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IMEM-CNR Institute

TEOS characterization of 2D materials – from graphene to TMDCs

30-03-2017

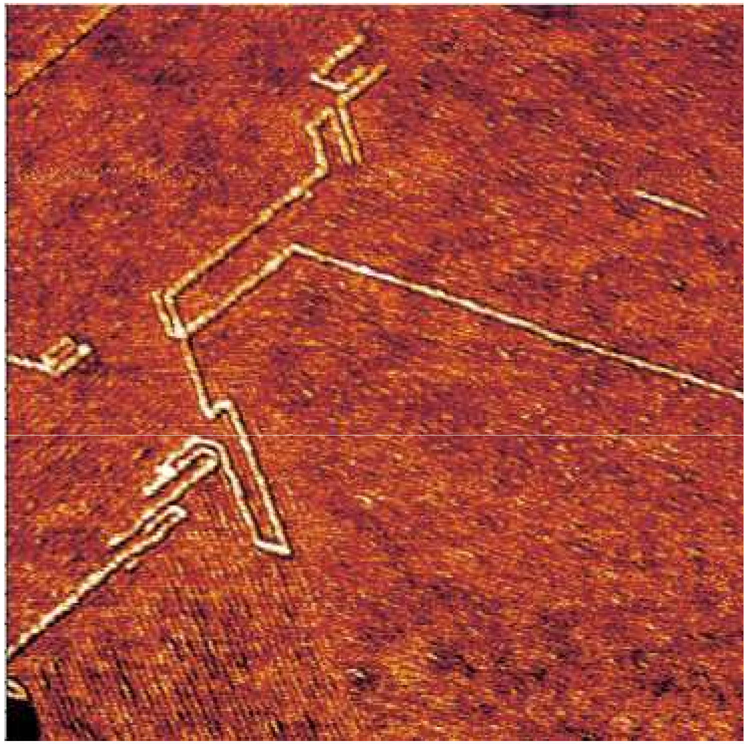
Graphene2017

Bringing Scanning Probe Microscopies…

- SPM bring 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

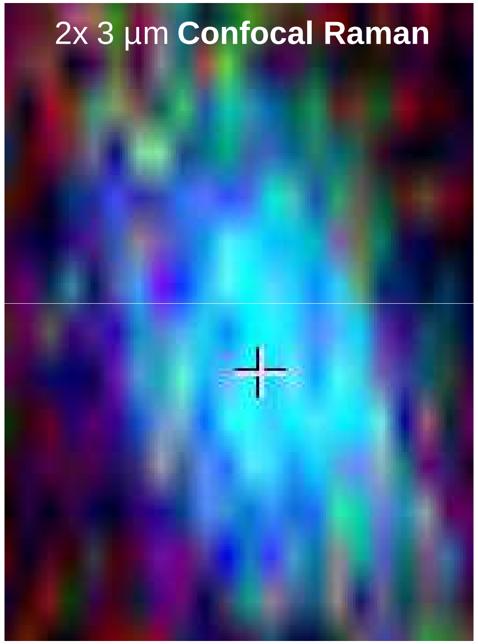
plays the role of a Nano-Antenna

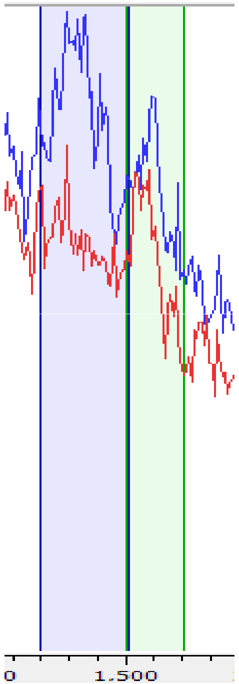
. Signal Enhancement

- *Near-Field Resolution*

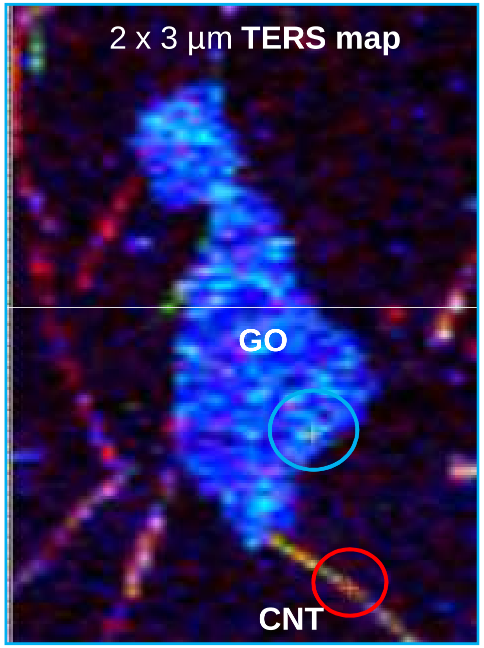
Conventional Raman VS TERS

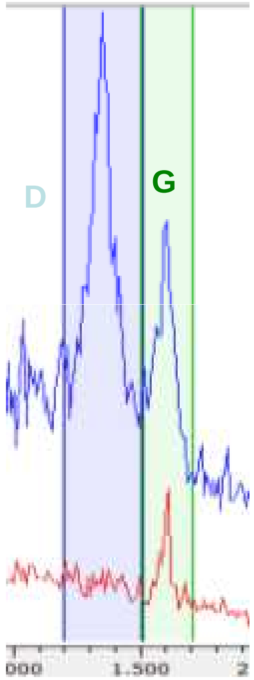
Confocal Raman and TERS of the same area, graphene oxide and CNTs on Au





Confocal Raman
13 mW; integration 1 s





TERS
130 µW; integration 0.2 s

Bringing SPM and Raman together

High resolution Raman spectrometer → Chemical and structural analysis

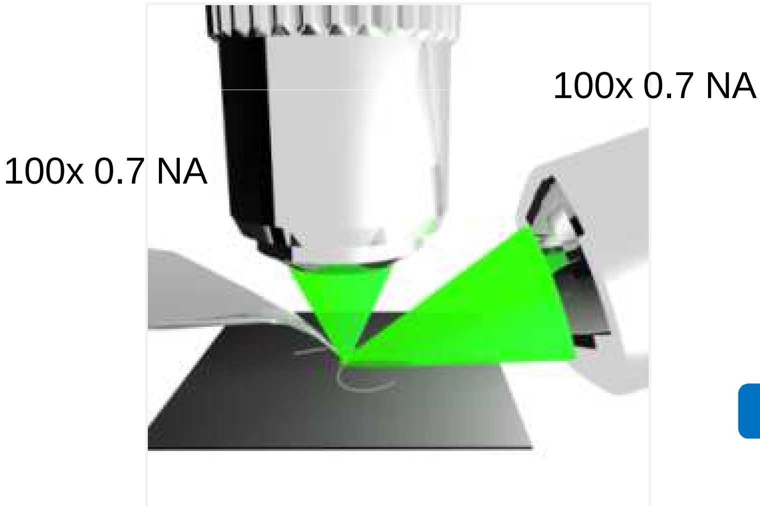
Scanning probe microscope (SPM) → Nano resolved surface mapping

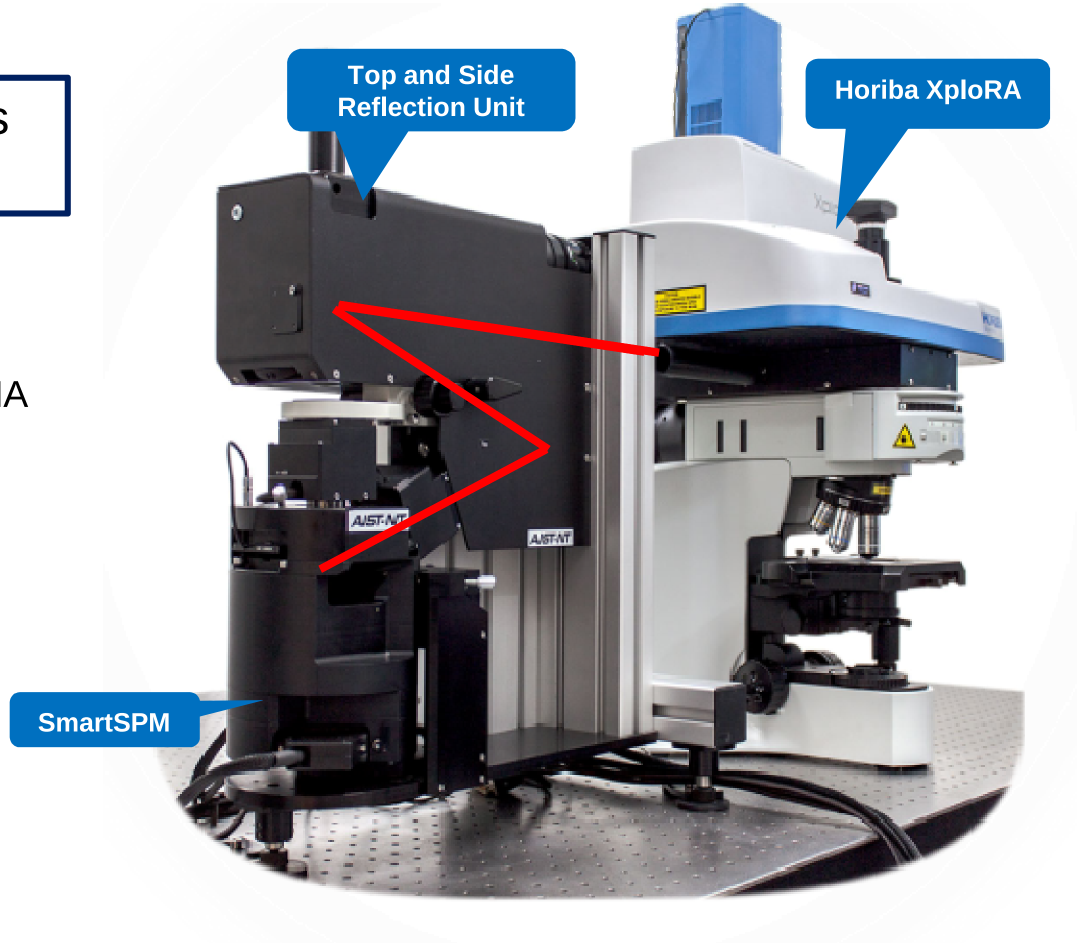
→ **Tip Enhanced Raman Spectroscopy (TERS)**
aka NanoRaman
aka Near-field Raman Spectroscopy

NanoRaman: Optical configurations

Top and Side illumination

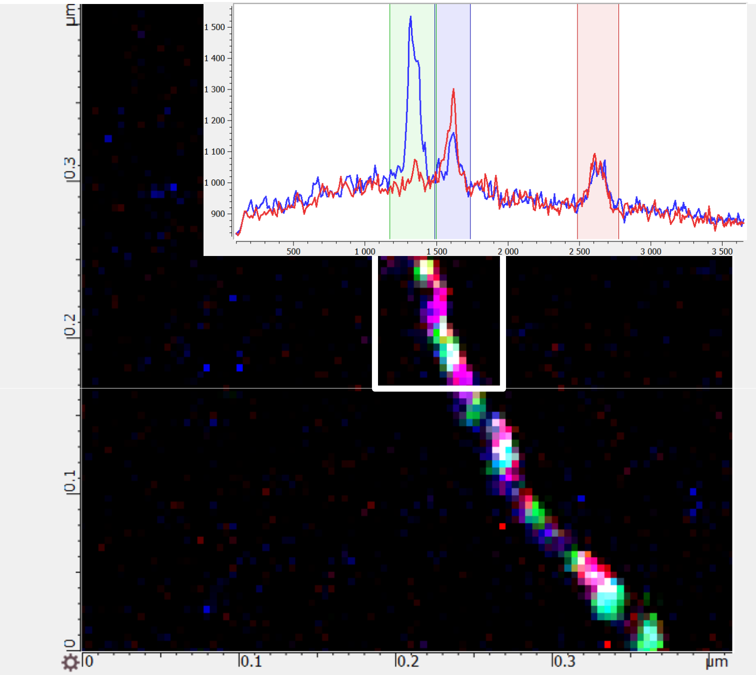
- Top: co-localized measurements
- Side: optimized for TERS



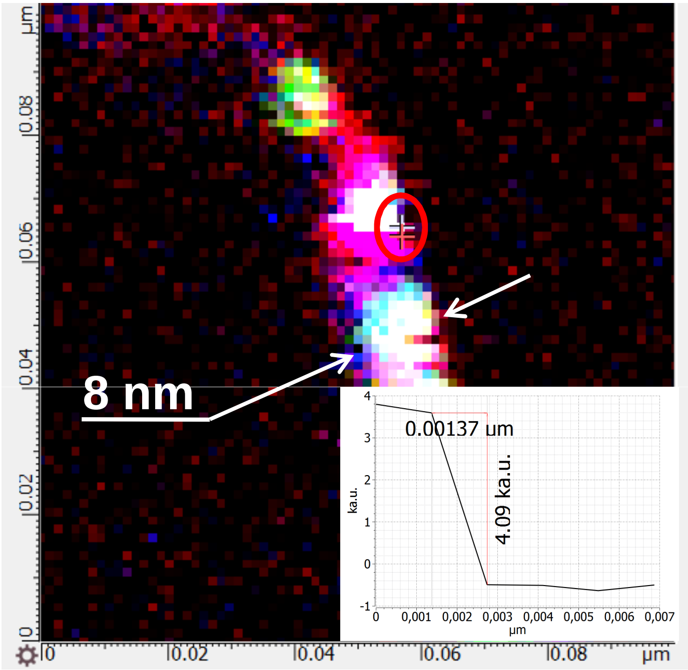


TERS: spatial resolution

CNTs maps out-of-lab conditions!



400 nm x 400 nm (100 x 100 pixels)

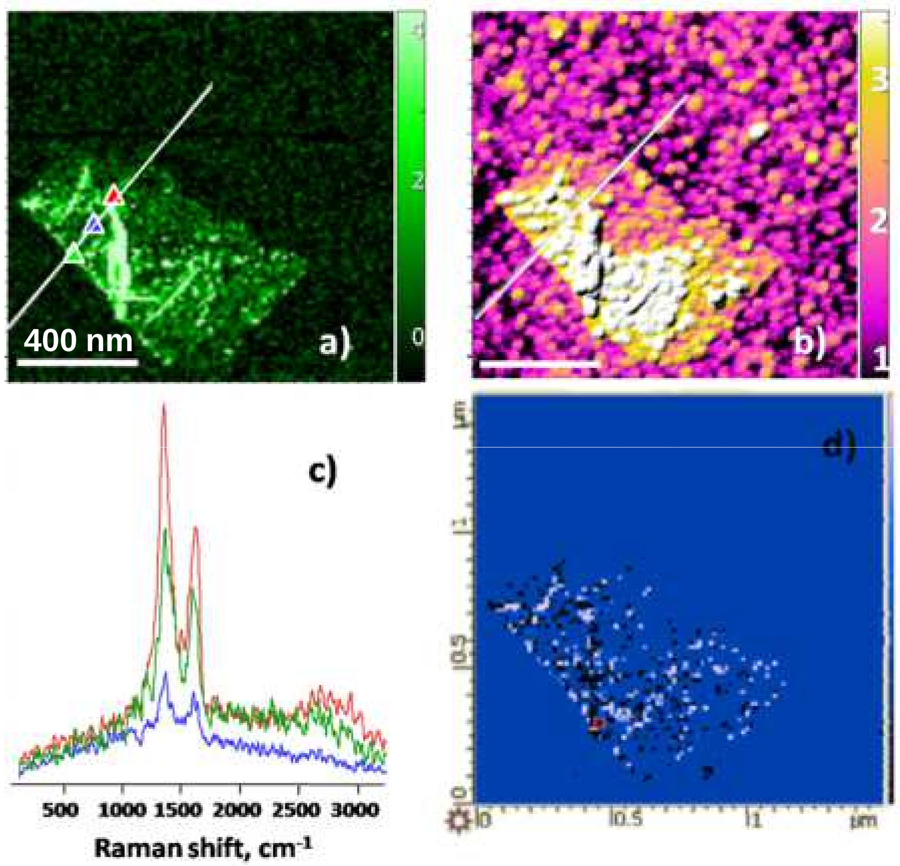


100 nm x 100 nm (75 x 75 pixels), 50 ms per pixel

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

Recorded @ SPIE San Diego, 2015

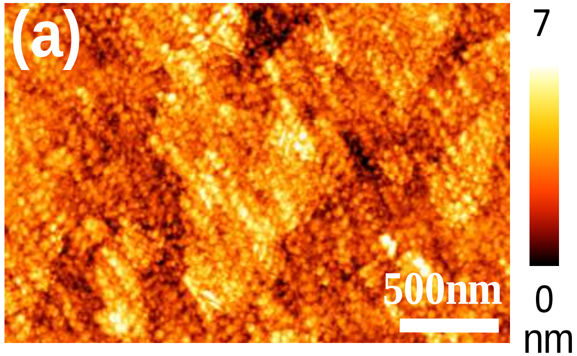
TERS Response of Graphene Oxide



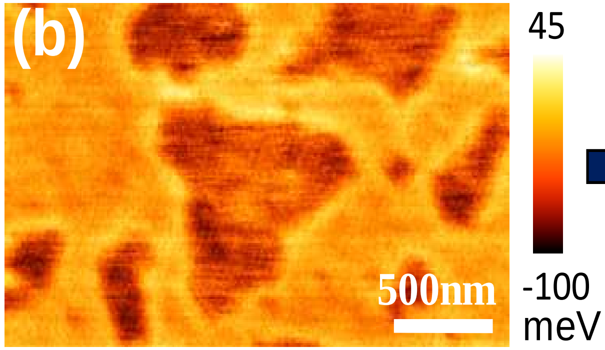
a) 100 pixels per line TERS map of D-band intensity
b) Topography image of the same flake
c) representative TERS spectra
d) distribution of the ratio of G to D band intensities

- Increase of both the D and G TERS band intensities at creases and wrinkles
- increase of TERS activity is not consequence of the increased thickness of the flake at folds

Combined TERS and KPFM mapping of GO-COOH

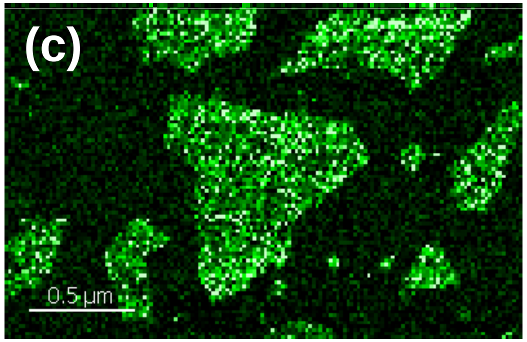


AFM topographic image

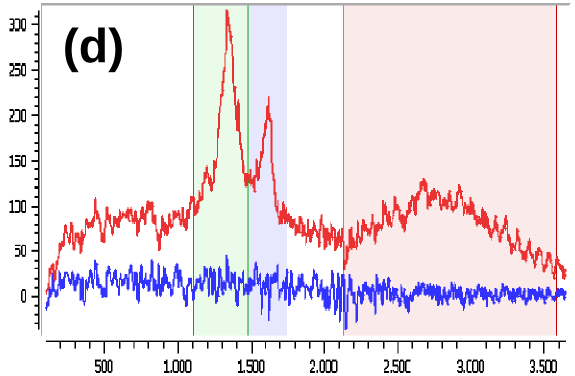


KPFM potential image

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



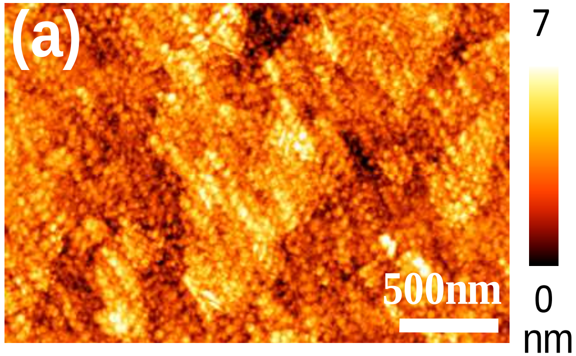
TERS image



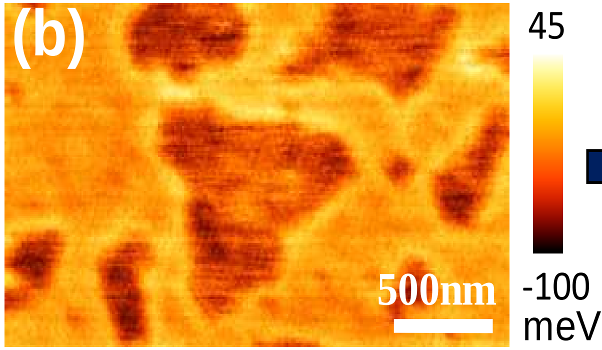
Typical TER spectra

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

Combined TERS and KPFM mapping of GO-COOH



AFM topographic image



KPFM potential image

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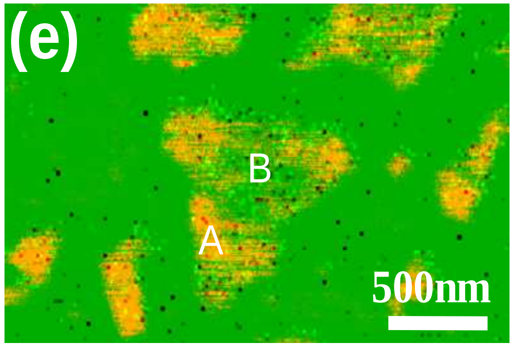
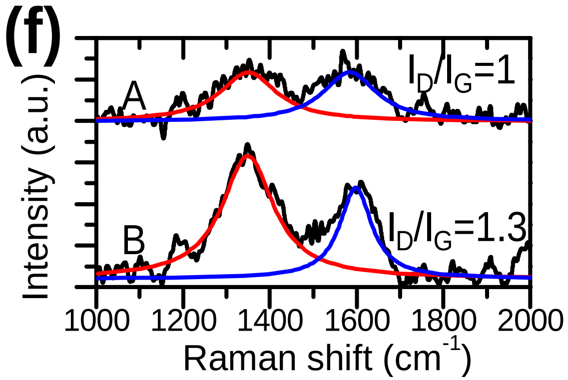


Overlay image using I_D/I_G and inverse KPD



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

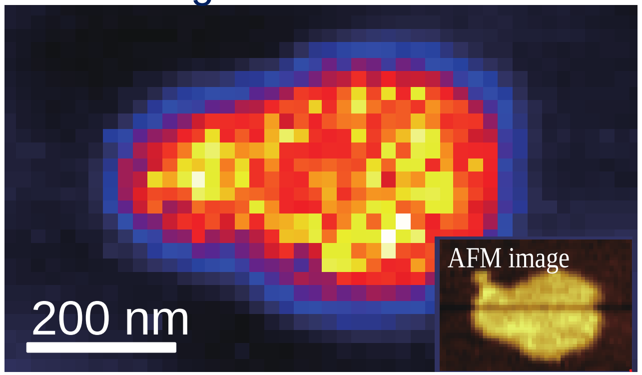
The Fermi level in an area of GO increases with I_D/I_G (ie with density of defects)

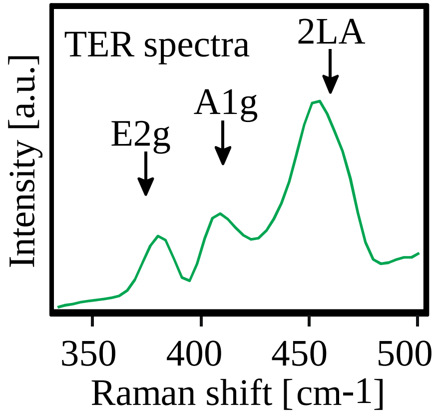
N. Kumar, W. Su (NPL), M. Chaigneau (HORIBA), in preparation

Non gap-mode TERS and TEPL: MoS_2

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

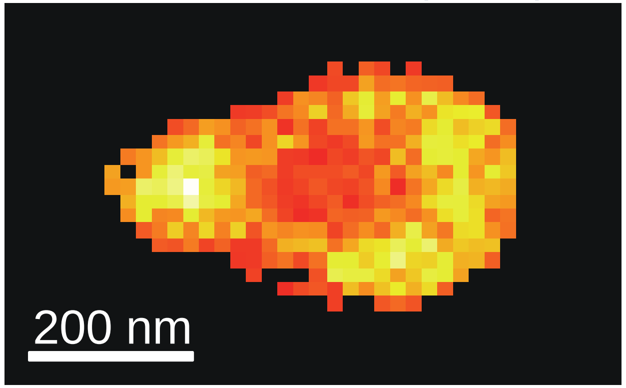
TERS image

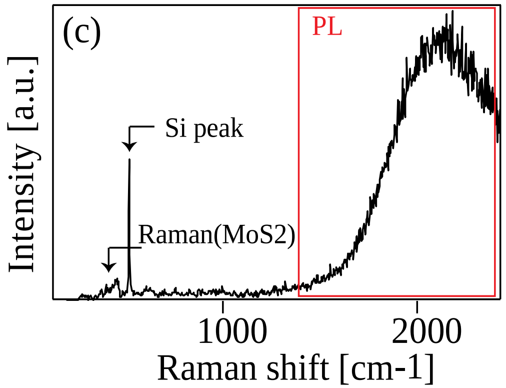




Monolayer flake
(supported by the distance between the E2g and A1g).

TE Photoluminescence (TEPL) image





Excitonic emission is enhanced around the edges

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

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Non gap-mode TERS and TEPL: MoS_2

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

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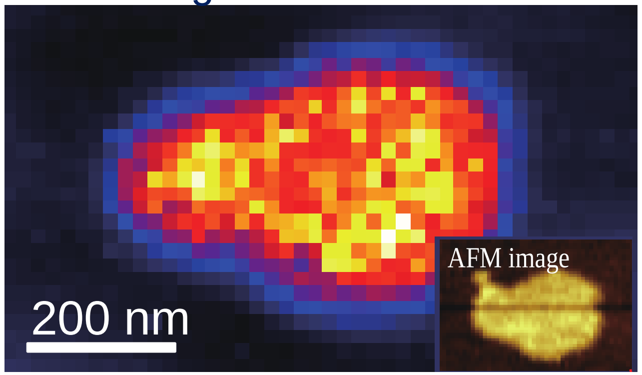
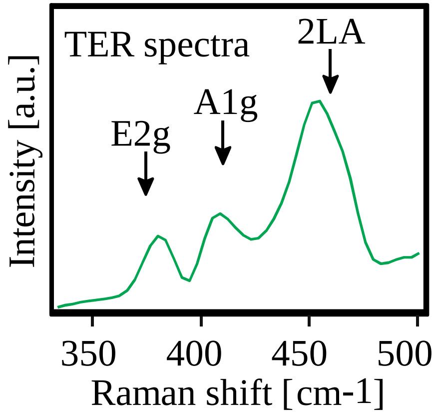
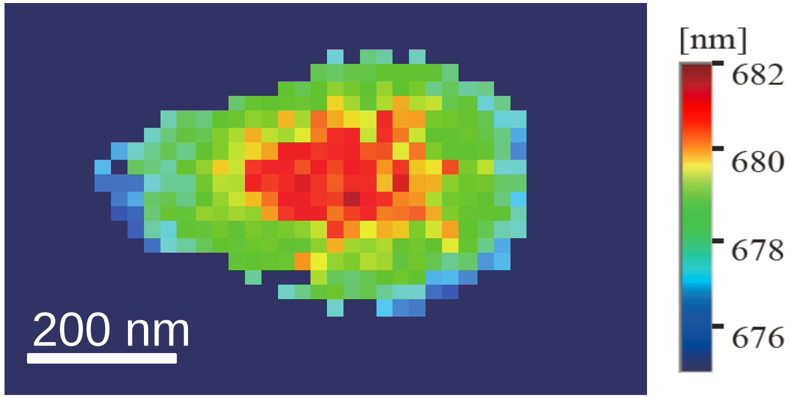




Monolayer flake
(supported by the distance between the E2g and A1g).

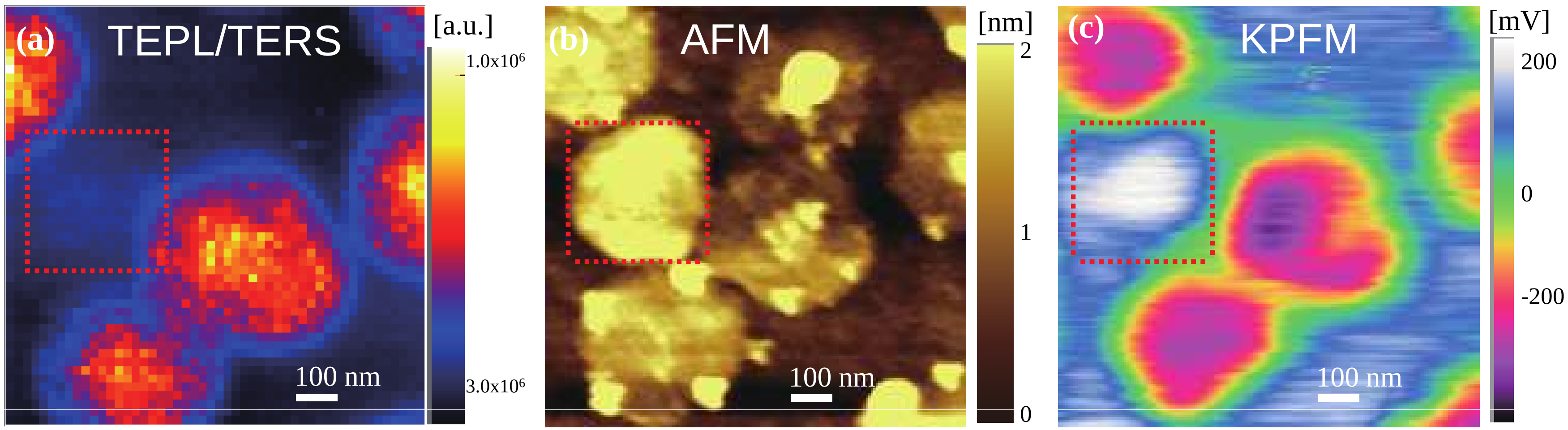
TEPL shift image



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



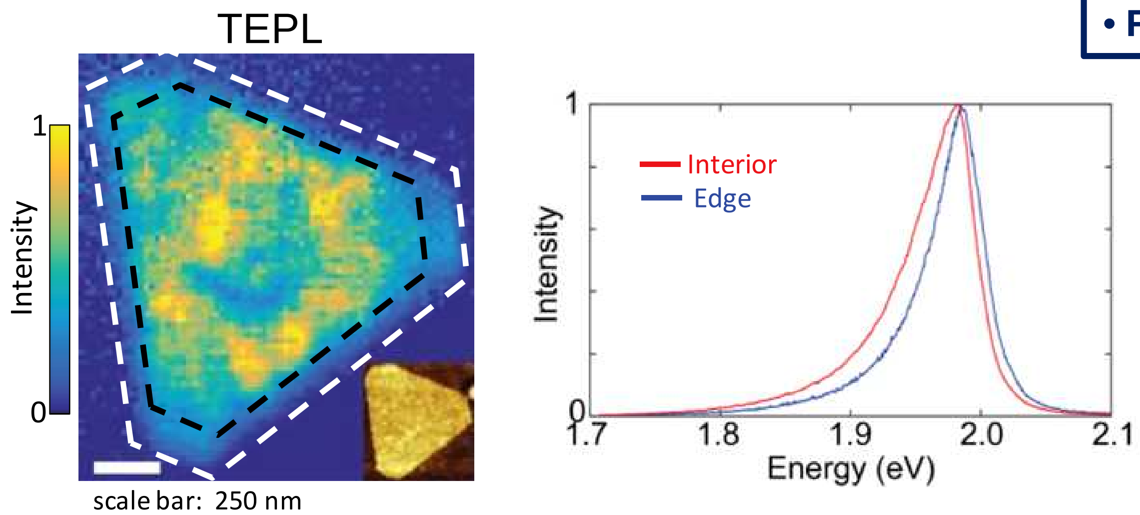
(a) TEPL map, (b) AFM image of monolayer and bilayer MoS2 flakes and (c) Kelvin Force image of the same area

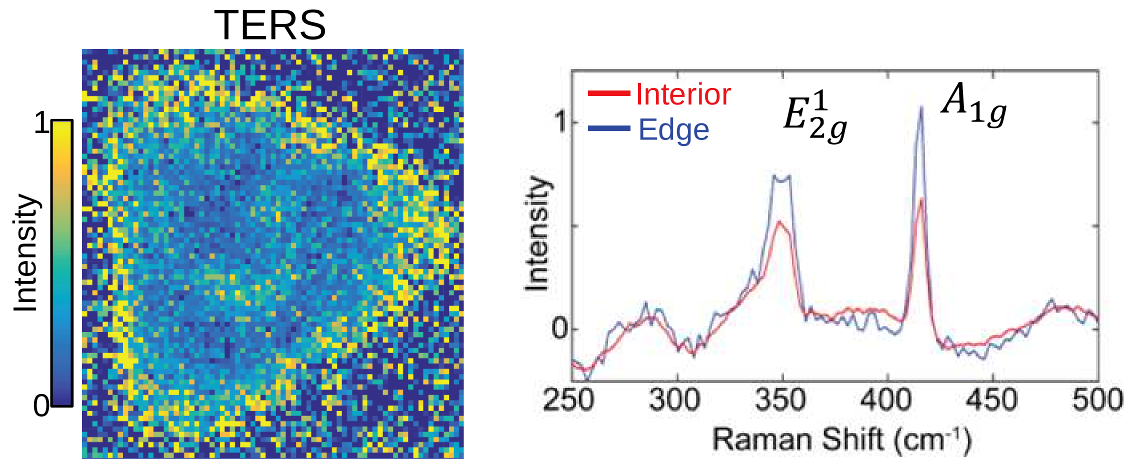
- PL intensity, and TERS (through separation between A1g and E2g peaks) are consistent in distinguishing monolayer and bilayer flakes
- Kelvin probe force map shows positive values (~100 mV) for bilayer flakes and negative values around -300 mV for monolayer flakes.
  →the Fermi energy increases in bilayer MoS2.

Non gap-mode TERS: WS_2

→ extend the TERS technique to others 2D TMDCs:

- CVD grown WS2 on <u>Si substrate</u>
- Ag tips, 638 nm
- Reflection configuration





Monolayer WS_2 edges vs interior: spectral signatures of different doping

Kastl, Chen, Kuykendall, Darlington, Borys, Krayev, Schuck, Aloni & Schwartzberg (LBL), Andrey Krayez (AIST-NT) (submitted).

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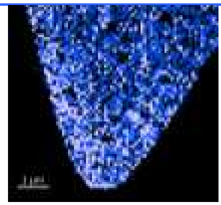
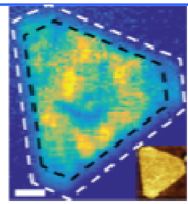
CONCLUSIONS

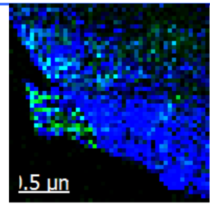
TERS and 2D materials



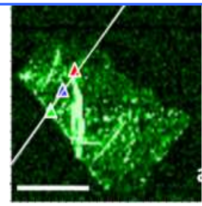
MoS_2



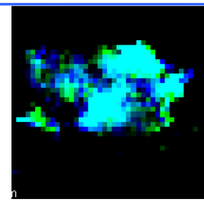
WS_2



WSe_2



GO



BiOCl

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

- **Without detailed NANOSCALE characterization of 1-d and 2D materials, their use in next generation devices is pretty much impossible.**

  TERS can provide reliable information on peculiarities of local structure with resolution <u>below 10 nm</u>.

- **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)

Thank you very much for your attention.

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