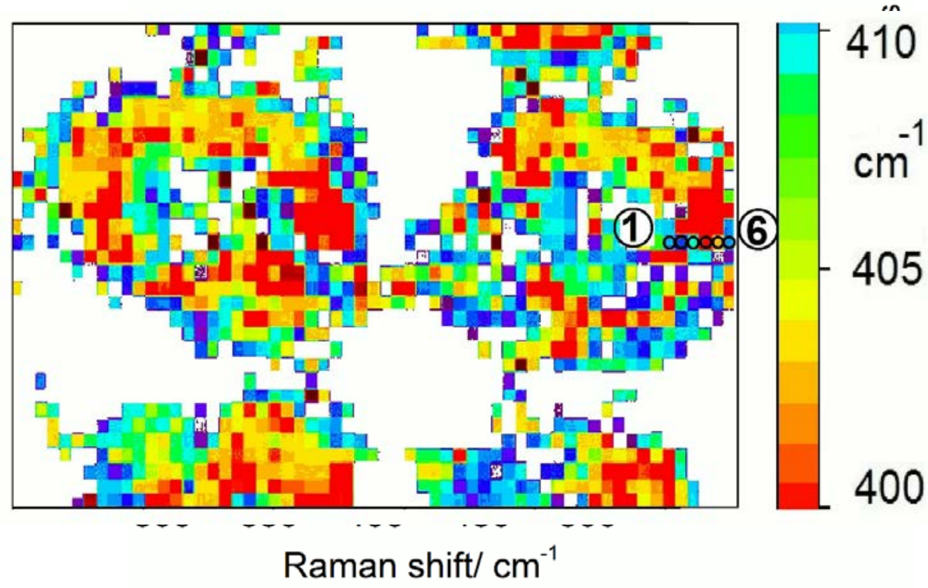


$$EF_{hot-spot} = Contrast_{TERS} \times \frac{d_{Raman}}{d_{tip}}$$

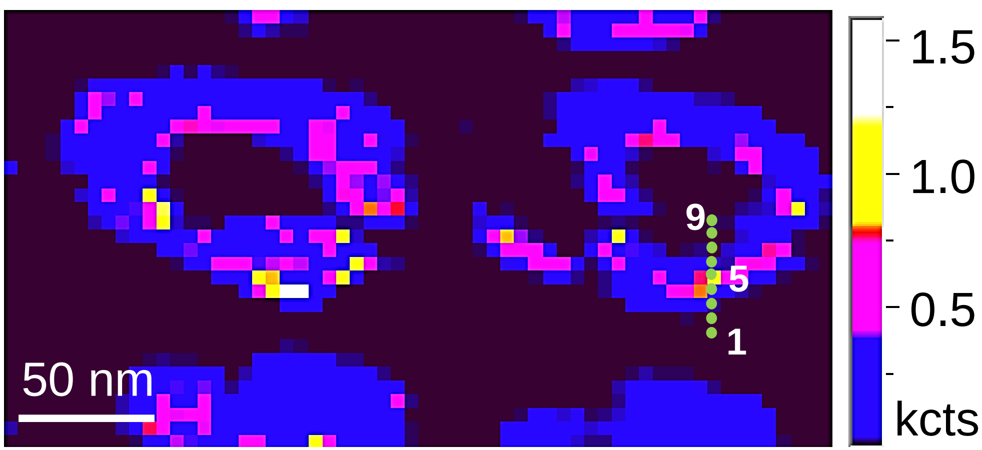
$$= \frac{I_{TERS}/d_{tip}}{I_{Raman}/d_{Raman}} = 5.6 \cdot 10^8$$

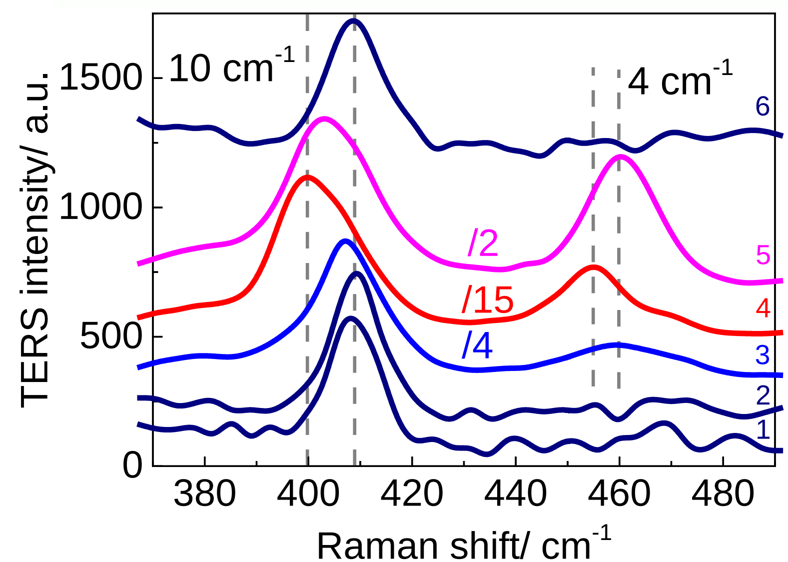
Investigation of Local Heterogeneities

- Strain
- Temperature rise
- Hot electron doping



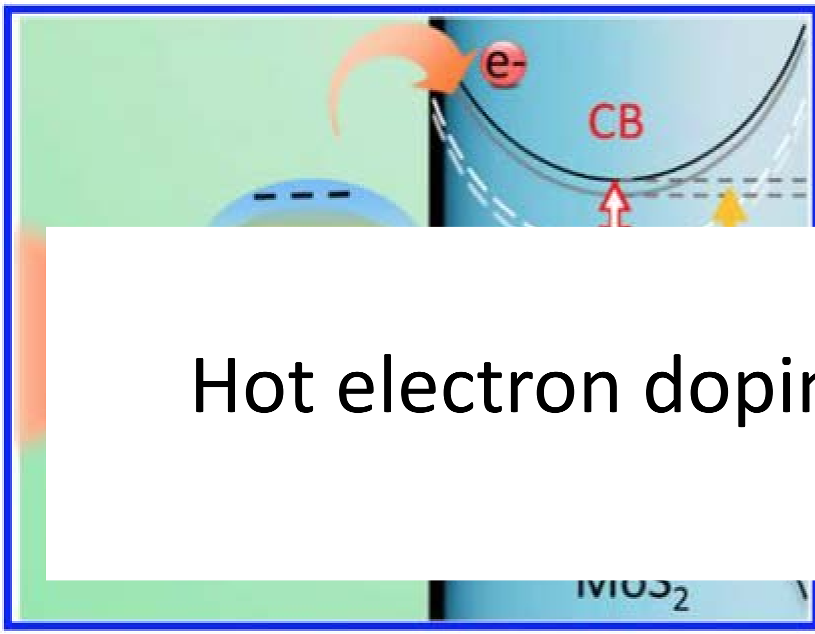
TERS map @ 410cm^{-1}





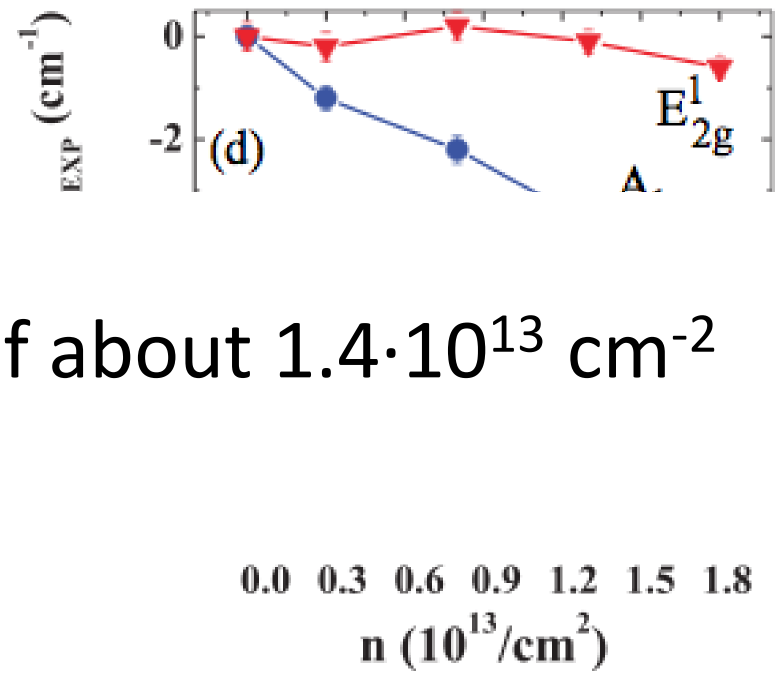
Disentangling Shifts in Raman Spectra

- Doping induced Raman shift ≈ 6 cm^{-1}



Hot electron doping of about $1.4 \cdot 10^{13}$ cm^{-2}

Doping gradient of phonon modes

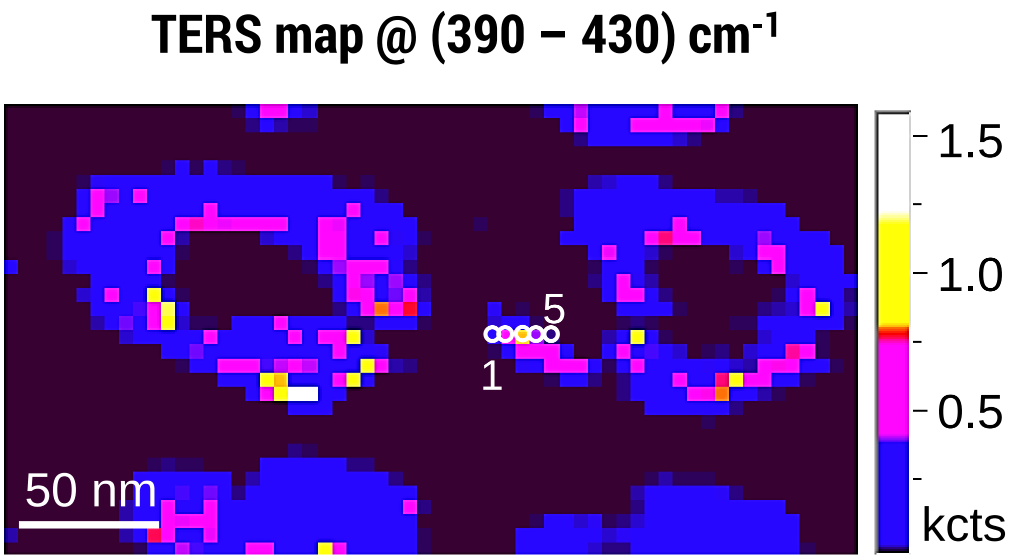


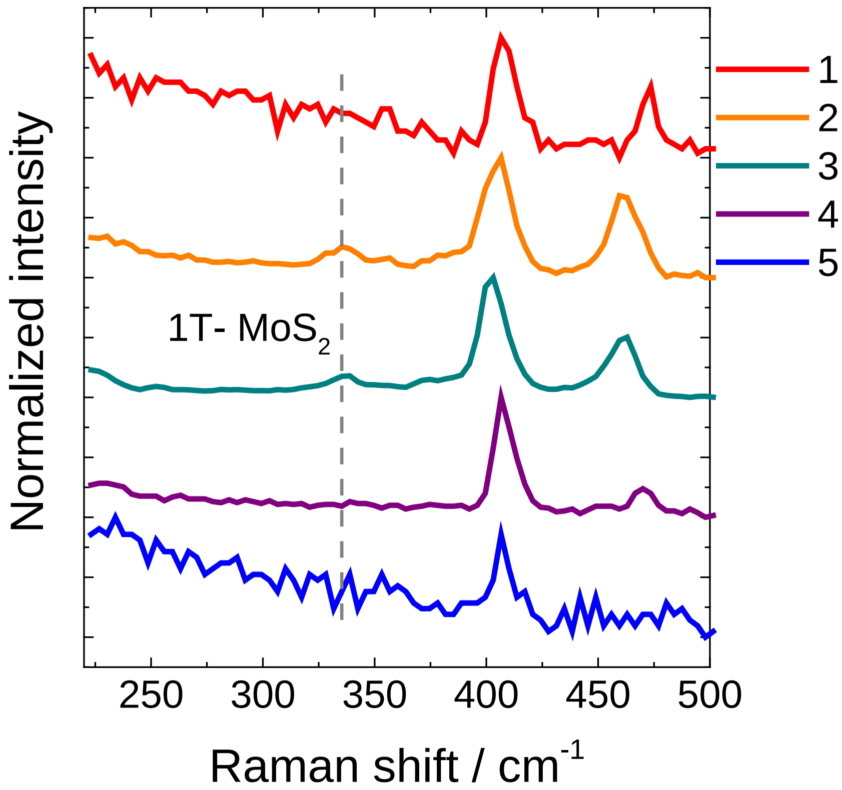
Chakraborty *et al. Phys. Rev. B* ***(2012), 85, 161403(R)***

1. Li *et al.*; ACS *Nano* **(2015),9, 10158**
2. Yu *et al., Adv. Func. Mat.* ***(2016), 26, 6394***
3. Najmaei *et al., ACS Nano* ***(2014), 8, 12682***

Doping gradient for A_{1g} mode = $\mathbf{0.23 \cdot 10^{13}\ cm^{-2}/cm^{-1}}$

Phase Change in Hot Spots





High resolution TERS map of monolayer MoS_2 on gold nanodiscs acquired with a gold tip and 785 nm excitation.

Corresponding TERS spectra along the circles shown in the map.

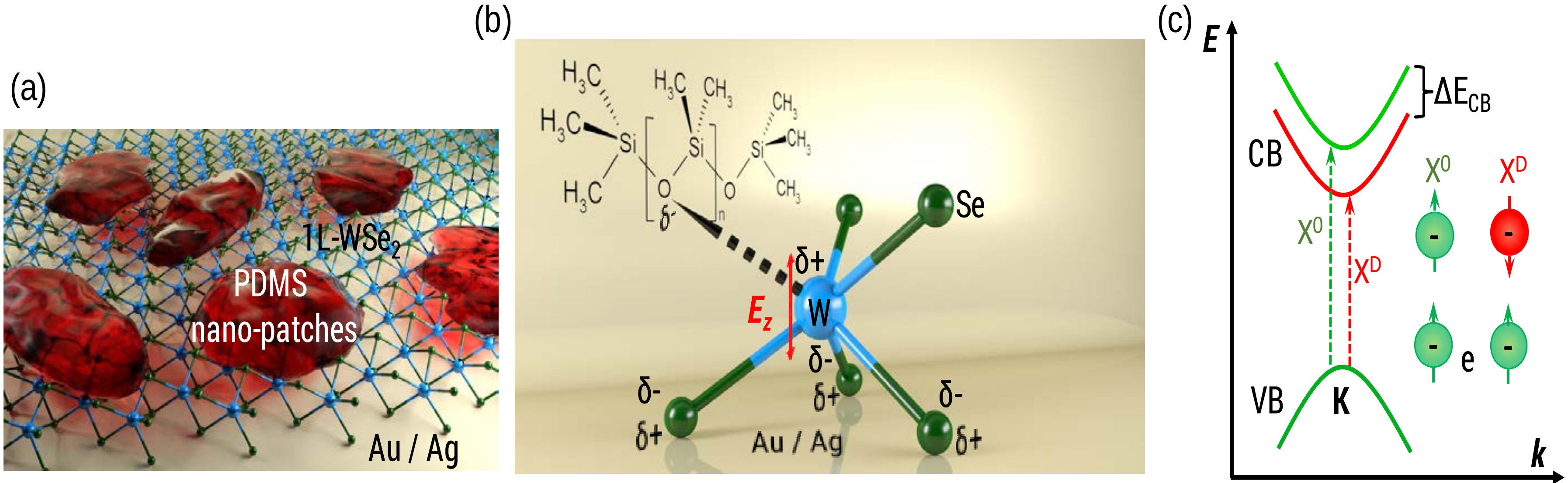
RESEARCH ARTICLE

ADVANCED OPTICAL MATERIALS
www.advopticalmat.de

Observation of Room-Temperature Dark Exciton Emission in Nanopatch-Decorated Monolayer WSe_2 on Metal Substrate

Mahfujur Rahaman, Oleksandr Selyshchev, Yang Pan, Rico Schwartz, Ilya Milekhin, Apoorva Sharma, Georgeta Salvan, Sibylle Gemming, Tobias Korn, and Dietrich R. T. Zahn*

Dark Excitons in WSe_2



Schematic of monolayer WSe_2 sandwiched between Au (or Ag) and PDMS nano-patches (a).

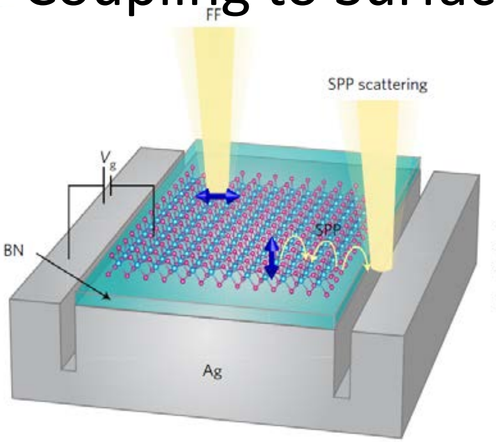
Two-way formation of out-of-plane dipole in WSe_2 (b): one via metal substrate (bottom) and the other via polar Si-O in PDMS (top).

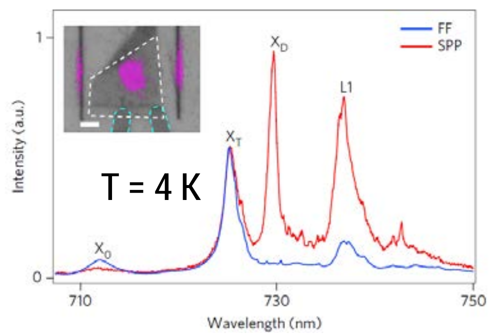
Formation of top dipoles via chalcogen vacancies are the most probable scenario.

Spin-dependent optical transitions in monolayer WSe_2 (c).

Dark Excitons in TMDCs

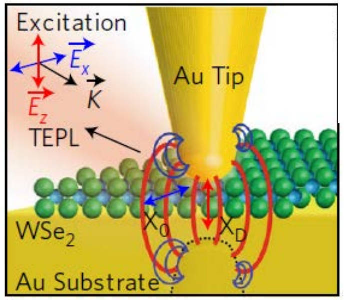
Coupling to Surface Plasmon Polariton

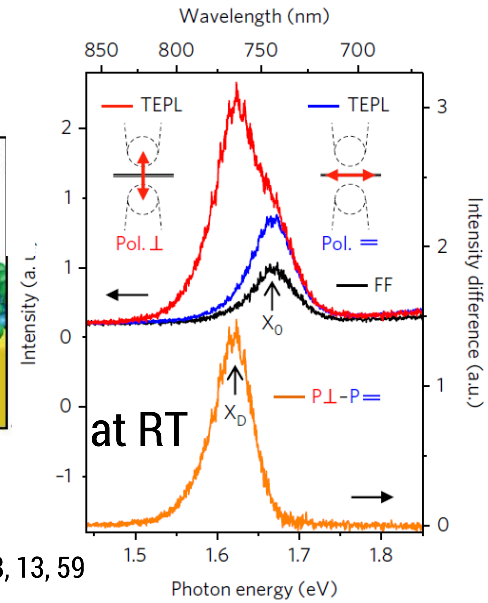




Zhou *et al.*, Nat. Nanotech., 2017, 12, 856

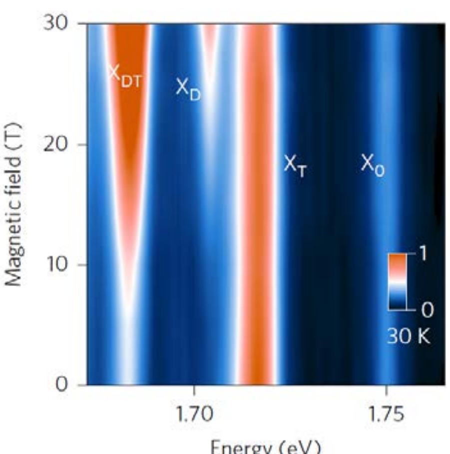
via Tip Purcell Effect

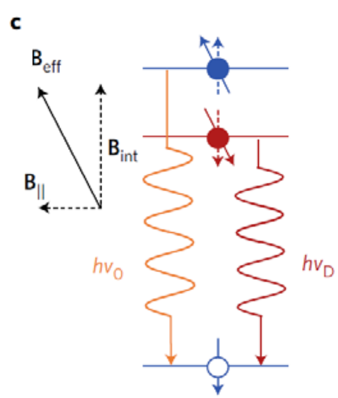




Park *et al.*, Nat. Nanotech., 2018, 13, 59

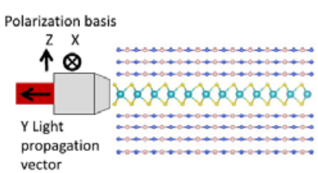
Magnetic Brightening

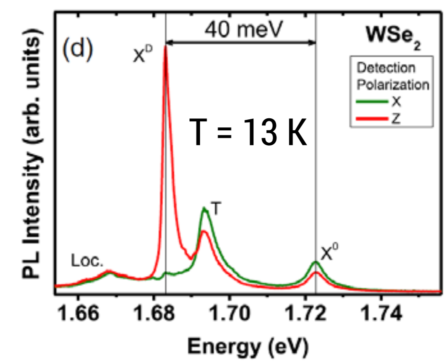




Zhang *et al.*, Nat. Nanotech., 2017, 12, 883

Using high NA objective

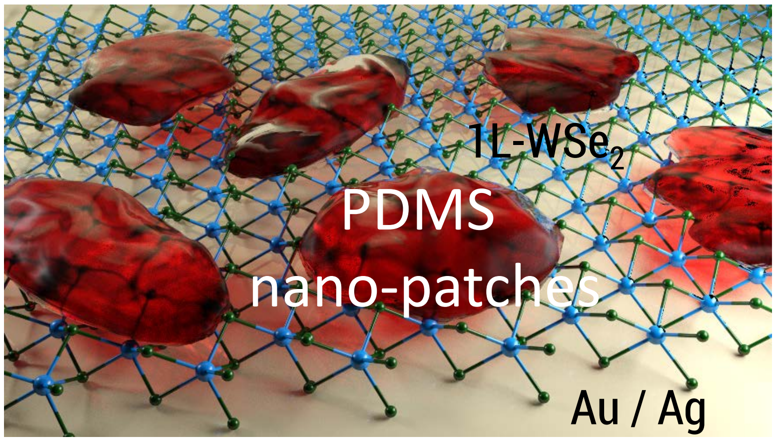




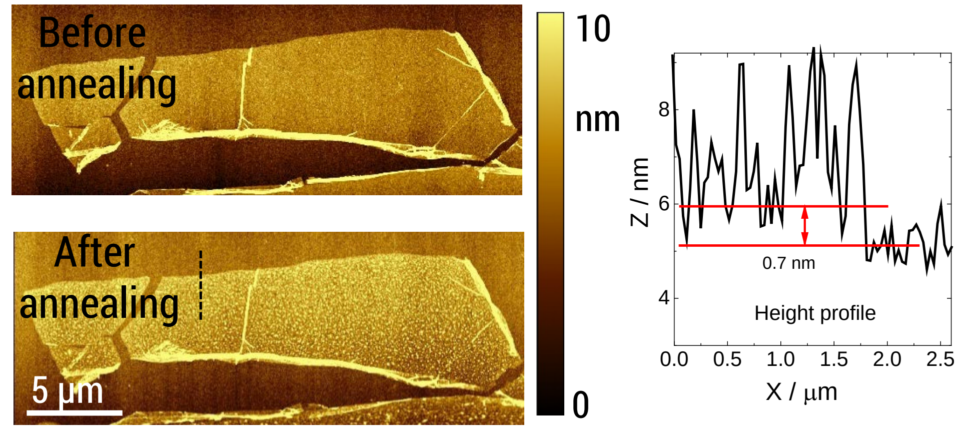
Zhu *et al.*, Phys. Rev. Lett., 2017, 119, 047401

Sample preparation

Sample schematic



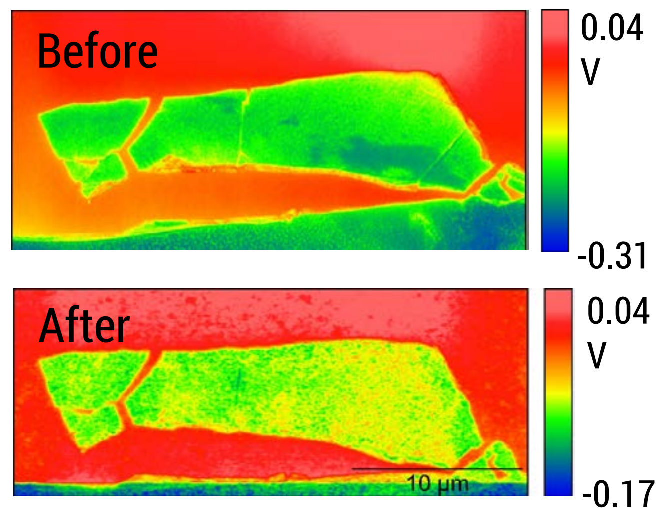
AFM topography



Sample preparation:

- Thermal evaporation of Au/Ag (100 nm) on Si
- 1L-WSe_2 was transferred on Au/Ag from PDMS using conventional dry transfer method
- Annealing @ 150 °C for 2 hours in N_2 atmosphere

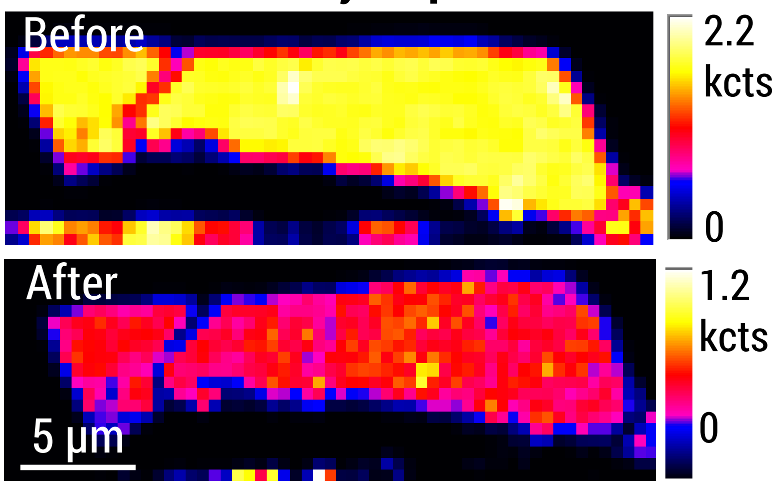
SP image



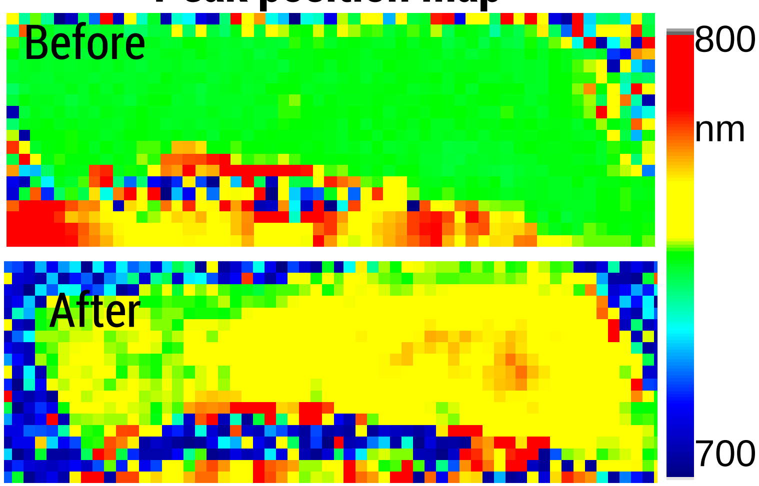
Micro-PL measurements

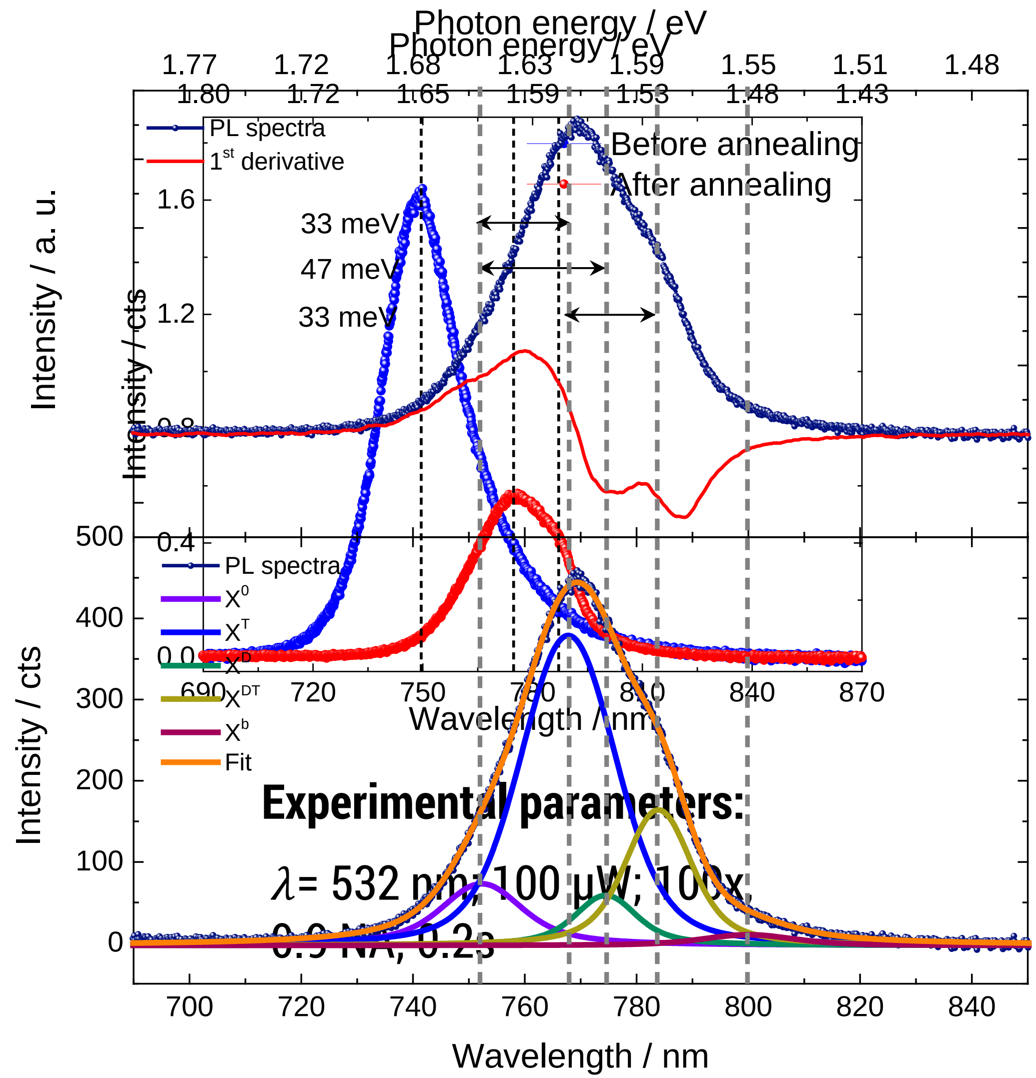
at Room Temperature

Intensity map



Peak position map





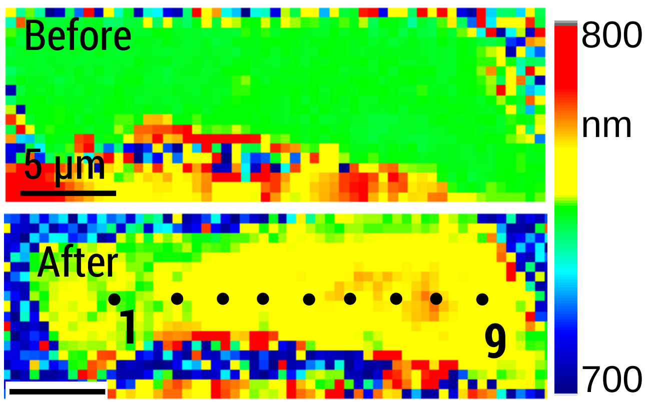
Experimental parameters:

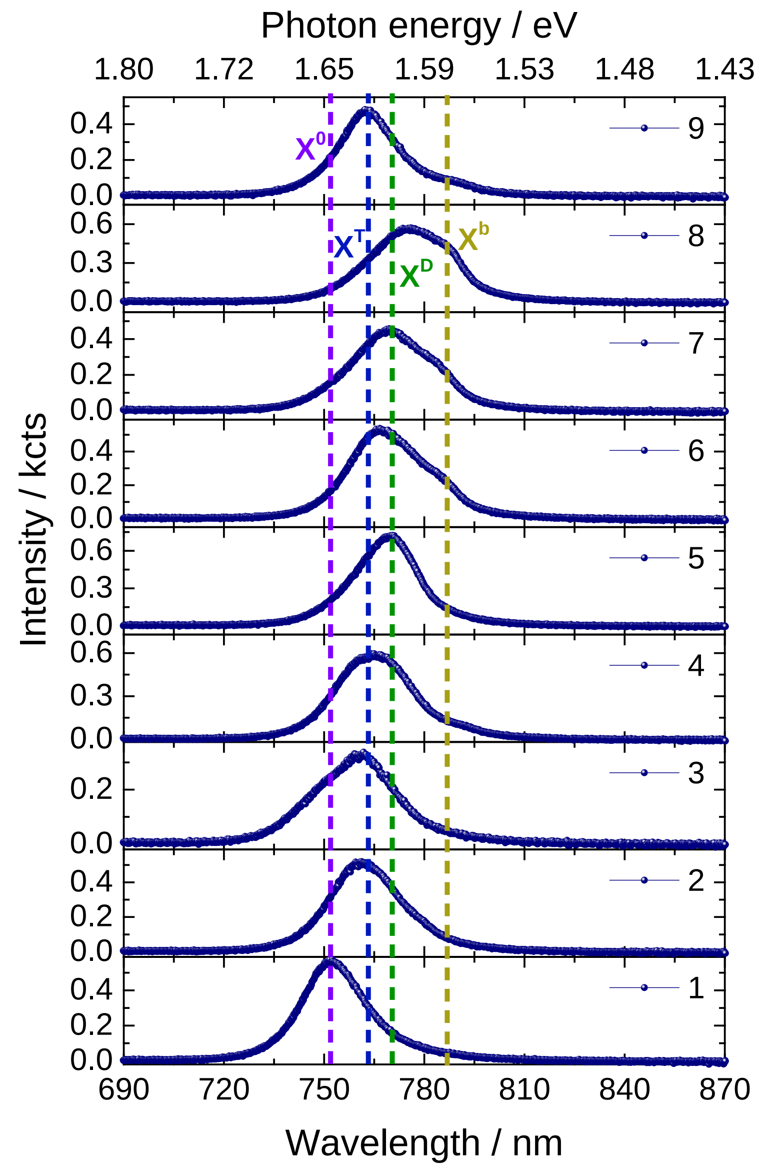
λ= 532 nm; 100 µW; 100x, 0.9 NA; 0.2 s

Micro-PL measurements

at Room Temperature

Peak position map

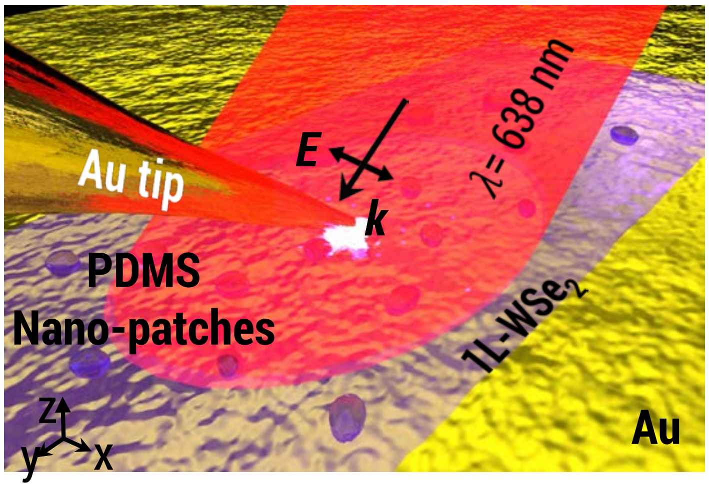




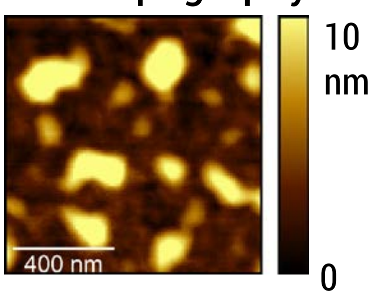
Nano-PL measurements

at Room Temperature

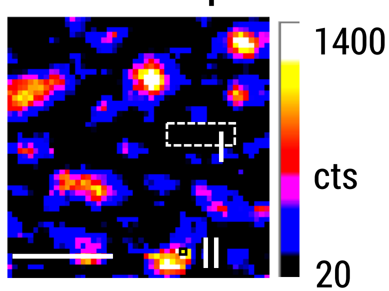
TEPL schematic



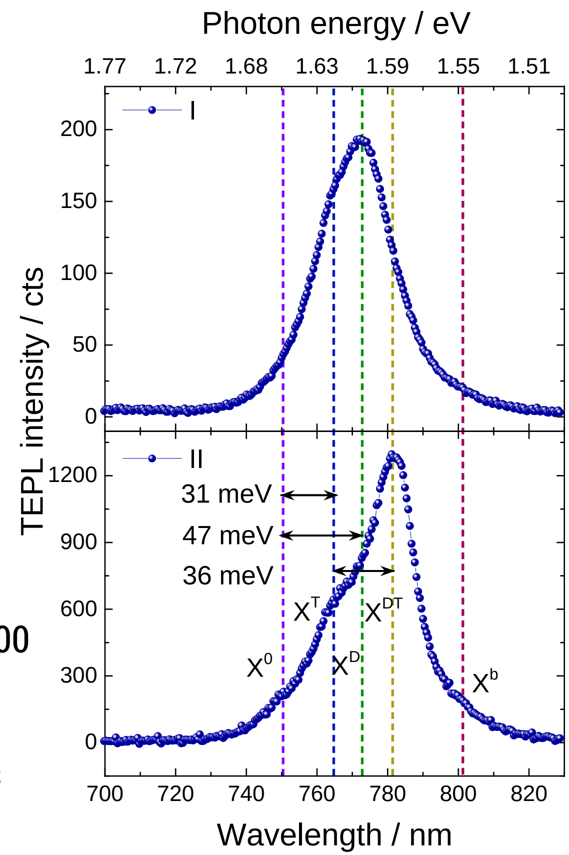
AFM topography



TEPL map



TEPL spectra

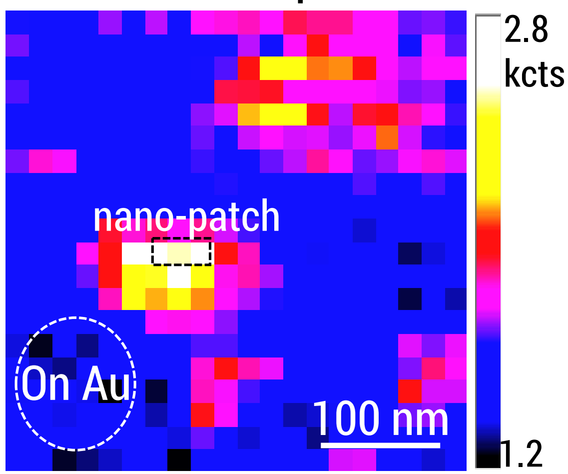


Correlation between TEPL and TERS

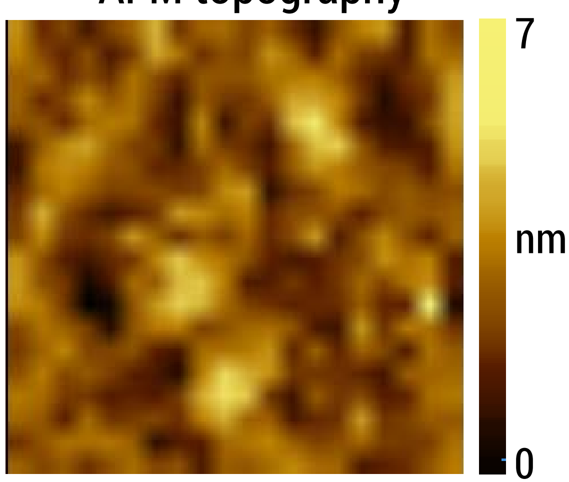
Qualitative determination of defect density

at Room Temperature

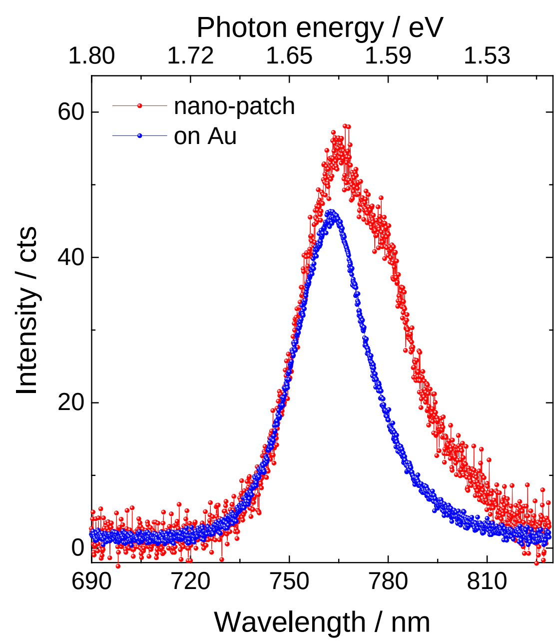
TEPL map



AFM topography

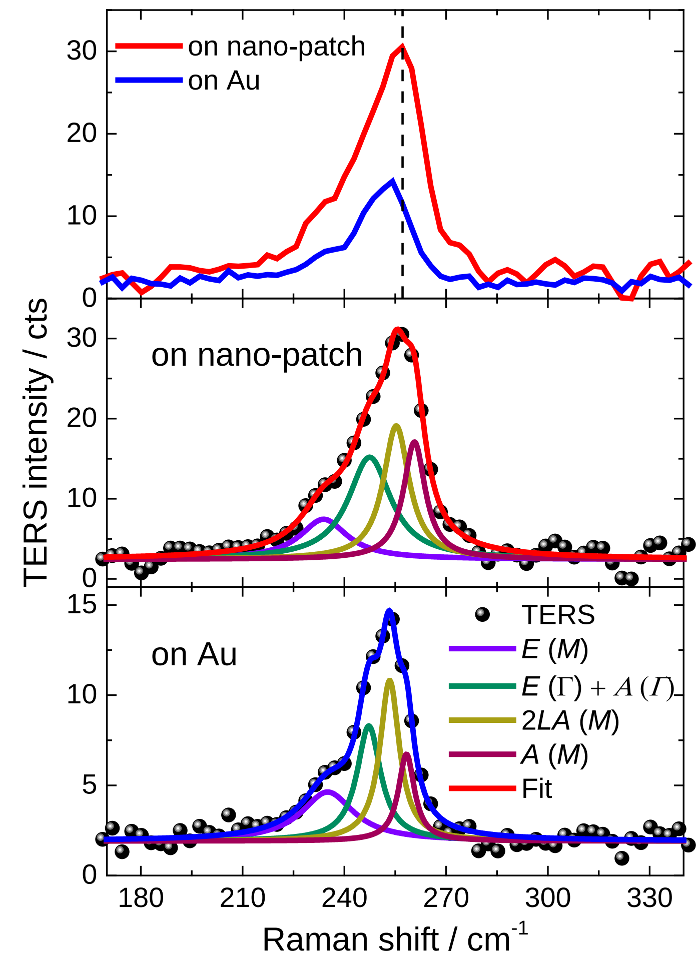


TEPL spectra



λ= 638 nm; 100 µW; 100x, 0.7 NA; 0.2s, 600 l/mm

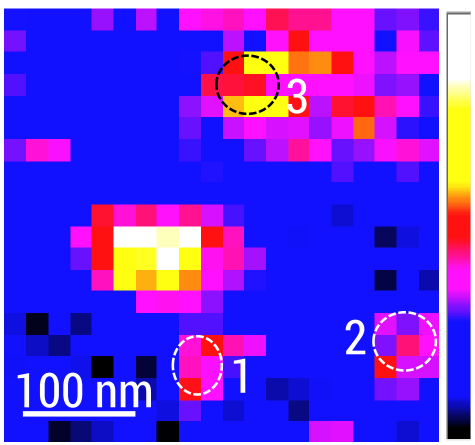
TERS spectra



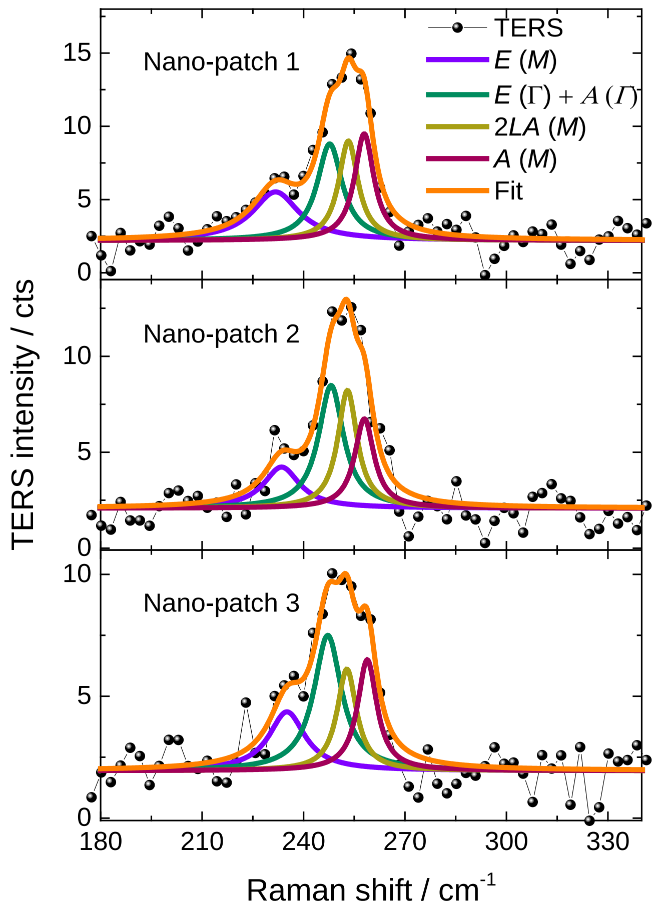
Correlation between TEPL and TERS

Qualitative determination of defect density

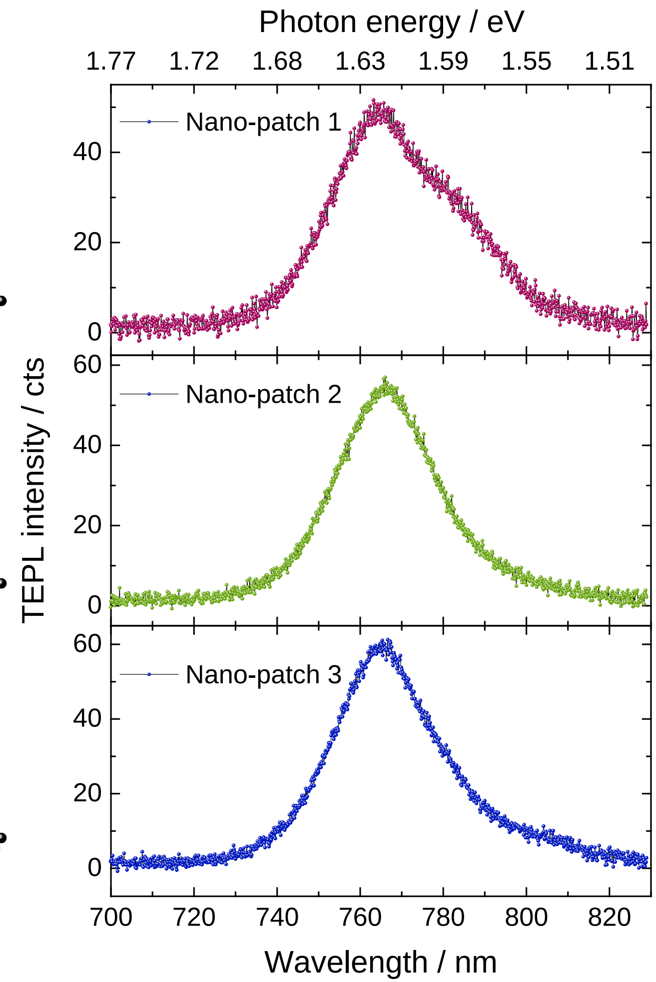
TEPL map



TERS spectra

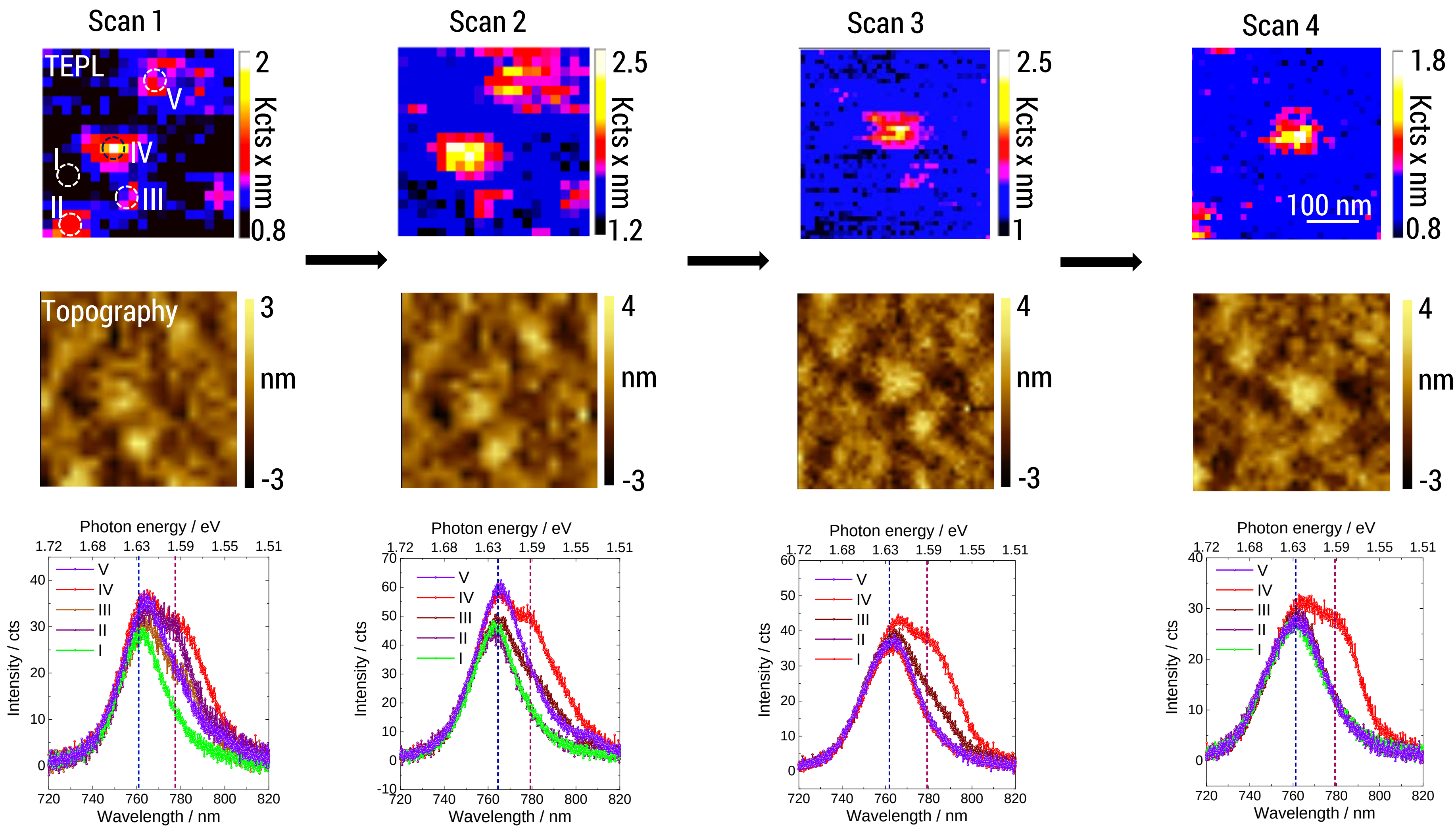


TEPL spectra



Nano-PL measurements

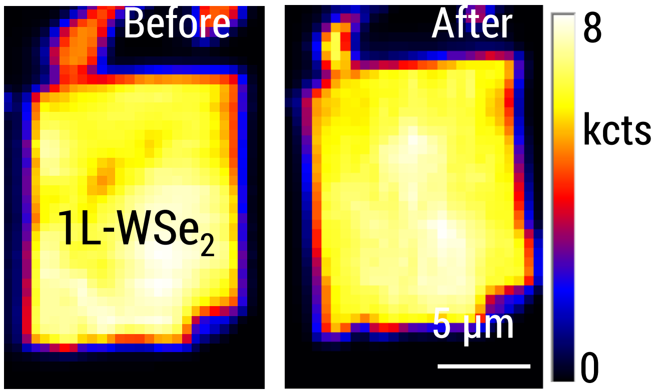
at Room Temperature



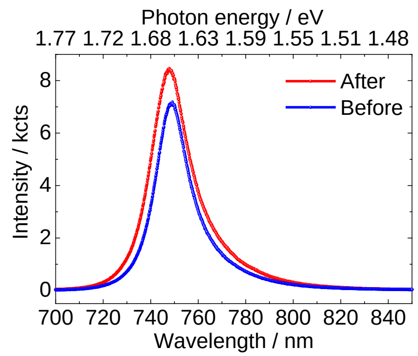
PL measurements on SiO_2 substrate

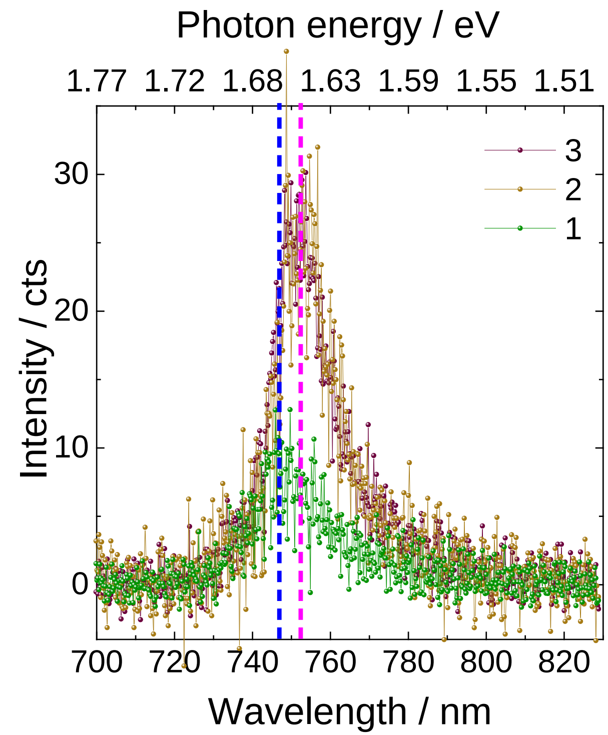
at Room Temperature

Micro-PL intensity map

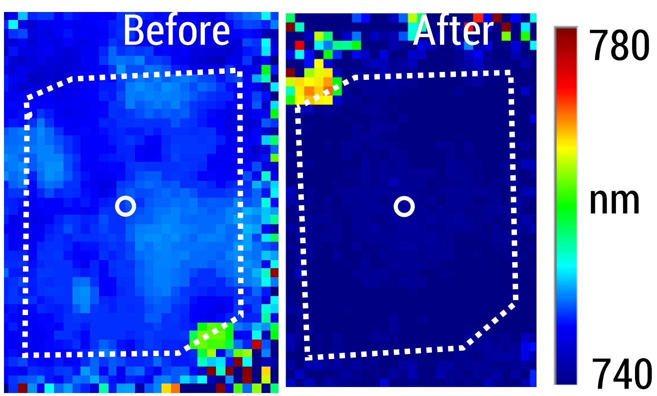


Micro-PL spectra

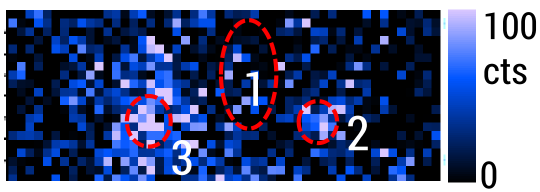




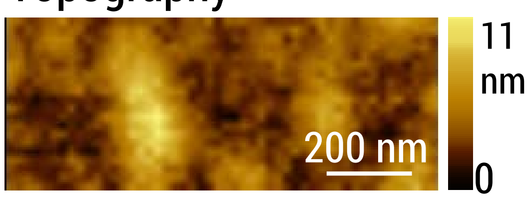
Micro-PL peak position map



TEPL map



Topography



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Topical Review

Plasmon-enhanced Raman spectroscopy of two-dimensional semiconductors

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The Chemnitz Semiconductor Physics Group

http://www.tu-chemnitz.de/physik/HLPH/

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Thank you very much for your attention!

Dr. Mahfujur Rahaman
Yang Pan
Ilya Milekhin

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