HORIBA

Explore the future

HORIBA France

Marc Chaigneau

Andrey Krayev, Yoshito Okuno

Tip Enhanced Optical Spectroscopy

Of 2D materials

21/09/2017

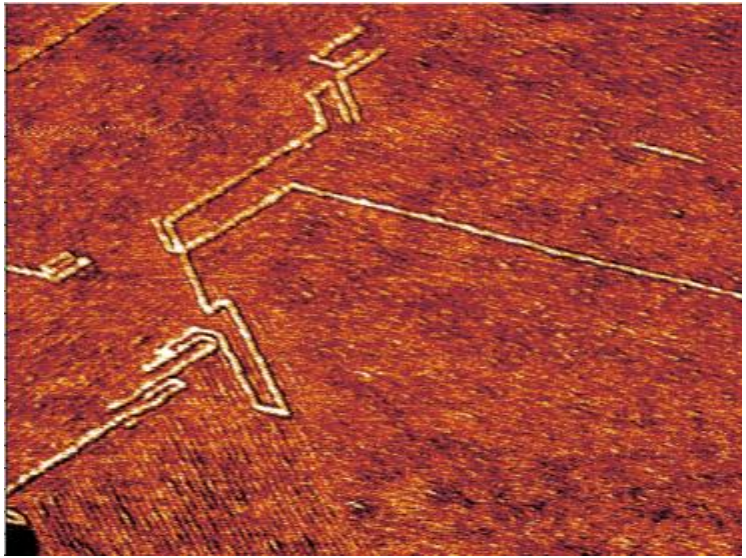
RPGR2017, Singapore

Bringing Scanning Probe Microscopies…

- **SPM** brings a lot of information on the **physical characteristics** of materials
  - *Topography*
  - *Mechanical properties*
  - *Electrical and magnetic properties*

- SPM is truly a nanoscale imaging technique…

…but it lacks ***chemical*** sensitivity



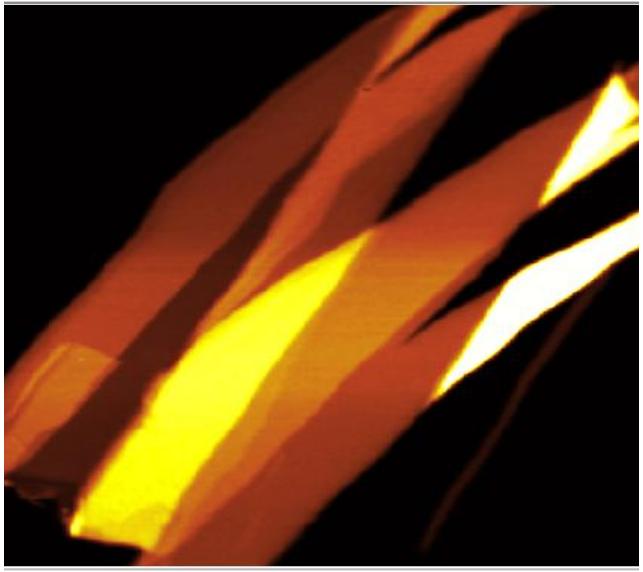
SS-DNA on HOPG functionalized with octadecylamine. 500nm frequency shift image.

... and Raman together

- Confocal Raman Microscopy is a very *specific* **chemical imaging**
  - Precise structural information, wide areas of application
  - Non-destructive technique, compatible with many environments
  - A wide spectrum of available laser sources

  (from UV to IR : possibility of resonant Raman scattering)

- **Drawbacks**
  - **Low cross-section (~ *10^{-30}*)**
  - **Limited spatial resolution**



Graphene- HORIBA

- 156 x 180 = 28080 spectra (step = 0.5 µm)
- 2 min 08 (EMCCD, SWIFT; Acq. Time 2 ms + 1.5 ms)

Let's break the Rayleigh criterion!

How? ➡

Nano Lightning Rod

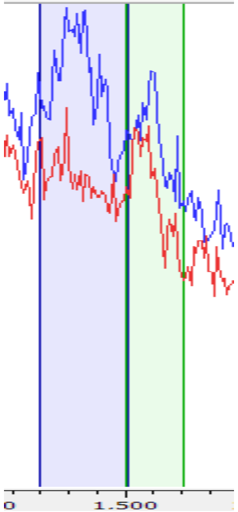
plays the role of a Nano-Antenna

. *Signal Enhancement*

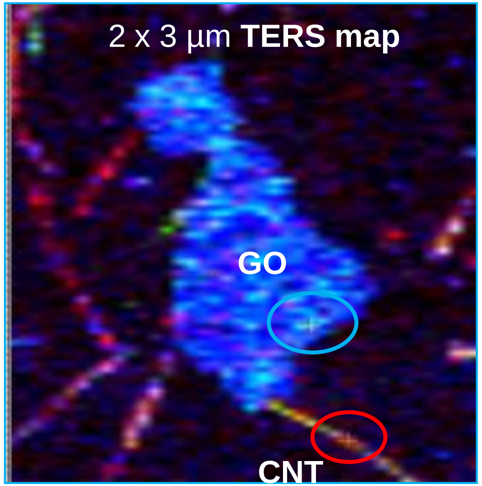
- ***Near-Field Resolution***

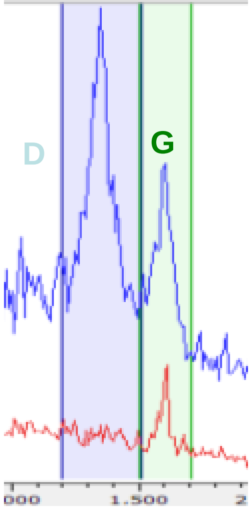
Conventional Raman VS TERS

Confocal Raman and TERS of the <u>same area</u>, graphene oxide and CNTs on Au



Confocal Raman
13 mW; integration 1 s





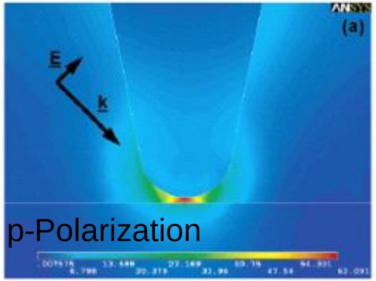
TERS
130 µW; integration 0.2 s

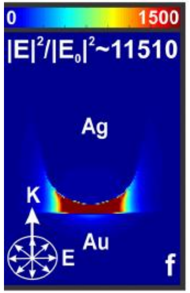
-TERS Instrumentation

(optical configuration, TERS tips, TERS in numbers)

- TERS applications for 2D materials

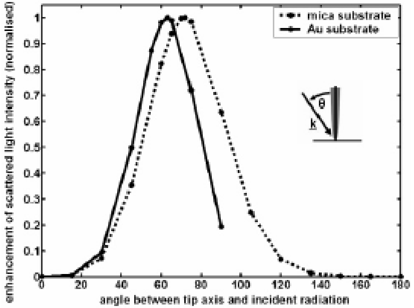
NanoRaman : Factors of influence





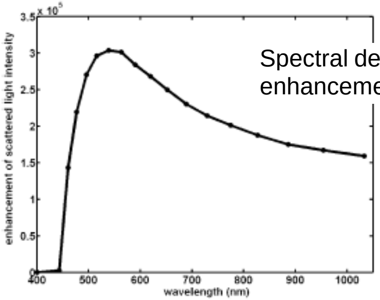
Electric field is preferentially enhanced if the polarization is **parallel to the tip's axis:**

- *p*-polarized light for TERS in reflection
- Radial polarization for TERS in transmission



Angular dependence of the enhancement

Optimum angle is 60-65° for TERS in reflection



Spectral dependence of the enhancement

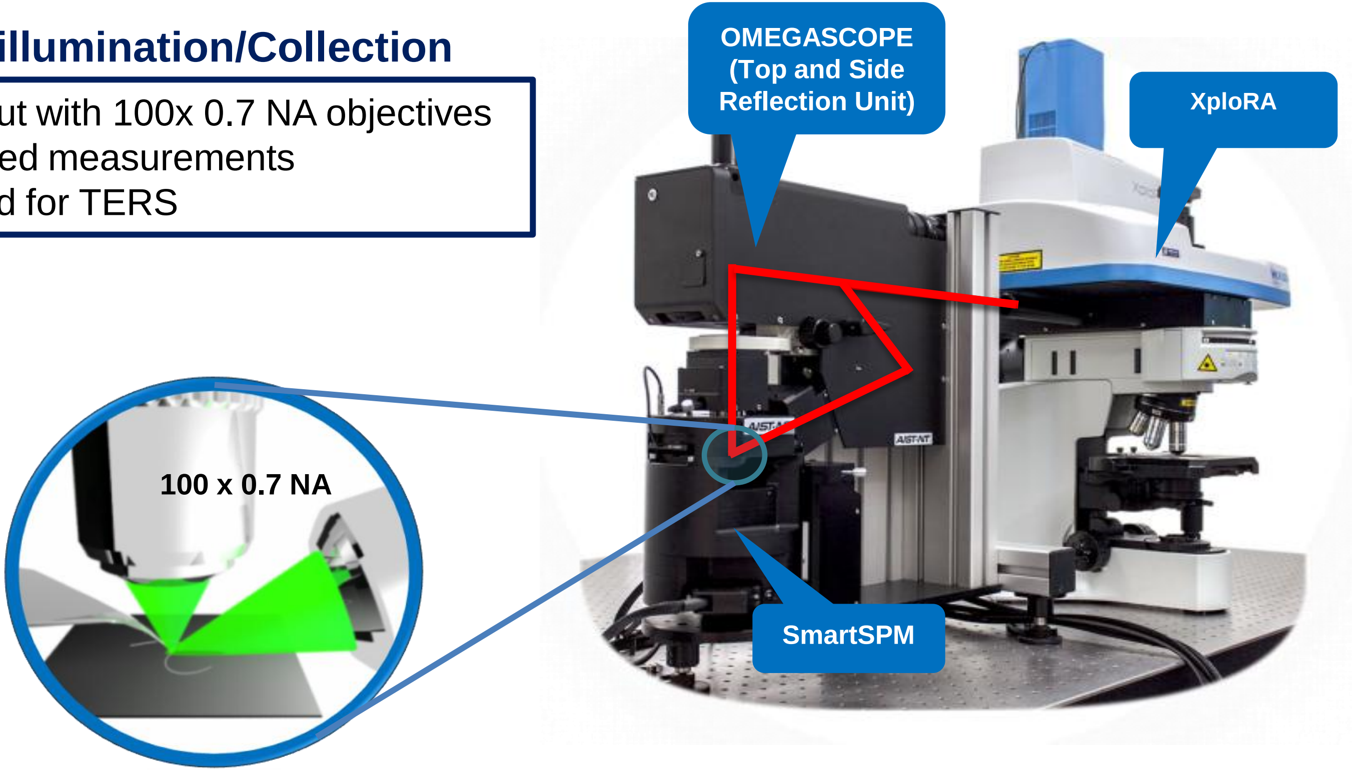
Noble metal (typically Au or Ag) is used for the TERS tips

J. Phys. Chem. B 110, 6692, 2006
Optics Express 21, 25271, 2013

NanoRaman: Optical configuration

Top and Side illumination/Collection

- High throughput with 100x 0.7 NA objectives
- Top: co-localized measurements
- Side: optimized for TERS



NanoRaman: Ag TERS probes

+ Innovative package to **enhance tip shelf life**

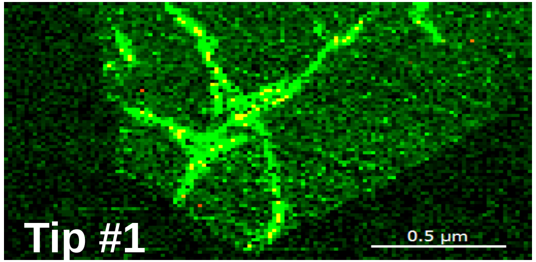
+ Raman active layer: **Ag** with protective layers

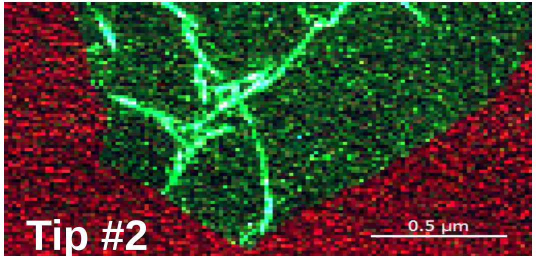
+ Great enhancement factor **EF =** $\mathbf{10^{5-6}}$

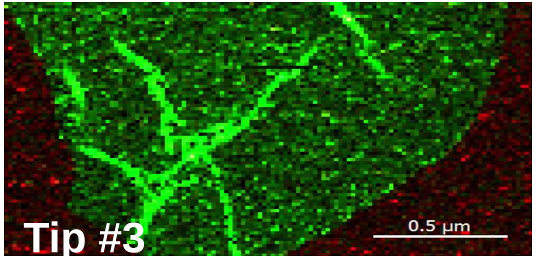
+ **Easy-of-use** thanks to the AFM regulation

+ Usable in **top/bottom** and **side** configurations

+ **9 tips out of 10 show the nanoresolution**!





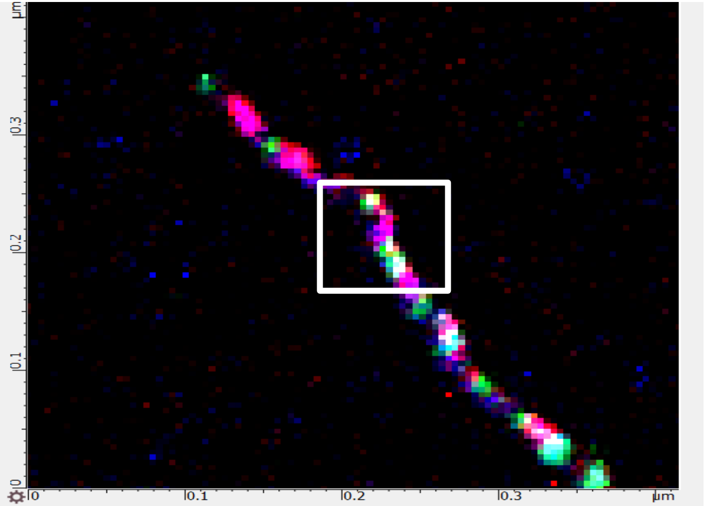


NanoRaman mapping

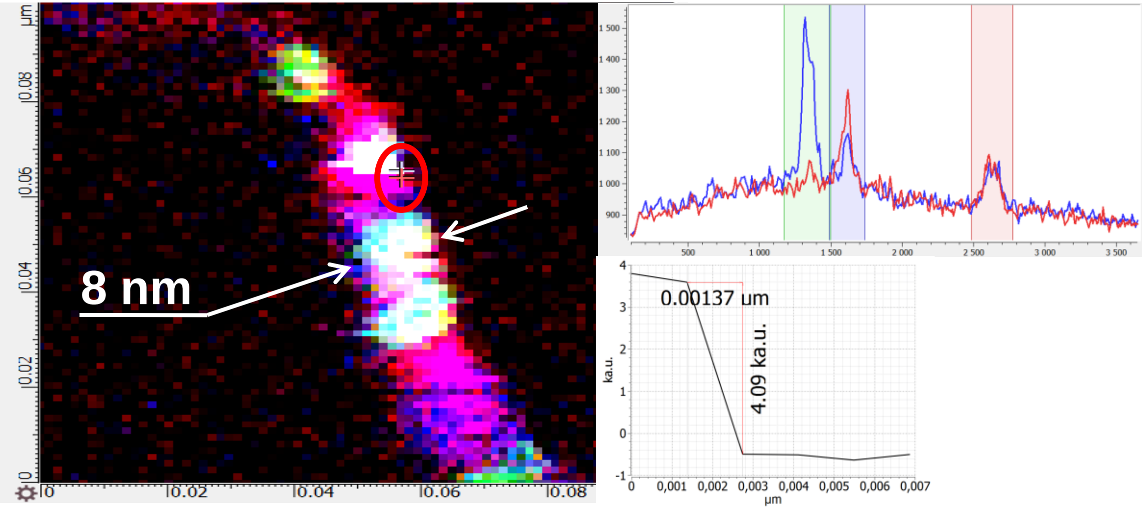
Movie

TERS: spatial resolution

CNTs maps out-of-lab conditions!



400 nm x 400 nm (100 x 100 pixels)

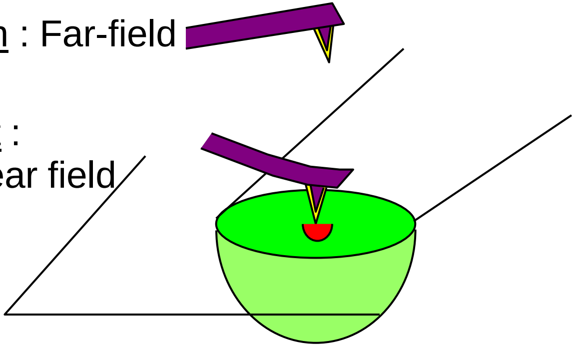


100 nm x 100 nm (75 x 75 pixels), 50 ms per pixel

Optical resolution capability: **8 nm**
Pixel step: **1.3 nm** → chemical sensitivity in both X and Y direction

Recorded by HORIBA @ SPIE San Diego

TERS: Contrast and Enhancement factor



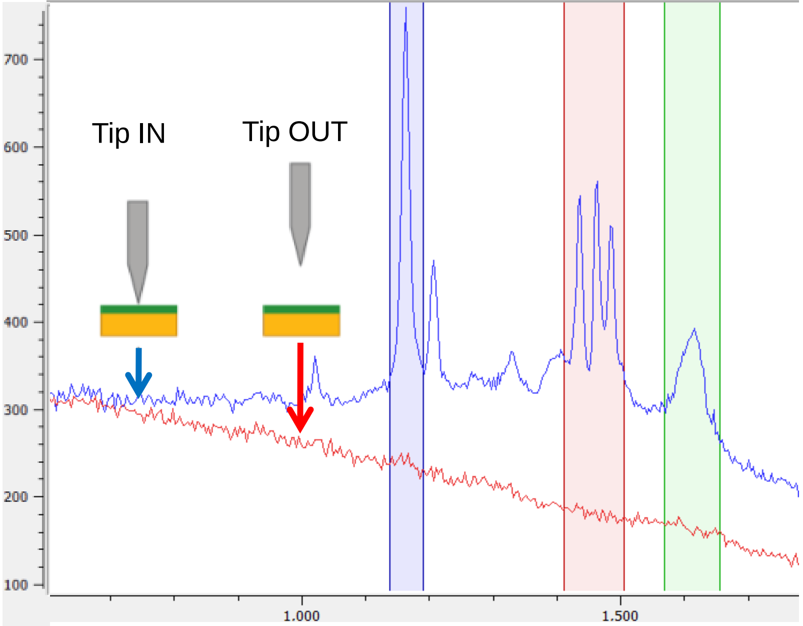
Tip withdrawn : Far-field

Tip in contact :
Far field + Near field

Contrast = I_{nf}/I_{ff}

Enhancement Factor

$$= \left(\frac{\overbrace{I_{nf} + I_{ff}}^{I_{\text{Tip IN}}}}{\underbrace{I_{ff}}_{I_{\text{Tip OUT}}}} - 1 \right) \frac{V_{ff}}{V_{nf}}$$



Tip enhanced Raman signal of Azobenzene molecules

C > 40 (up to 100)

F = 4 × 10^5 (up to $10^{6\text{-}7}$)

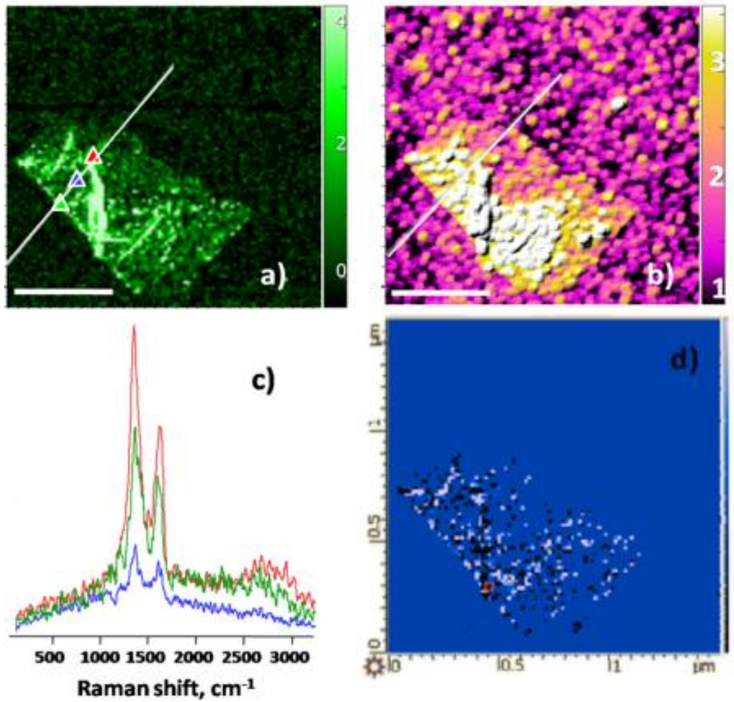
-TERS Instrumentation

(optical configuration, TERS tips, TERS in numbers)

- TERS applications for 2D materials

2D materials: Graphene and beyond

Why TERS? → to characterize **2D materials** in terms of size, shape, **electronic properties, distribution of defects and contaminants**

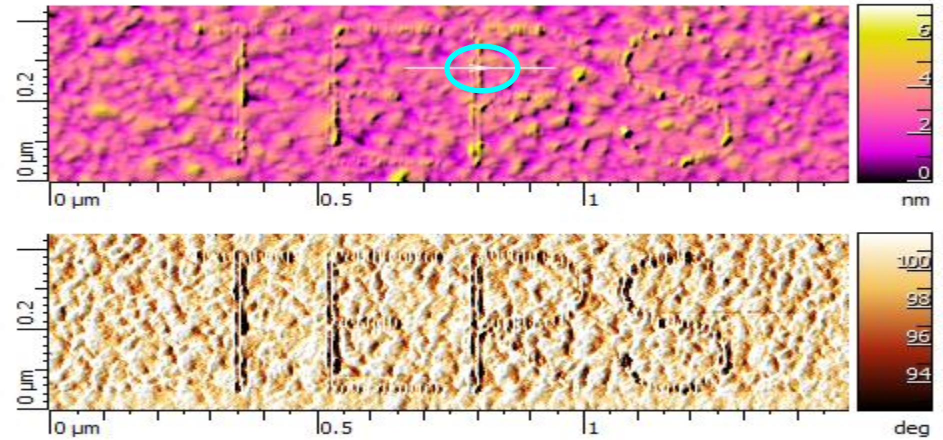


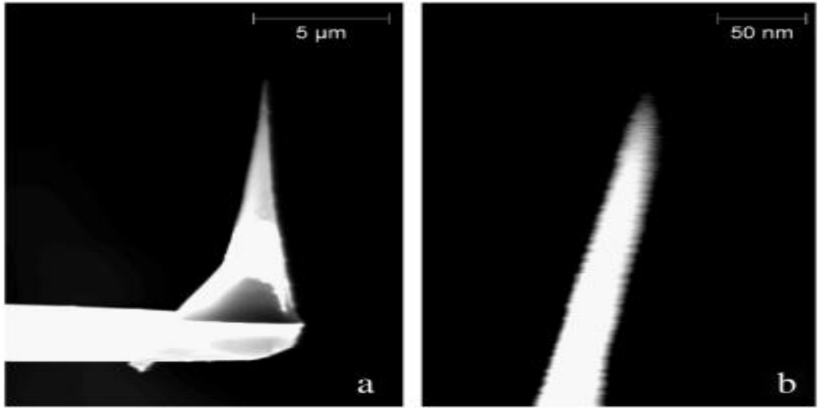
a) 100 pixels per line TERS map of D-band intensity
b) Topography image of the same flake
c) representative TERS spectra
d) distribution of the ratio of G to D band intensities

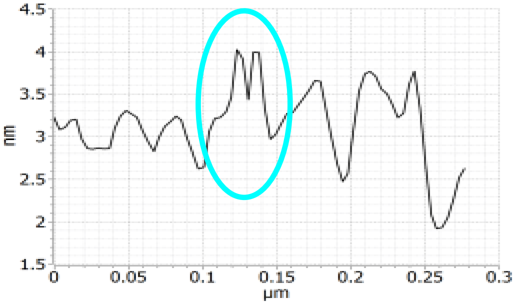
The defects density increases with the ratio I_D/I_G
→ Single point defect can be imaged in graphene and graphene oxide flakes with TERS

Patterning of Graphene Oxide

Patterning of graphene oxide flakes by “pulsed-force lithography”

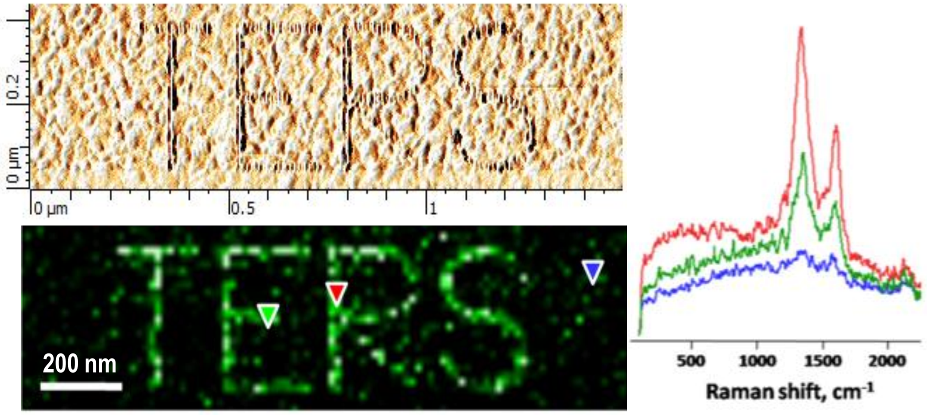


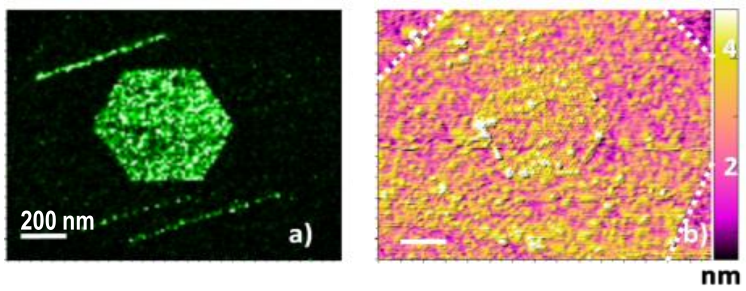




Thanks to elimination of lateral drag in pulsed force lithography and thanks to extreme hardness of diamond tips, it’s possible to create high quality patterns in single layer graphene oxide sheet

TERS response from patterned GO

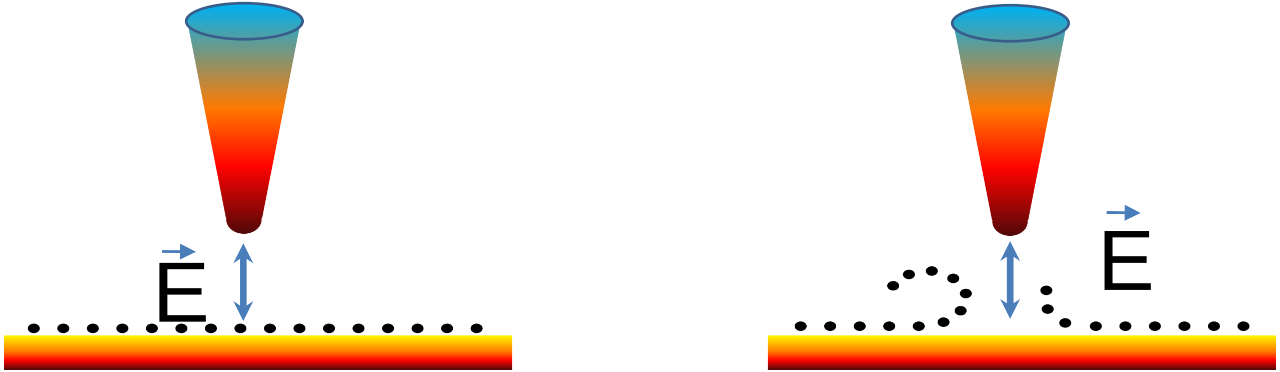




Patterns, both 1-D and 2-D, imprinted into SL-graphene oxide, demonstrate <u>1-2 orders of magnitude</u> stronger response compared to adjacent flat, non–patterned areas and comparable to the signal from folds and creases

TERS response from patterned GO

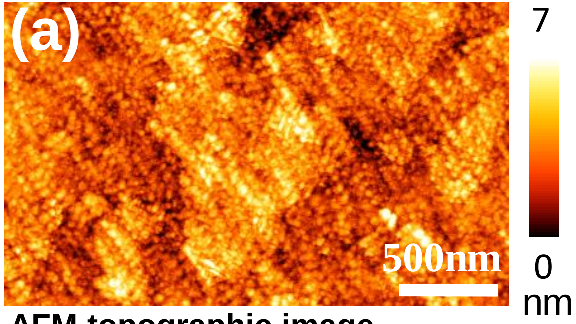
Improved Alignment of the Optical Electric Field with the Plane of 2-D Carbon Flakes



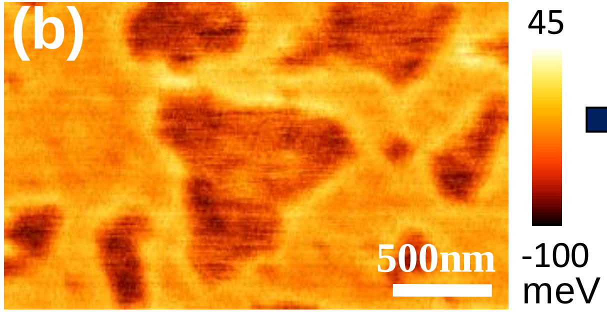
D, G, D', 2D modes in graphene are in- plane vibrations. When we increase the projection of the optical electric field in the tip-sample gap on the plane of 2D carbon, we should dramatically increase TERS response

Same should be valid for other 2-D materials- TMDCH!

Combined TERS and KPFM mapping of GO-COOH

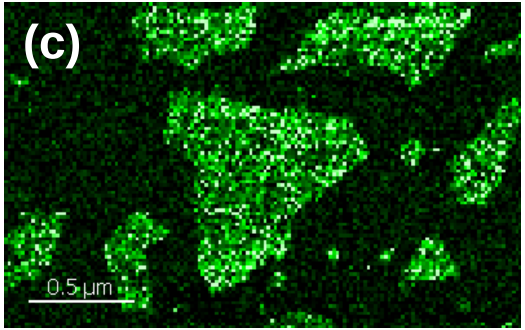


AFM topographic image

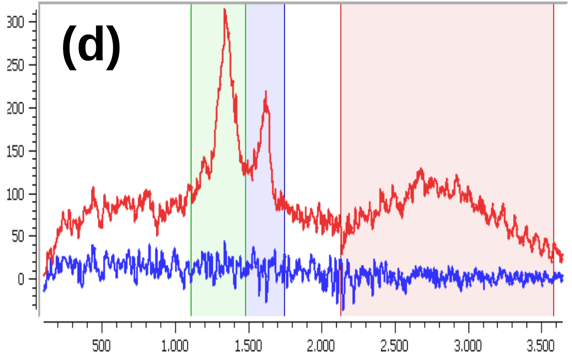


KPFM potential image

the calculated Fermi level of GO varies from 5eV to 5.14eV



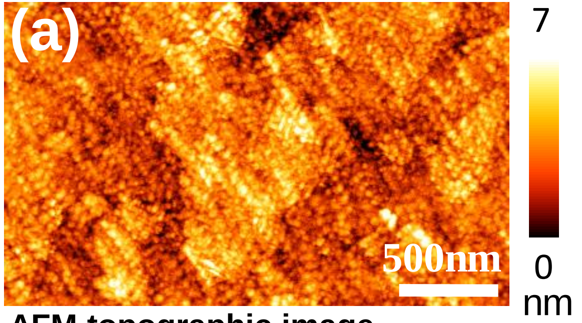
TERS image



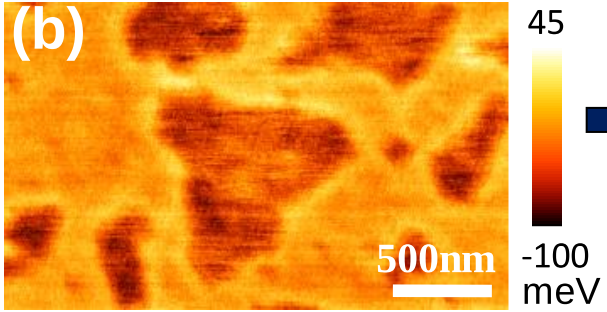
Typical TER spectra

N. Kumar, W. Su (NPL), M. Chaigneau (HORIBA), in preparation

Combined TERS and KPFM mapping of GO-COOH



AFM topographic image



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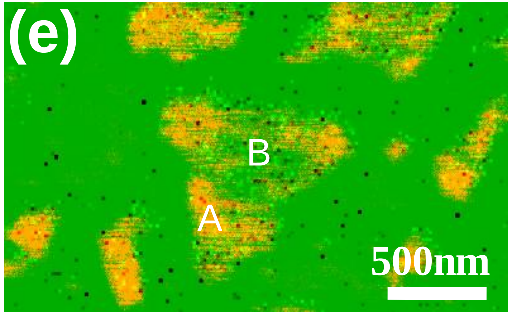
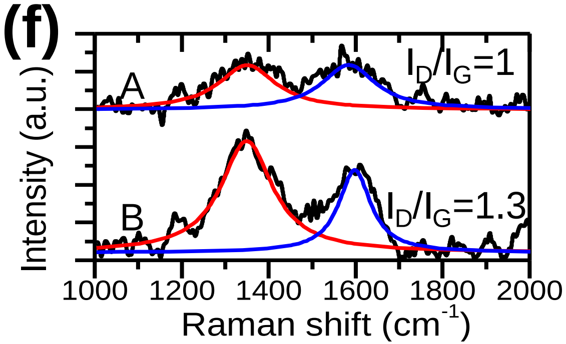


Overlay image using I_D/I_G and inverse KPD



average TERS spectra from region A and B

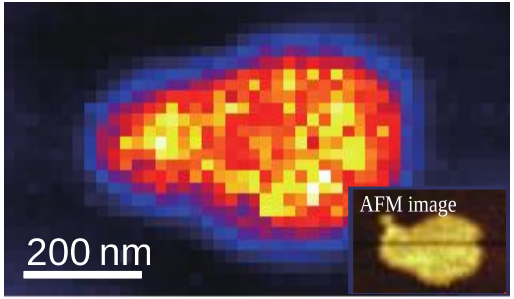
The high KPD areas always have high intensity of I_D/I_G, while low KPD areas always have low intensity of I_D/I_G

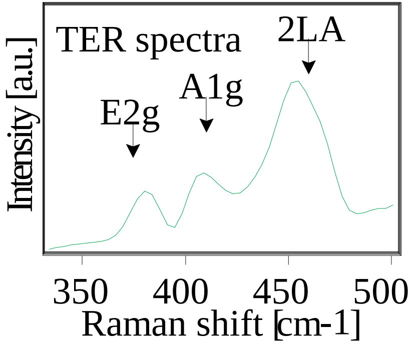
The Fermi level in an area of GO increases with I_D/I_G (ie with density of defects)

TERS/TEPL of MoS2 on Si-SiO$_2$

CVD grown MoS$_2$ on Si substrate, Ag tip, 594 nm, reflection configuration

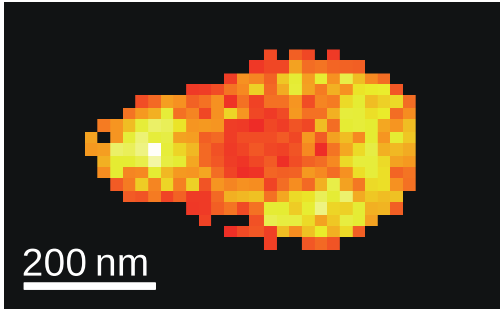
TERS image

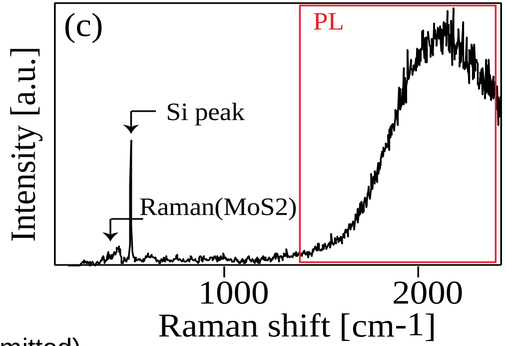




Monolayer flake
(supported by the distance between the E2g and A1g).

TE Photoluminescence (TEPL) image





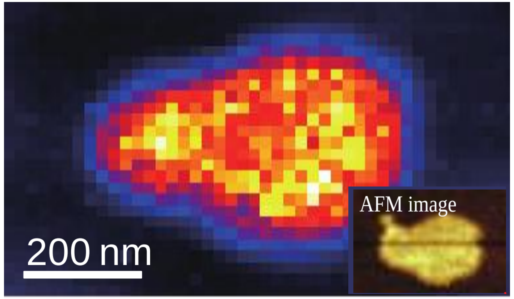
PL emission is enhanced around the edges

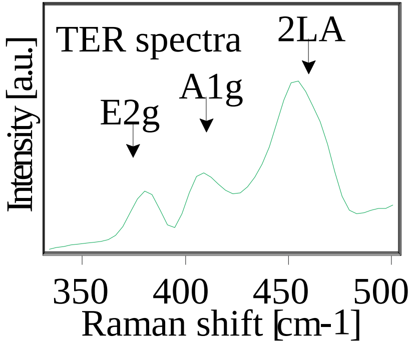
Y. Okuno, M. Chaigneau, HORIBA Scientific, F. Fabbri, IMEM (submitted).

TERS/TEPL of MoS2 on Si-SiO_2

CVD grown MoS_2 on Si substrate, Ag tip, 594 nm, reflection configuration

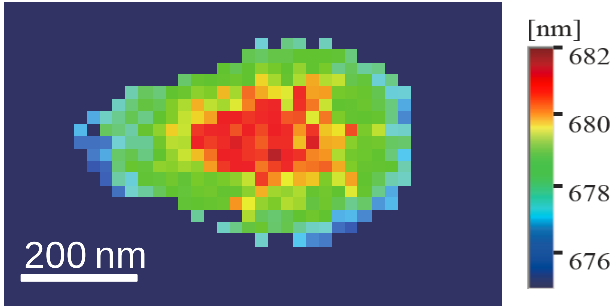
TERS image





Monolayer flake
(supported by the distance between the E2g and A1g).

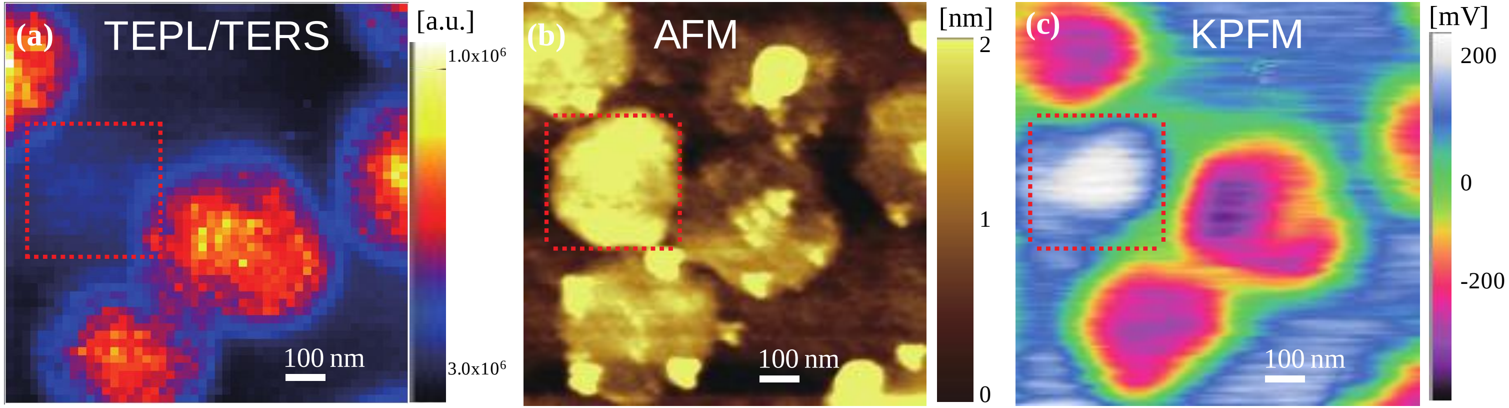
TEPL shift image



Edge-induced modification in the Fermi level of the MoS2 ML flake

Y. Okuno, M. Chaigneau, HORIBA Scientific, F. Fabbri, IMEM (submitted).

Combined TERS and KPFM mapping of MoS_2



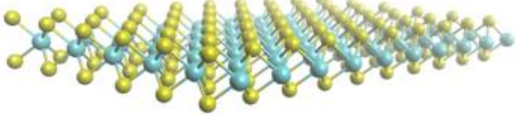
(a) TEPL map, (b) AFM image of monolayer and bilayer MoS2 flakes and (c) Kelvin Force image of the same area

- PL intensity, and TERS (through separation between A1g and E2g peaks) are consistent in distinguishing monolayer and bilayer flakes

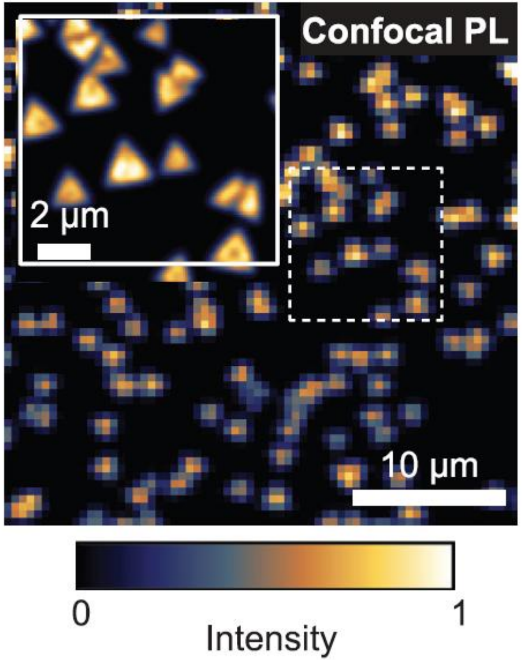
- Kelvin probe force map shows positive values (~100 mV) for bilayer flakes and negative values around -300 mV for monolayer flakes.
→the Fermi energy increases in bilayer MoS_2.

Nanoscale excitonic heterogeneity in monolayer WS_2

Monolayer WS_2



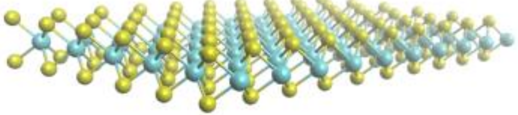
- Sulfur atoms
- Tungsten atoms



➡ **Confocal PL over a large area shows relatively uniform emission over many small WS2 flakes**

Nanoscale excitonic heterogeneity in monolayer WS$_2$

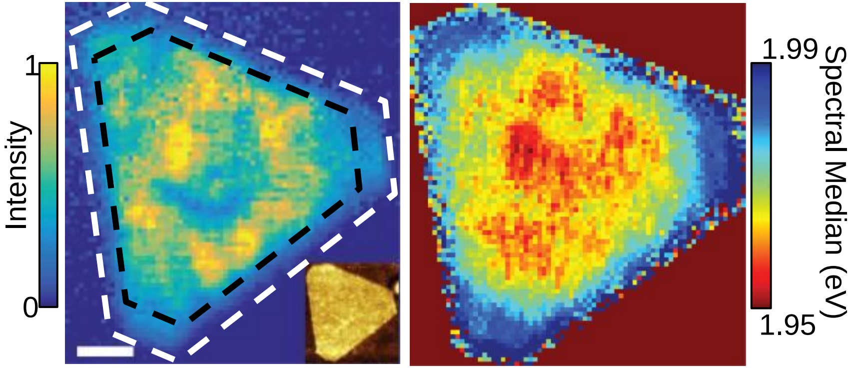
Monolayer WS$_2$



● Sulfur atoms

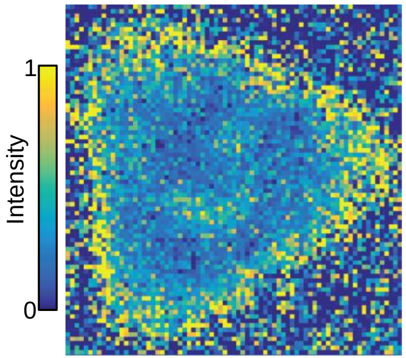
● Tungsten atoms

TEPL



scale bar: 250 nm

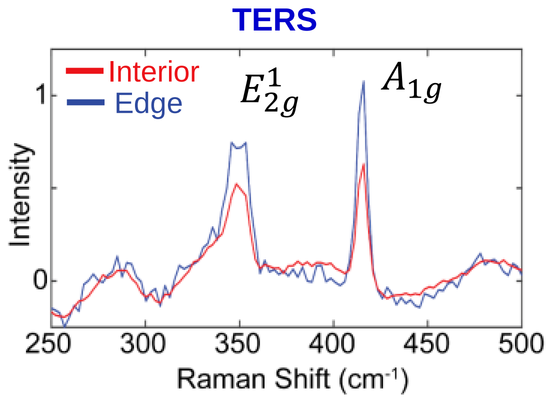
TERS

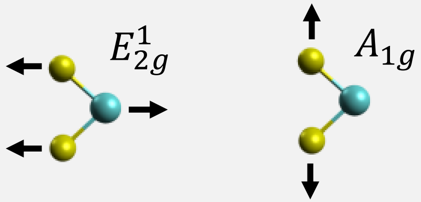


- **Nanoscale variations in PL emission intensity and energy.**
- **Distinct edge region (~110 nm wide)**
  - **Weaker PL.**
  - **Higher-energy PL.**
  - **Brighter TERS.**

Kastl, Chen, Kuykendall, Darlington,
Borys, Krayev, Schuck, Aloni & Schwartzberg (2D Mater. 4 (2017) 021024).

Monolayer WS_2 edges vs interior: spectral signatures of different doping



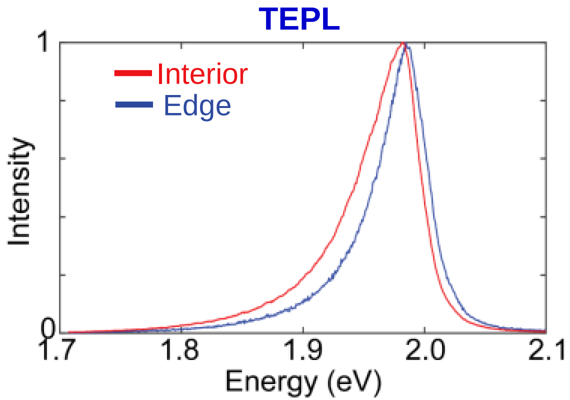


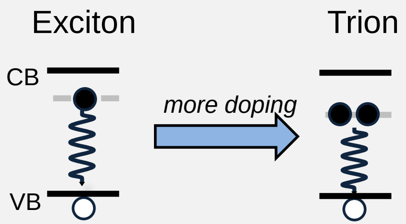
- Ratio of mode intensities depends on free carrier density.
- Smaller carrier density at the edge.

cf., *Phys. Rev. B* **85**, 161403 (2012).

Spectral signatures:

Free-carrier concentration is larger in the interior region



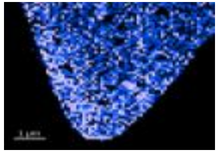


- More trion emission from the interior region.

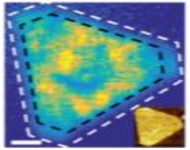
CONCLUSIONS

- TERS ***IS READY*** for real-life analytical application on number of scientifically/industrially interesting samples
- Without detailed NANOSCALE characterization of nanomaterials, their use in next generation devices is pretty much impossible.
- TERS can provide reliable information on peculiarities of local structure with resolution below 10 nm.
- TERS is extended to two-dimensional materials with dominating out-of-plane Raman-active modes such as WS_2, MoS_2 ,WSe_2 …

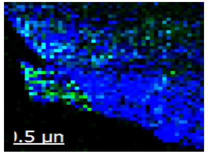
TERS and 2D materials



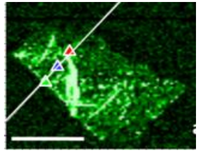
MoS_2



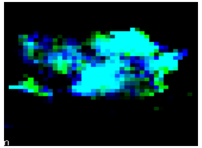
WS_2



WSe_2



GO



BiOCl

CONCLUSIONS

- TERS ***IS READY*** for real-life analytical application on number of scientifically/industrially interesting samples

- Without detailed NANOSCALE characterization of nanomaterials, their use in next generation devices is pretty much impossible.
- TERS can provide reliable information on peculiarities of local structure with resolution below 10 nm.

- TERS is extended to two-dimensional materials with dominating out-of-plane Raman-active modes such as WS_2, MoS_2 ,WSe_2 …

- AFM (topographic/structural) + TERS (chemical) + TEPL (optoelectronic) + KPFM / cAFM (local work function / local conductivity)

CONCLUSIONS

new trends

- Non linear TERS: Stimulated TERS demonstrated!

- UHV TERS

- TERS in liquids

- ElectroChemical Tip Enhanced Raman Spectroscopy

…

Thank you very much for your attention

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