NICOLET CZ
MOLECULAR SPECTROSCOPY

Ramanova mikroskopie pro strukturální stadium moderních baterií

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Perspektivy analýzy nových materiálů a zdrojů energie
Ostrava 2022

thermoscientific

Chemical, Elemental and Structural Analysis of Batteries

Application Compendium

Informace ve spektrech

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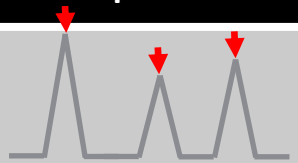
Raman spektra	Změna	Informace	Příklad
	Charakteristické frekvence	Základní identifikace, Rozlišení polymorfů atd.	Rutile a anatas - TiO_2 PS, PET atd.
	Intenzita	Kvantitativní analýza	Koncentrace ve vodných roztocích, tloušťka vrstvy v polymeru atd.
	Změna frekvence (vlnočtu)	Stress/strain	520 cm^{-1} posun pásu Si
	Změna položířky pásu	Disorder či defekty	Crystalline 520 cm^{-1} and amorphous 480 cm^{-1} peak in Si; D band in CM
	Změna intenzity, frekvence i položířky pásů	Vliv teploty, či tlaku	Phase transformation, melting, crystallization
	Změna poměru pásů (polarizovaná excitace)	Symetrie a orientace molekuly	459 cm^{-1} band (A1) of CCl_4; $LiNbO_3$ Raman peaks; Isotactic polypropylene films atd.

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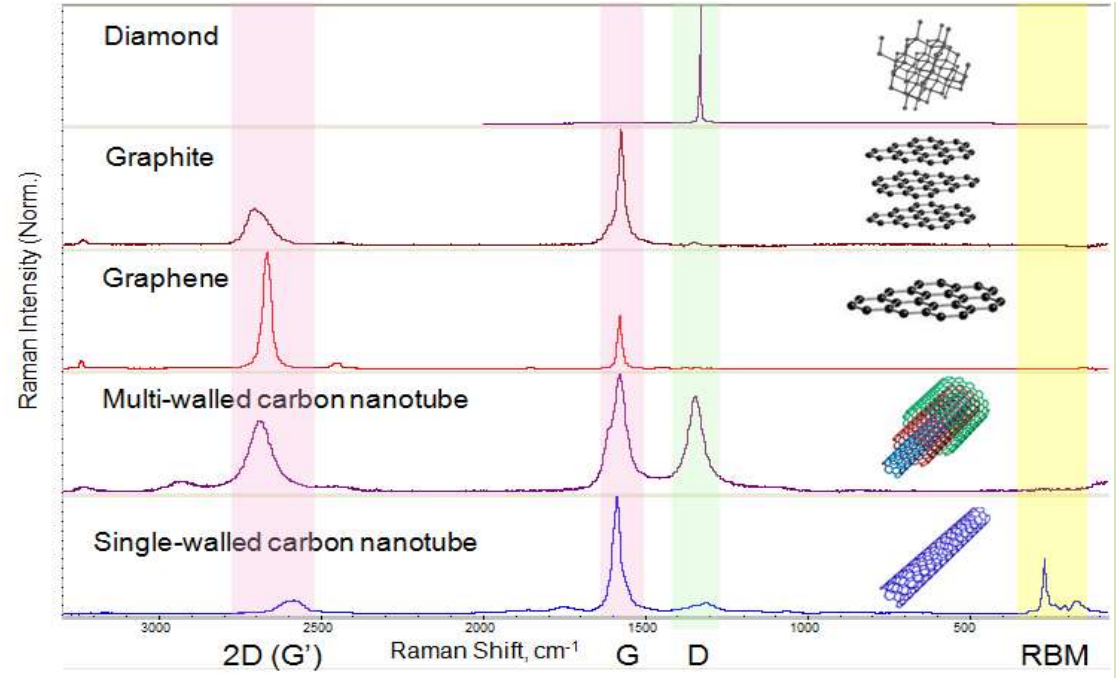
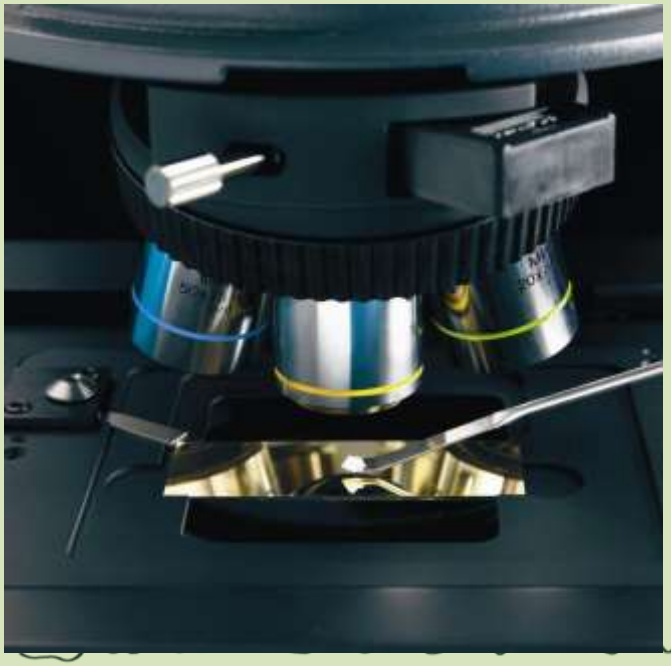
Analyzing cathodes, anodes, and electrodes with Raman spectroscopy: Improving lithium-ion batteries

- Ramanova mikroskopie (DXR3, DXR3xi)
- Obvykle žádná příprava vzorků
- Vývoj a výzkum, ale i rychlá kontrola kvality
- Ideálně Raman + XPS, SEM
- Prostorové rozlišení mappingu až 0,4 mikrometry
- Speciální elektrochemické cely (anody, katody, elektrolyty, kontrola elektrických podmínek a procesu nabíjení a vybíjení)





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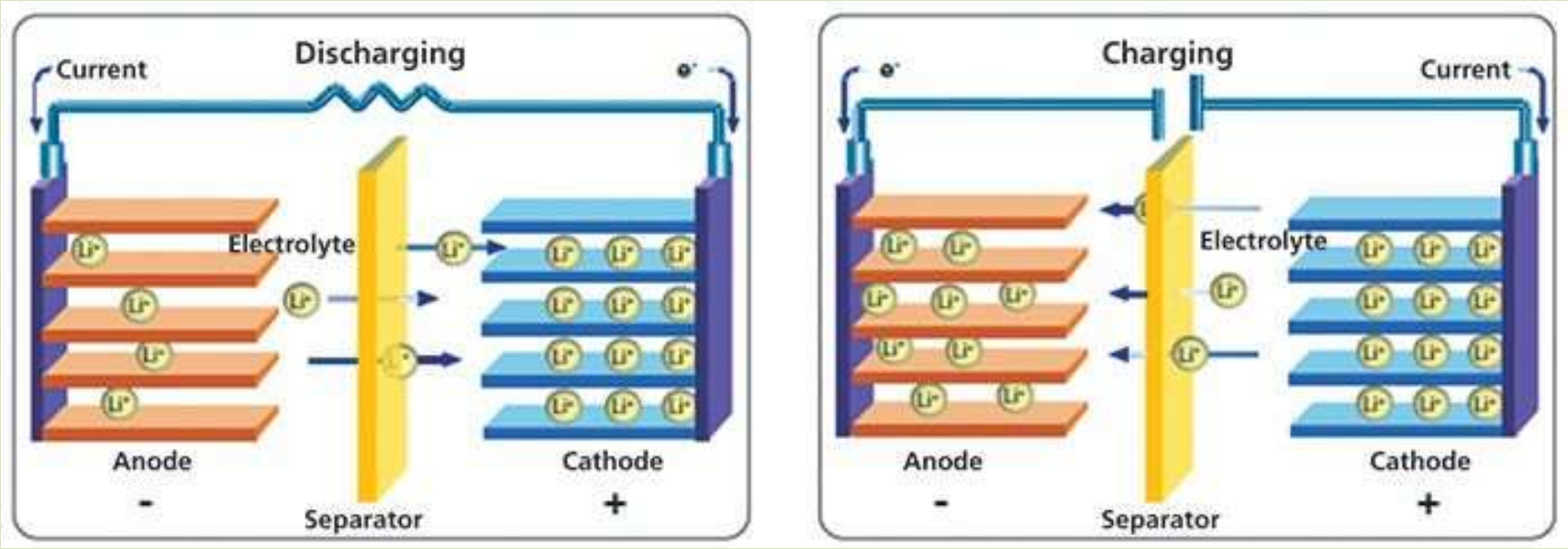
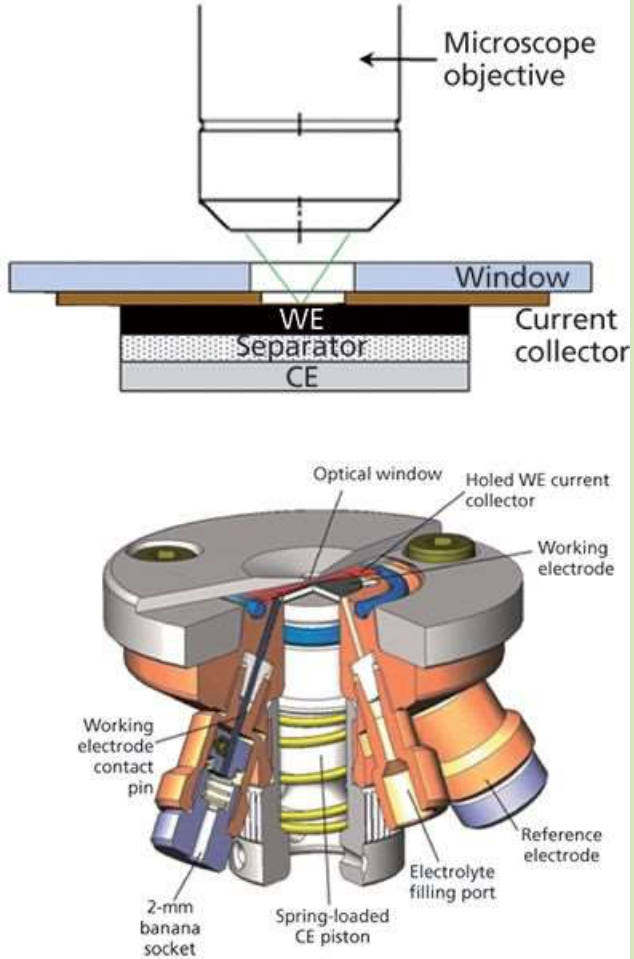
Analyzing cathodes, anodes, and electrodes with Raman spectroscopy: Improving lithium-ion batteries: Lithiation of Graphite (anode material)



Process of Li^+ ions entering the graphitic structure of the anode is called *intercalation*. Intercalation causes changes in the anode structure-primarily a **swelling** of the graphite structure.

Analyzing cathodes, anodes, and electrodes with Raman spectroscopy: Improving lithium-ion batteries: Lithiation of Graphite (anode material)



- ECC-Opto-Std optical electrochemical cell (EL-CELL).
- Enables the investigation of batteries
- Working electrode material is placed under a sapphire (Al_2O_3) window
- Electrode material (graphite powder in this example) is spread onto a copper grid = current collector.
- Working electrode is sandwiched from below, with a glass fiber separator soaked with the electrolyte solution and lithium metal as the counter electrode
- Raman measurement during lithiation (charging) – 480 minutes

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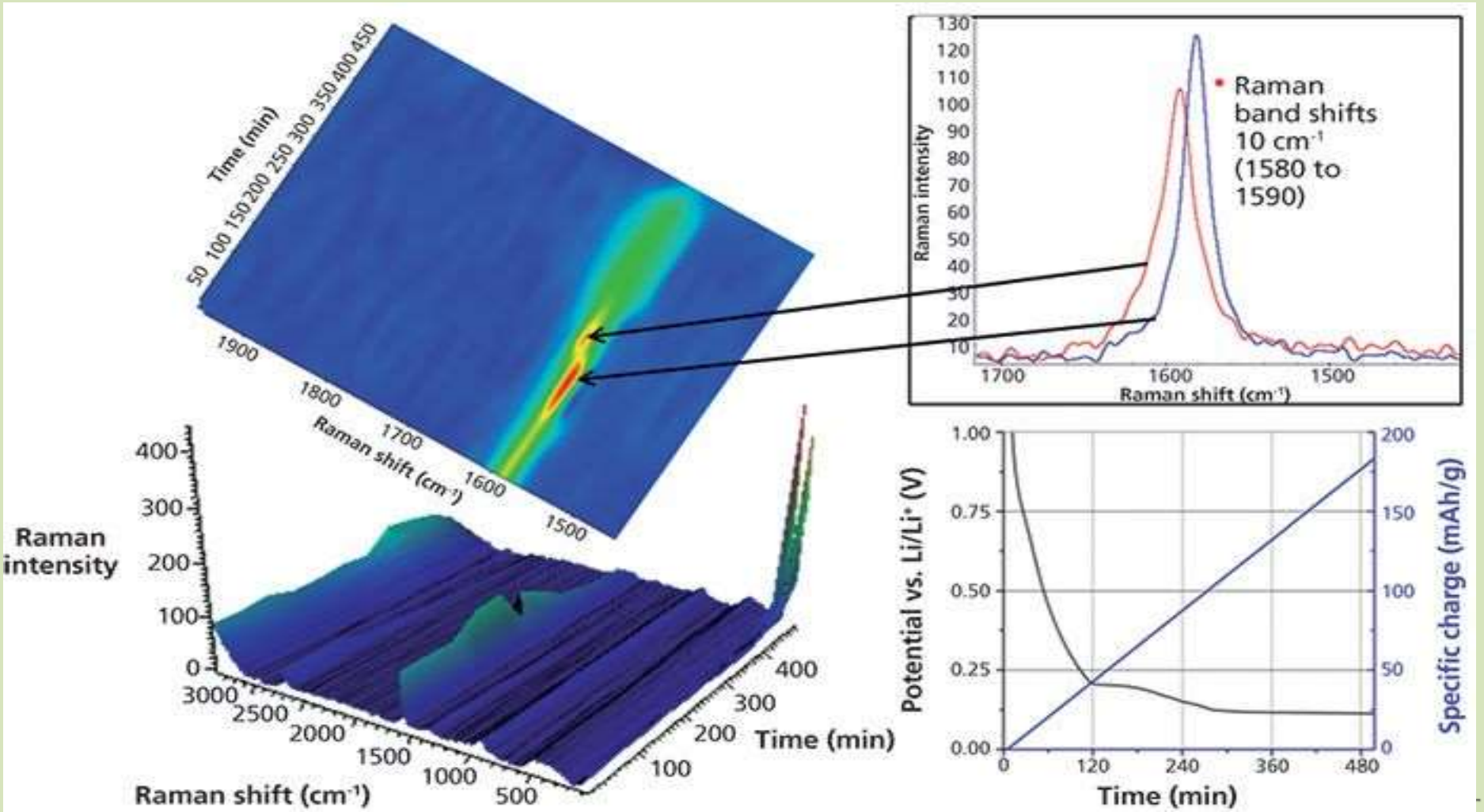
Analyzing cathodes, anodes, and electrodes with Raman spectroscopy: Improving lithium-ion batteries: Lithiation of Graphite (anode material)



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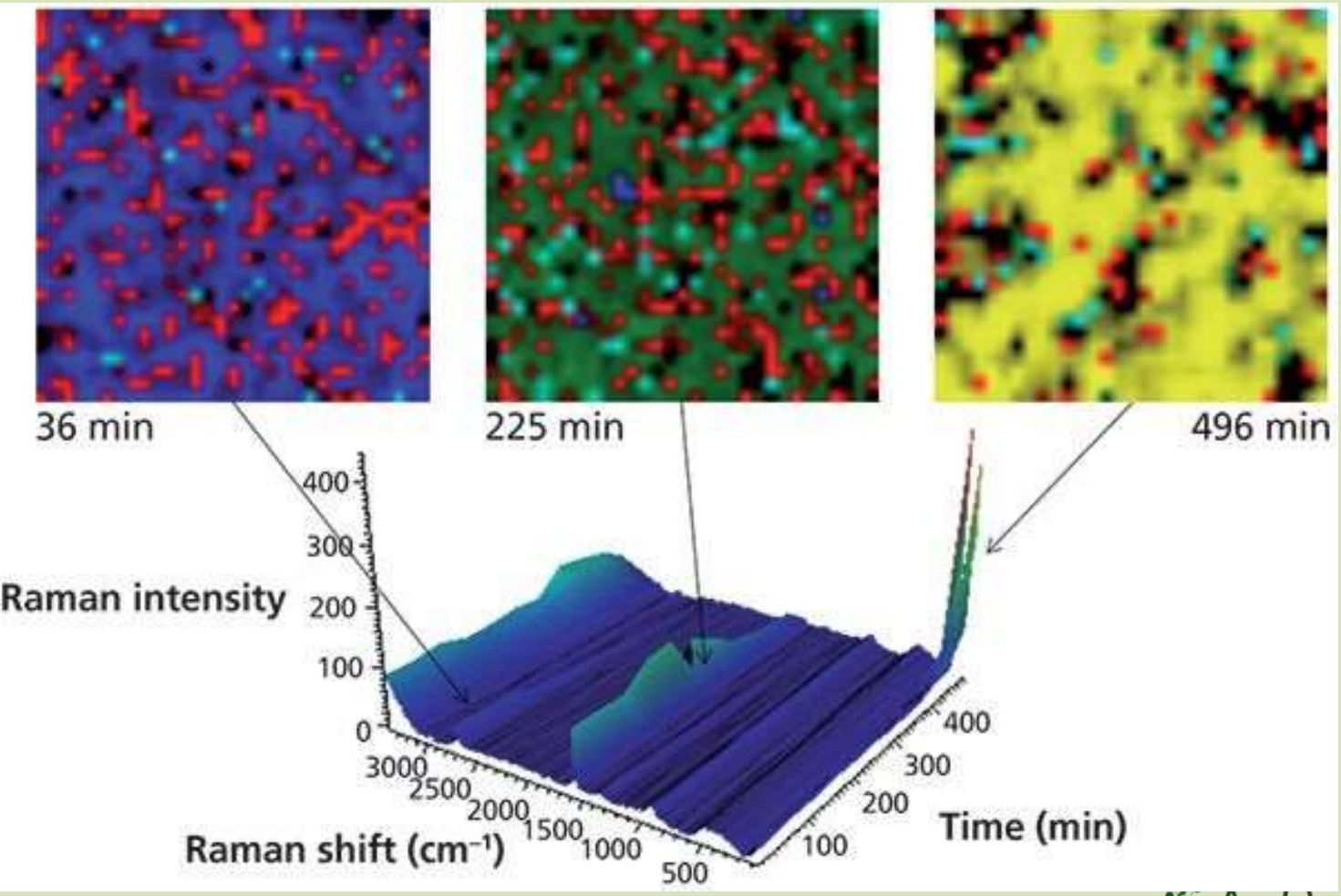
Analyzing cathodes, anodes, and electrodes with Raman spectroscopy: Improving lithium-ion batteries: Lithiation of Graphite (anode material) – MCR IMAGING



- blue
  1580 cm^{-1} band
- green
  1590 cm^{-1} band
- yellow
  154 cm^{-1} band
- Red:
  carbon black (conductivity enhancer)

Infračervená nanoskopie a imaging s rozlišením 10 nm: nano-FT-IR

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Překonání difrakčního limitu pro infračervenou mikrospektroskopii: technika IR-SNOM

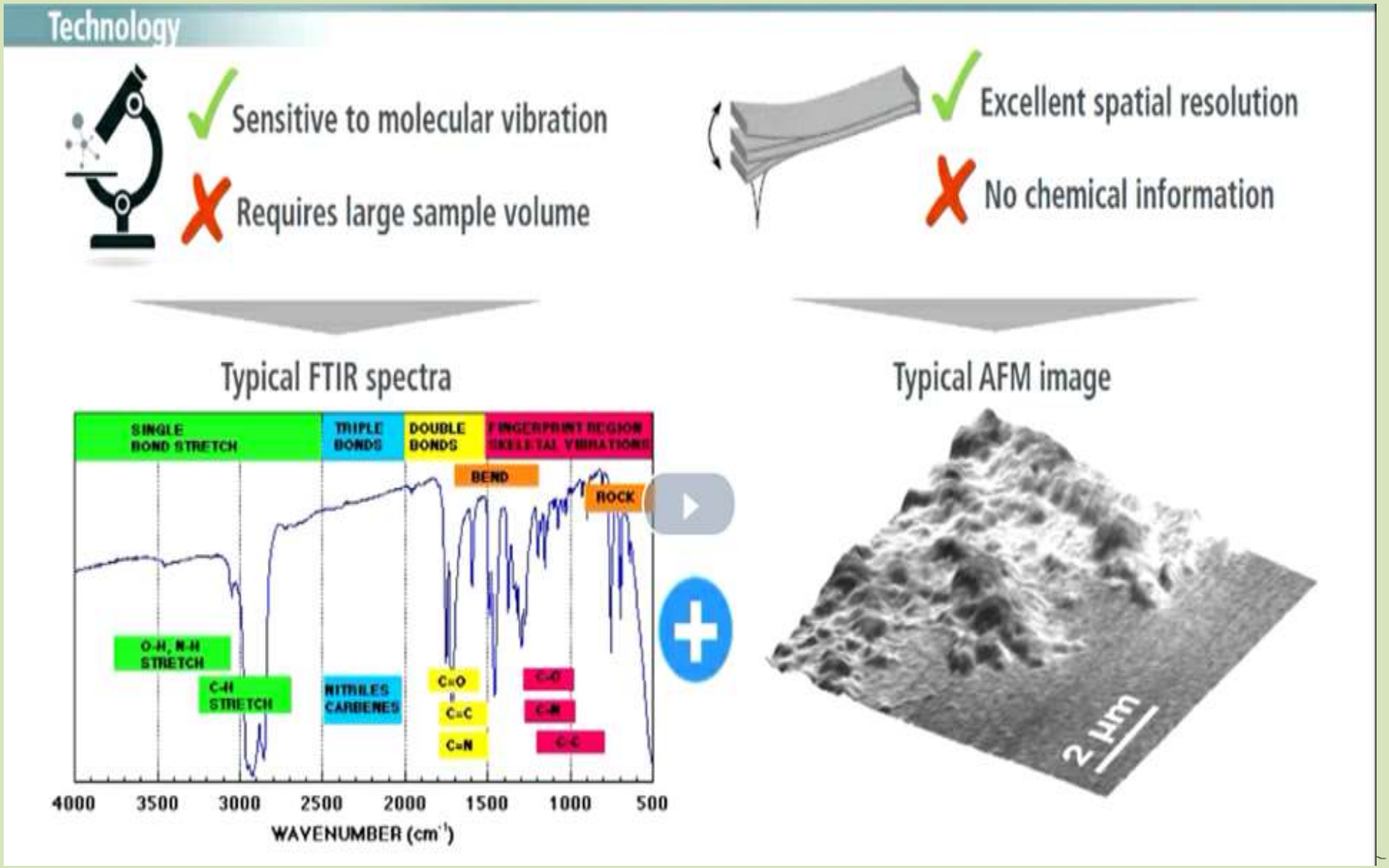
- **FT-IR (cca 5 x 5 µm)**
- **RAMAN (cca 0,4 µm)**
- **IR-SNOM: 10 nm!**

Hlavní aplikace

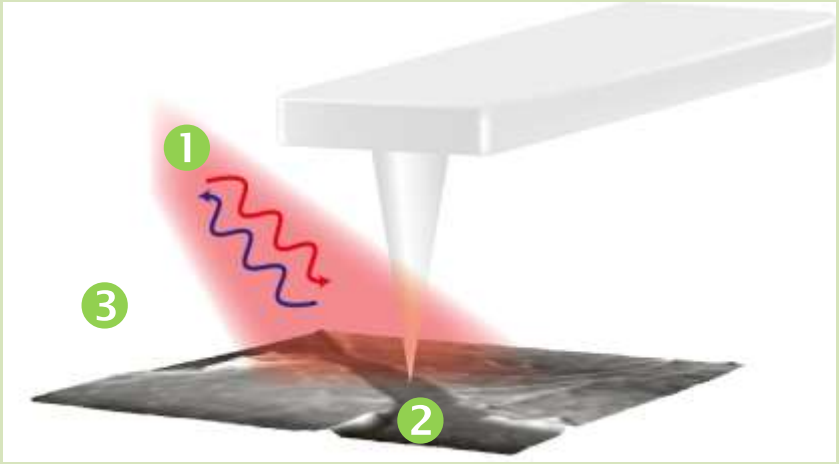
- Polymerní výzkum a průmysl
- Korozní inženýrství
- Nanostrukturní mapování
- Biomateriály
- Lékařství
- Analýza grafenických materiálů
- Analýza nanovláken
- QC/vývoj polovodičů
- Struktury plasmonů

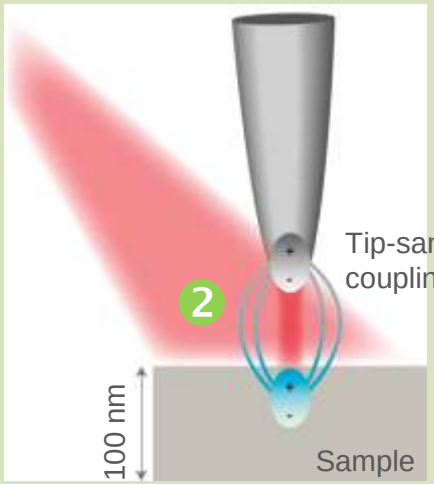
s-SNOM (**s**cattering-type **S**canning **N**ear-field **O**ptical **M**icroscopy)

IR-SNOM: Kombinace AFM a FTIR (IR) mikroskopie



Prostorové rozlišení nezávisí na vlnové délce!





1 › Fokusace laserového paprsku na vodivý AFM hrot

2 › Zachycení světla na vrcholu hrotu vytváří velmi prostorově malý „nano-fokus“, který generuje optickou interakci (v tzv. blízkém poli) ve vzorku

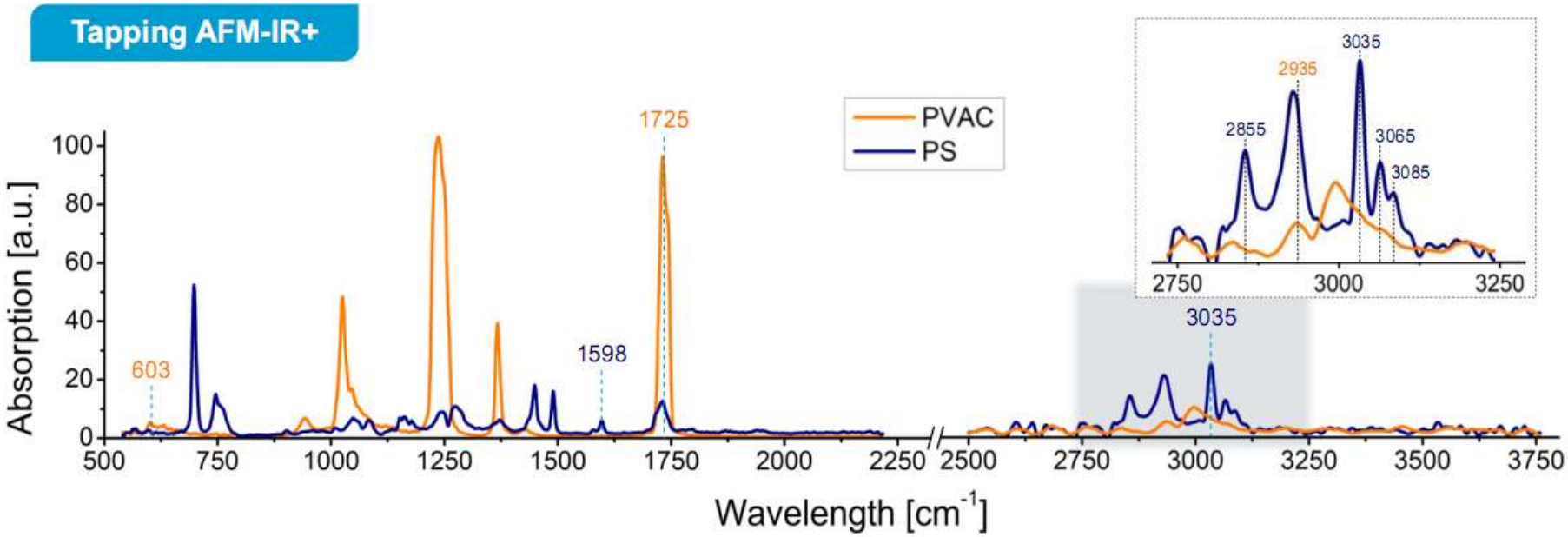
3 › Rozptýlení vysoce lokalizované informace z blízkého pole zachytí optická detekce záření pomocí inovativních interferometrických detekčních schémat – vznikají chemické mapy (imaging) a např. infračervená spektra FT-IR (IR)

IR-SNOM: zdroje záření = UV, VIS, NIR, MID-IR, THz !
Laditelné lasery, kaskádové lasery atd.

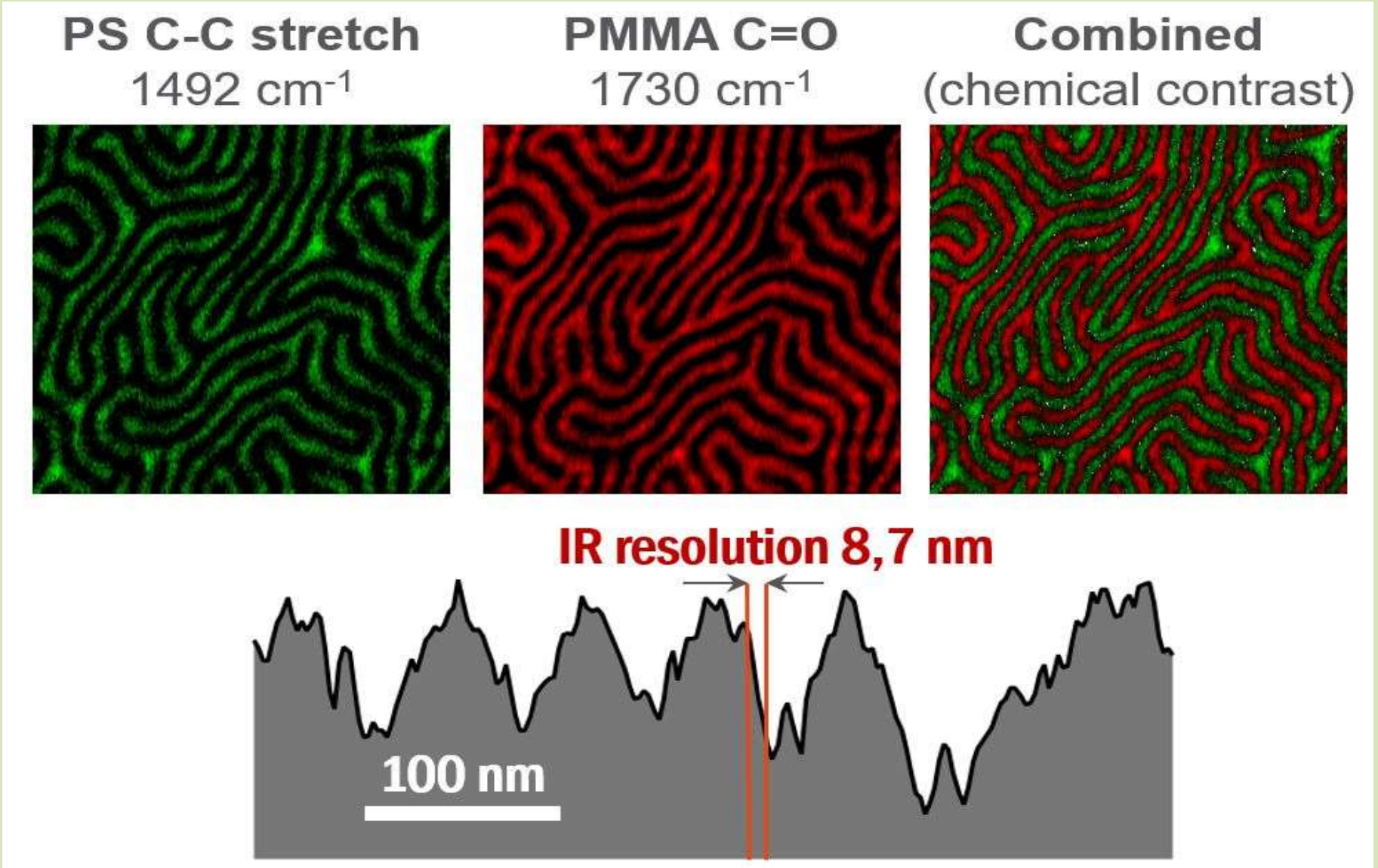
Novinka 2022 single widely tunable laser wOPO

ONE SOURCE TO RULE THEM ALL!

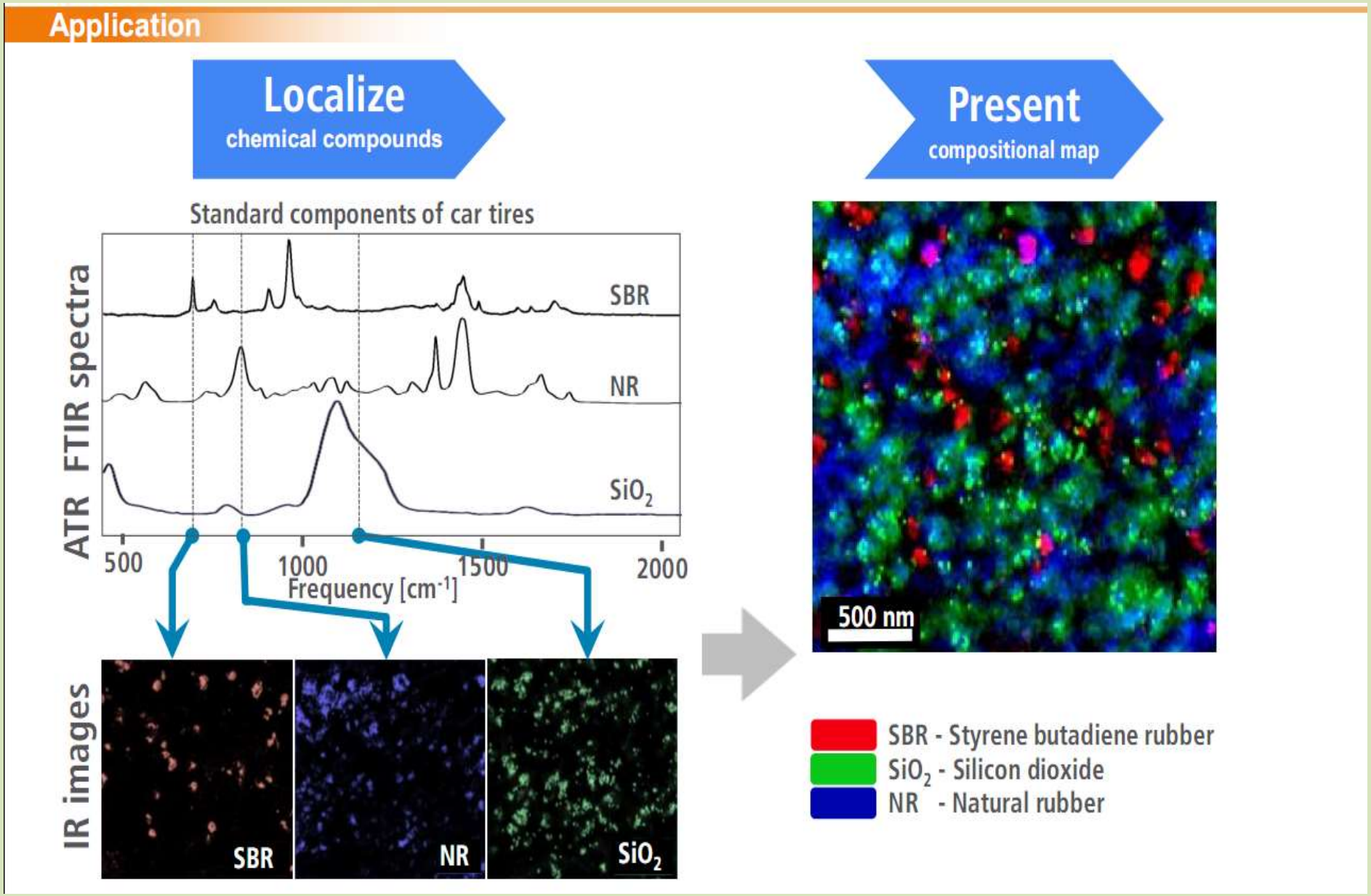
- Unikátní široký ladící rozsah: 1.4 – 18.4 µm (7 140 – 540 cm^{-1})
- Narrow linewidth <4 cm-1 in the entire tuning range
- Ultrafast frequency sweeping up to 14000 cm-1/sec
- Widest application potential: organické i anorganické vzorky
- Easy to use: fully motorized with fast automatic switching between spectral ranges
- Superior stability: completely integrated, single housing design



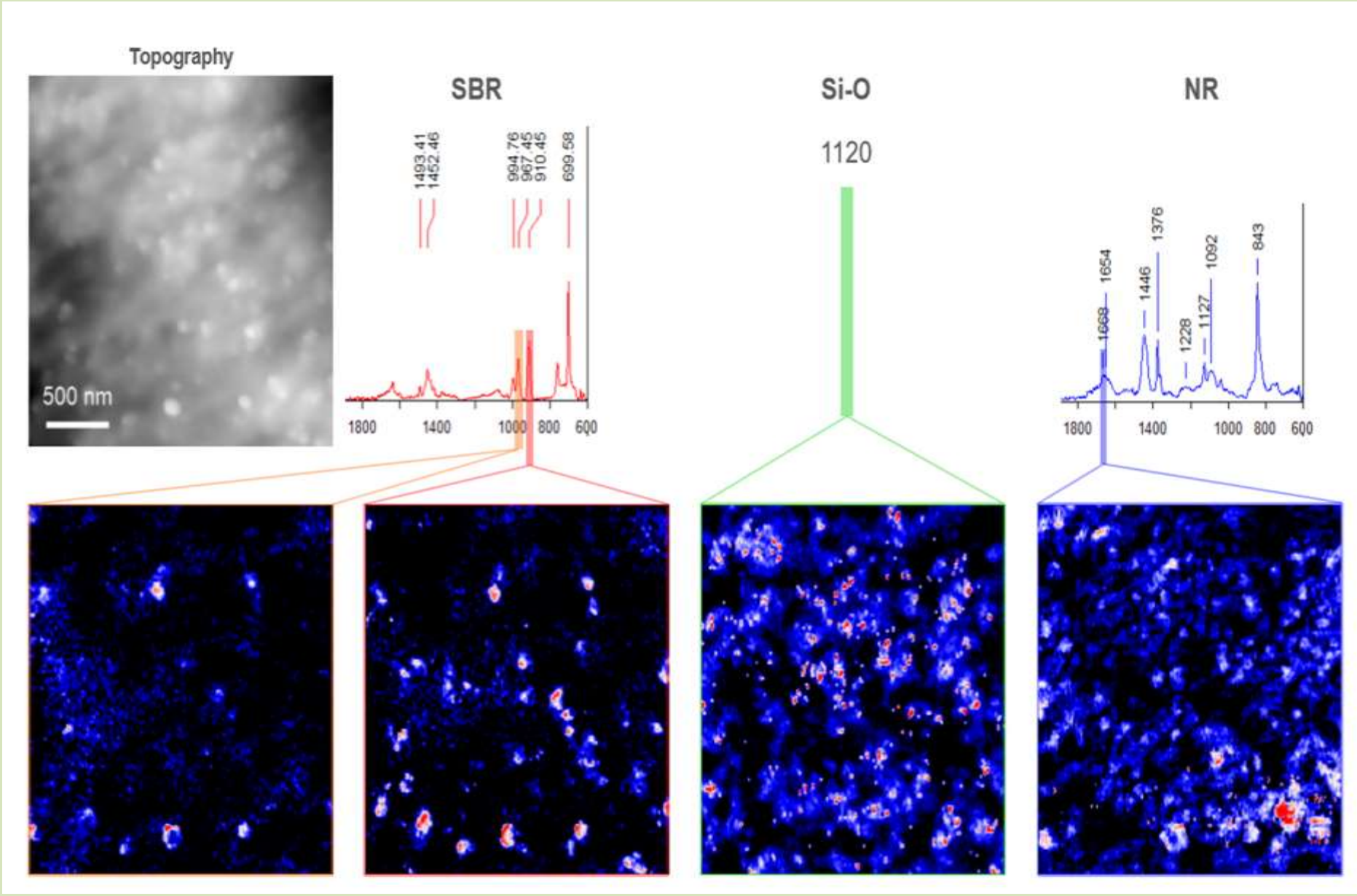
Příklad IR-SNOM mapování: PMMA/PS polymer blend: laditelný laser jako zdroj IR záření



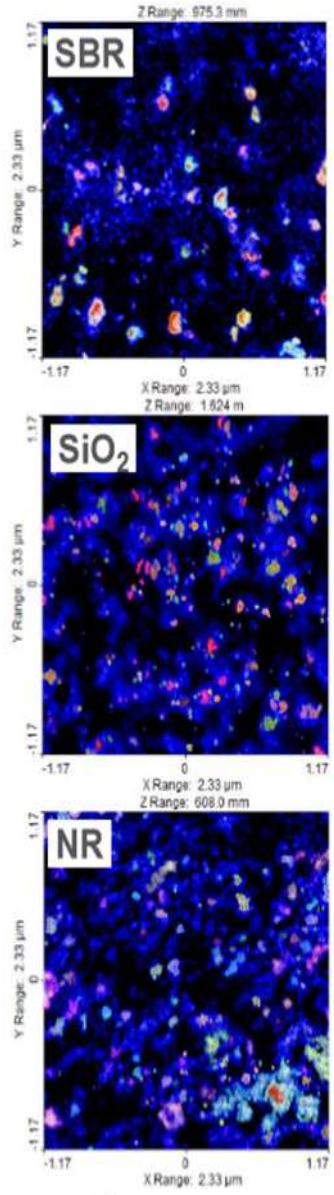
Příklad IR-SNOM: mapování vzorku pneumatik

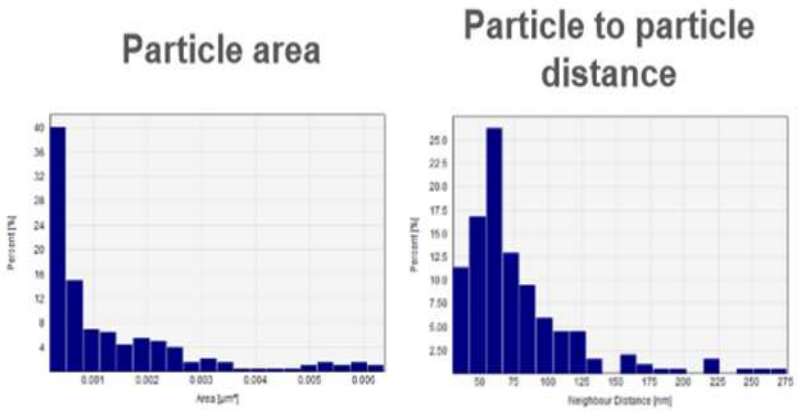


Příklad IR-SNOM: mapování vzorku pneumatik



Příklad IR-SNOM: mapování vzorku pneumatik





› Statistical analysis e.g. SPIP software

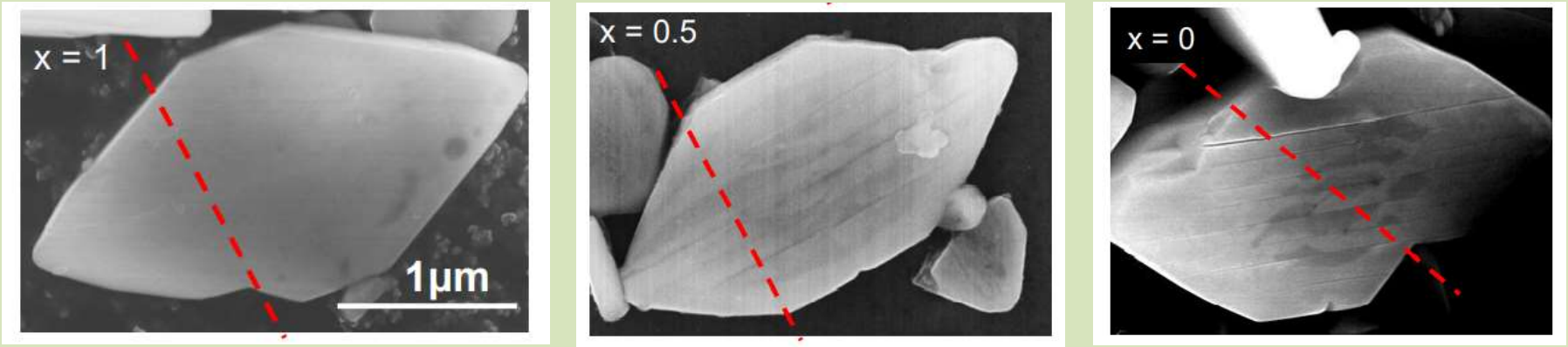
Channel/ compound	Particle diameter (mean)	Area coverage	Particle to particle distance (mean)
SBR	56 ± 34 nm	3.9 %	133 ± 82 nm
SiO_2	36 ± 19 nm	4.8 %	78 ± 42 nm
NR	47 ± 43 nm	10.9%	92 ± 47 nm

High image quality of s-SNOM scans enables statistical analysis of individual compounds

Příklad IR-SNOM: IR Near-Field Spectroscopy and Imaging of Single Li$_x$FePO$_4$ Microcrystals

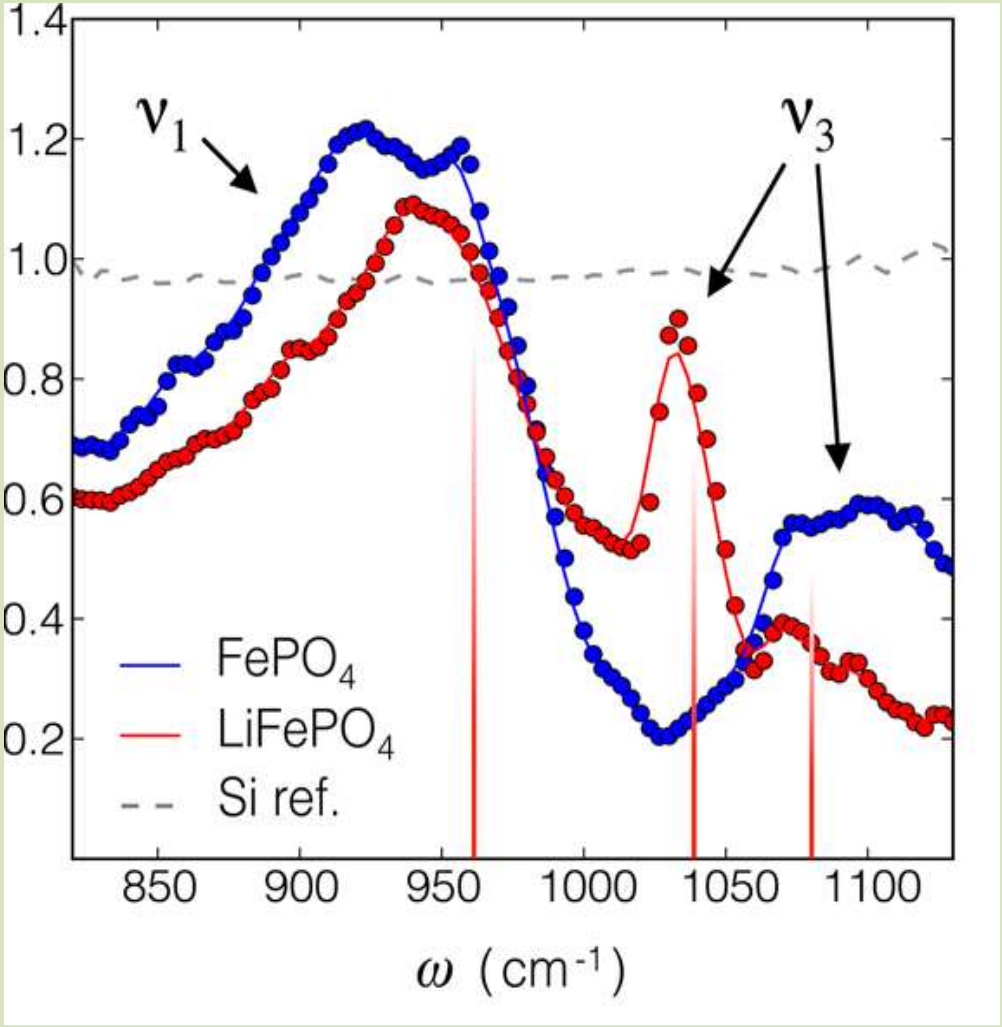
This study demonstrates the unique capability of infrared near-field nanoscopy combined with Fourier transform infrared (FTIR) spectroscopy to map phases distributions in microcrystals of Li$_x$FePO$_4$, a positive electrode material for Li-ion batteries.

Charging and discharging of the cathode material LiFePO$_4$ - delithiation

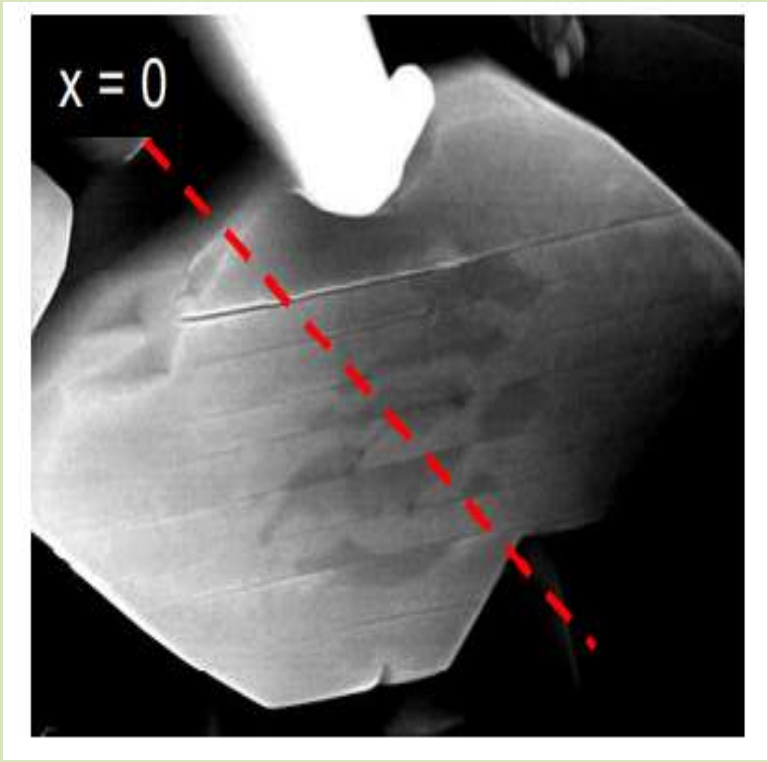


Li$_x$FePO$_4$ – delithiace, SEM images of single LiFePO$_4$, Li$_{0.5}$FePO$_4$, and FePO$_4$ microcrystals, revealing cracks along the crystal surface after delithiation.

Příklad IR-SNOM: IR Near-Field Spectroscopy and Imaging of Single Li_xFePO_4 Microcrystals



Nano-FTIR spectra of pure-phase $LiFePO_4$ and $FePO_4$ microcrystals



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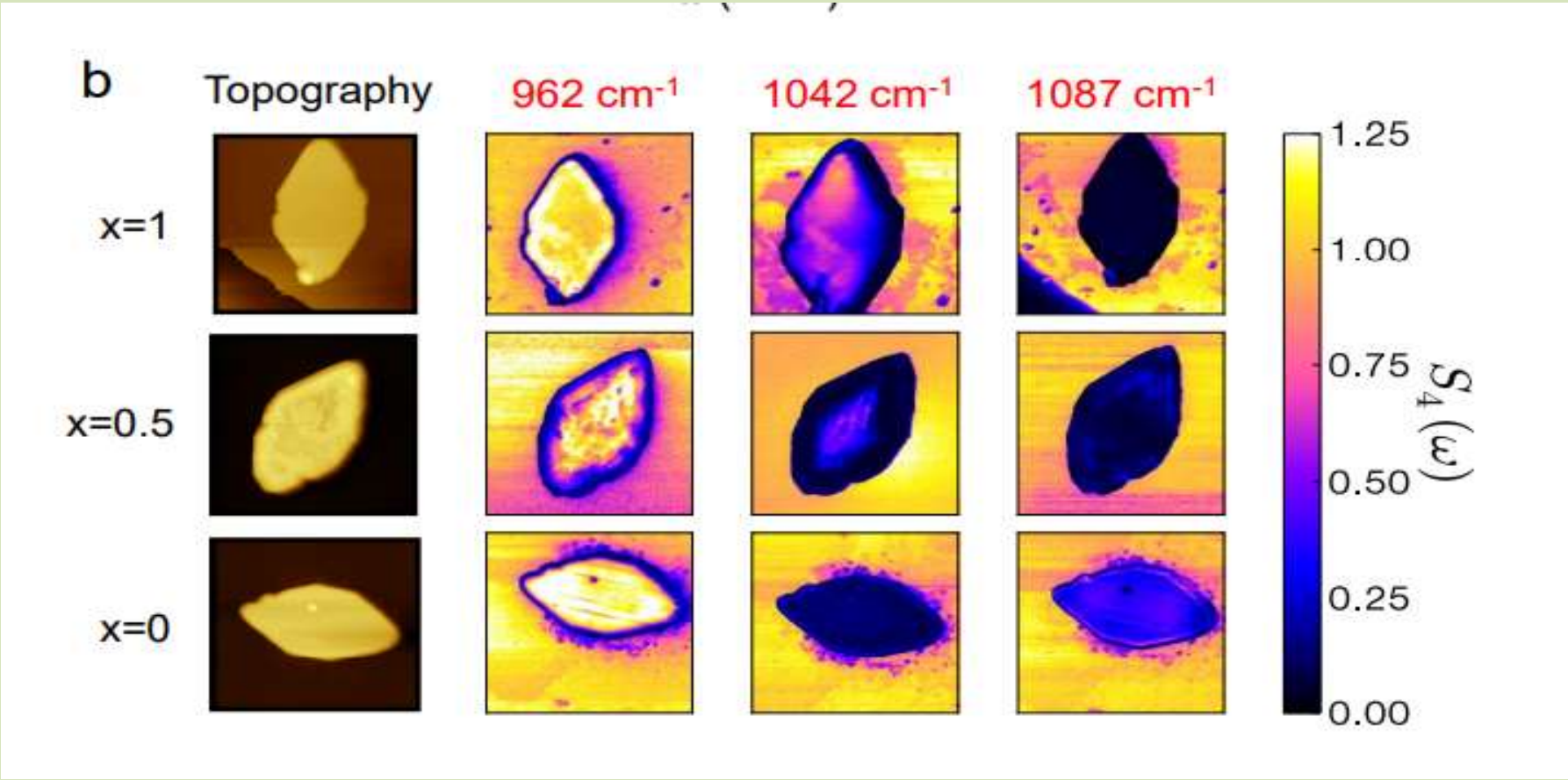
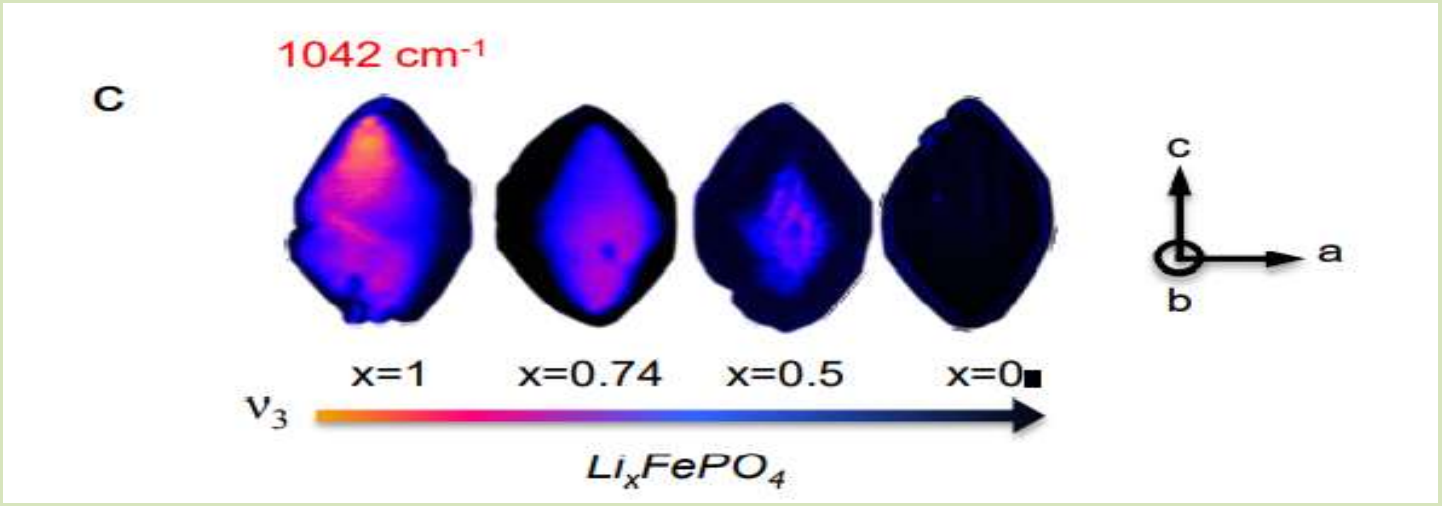
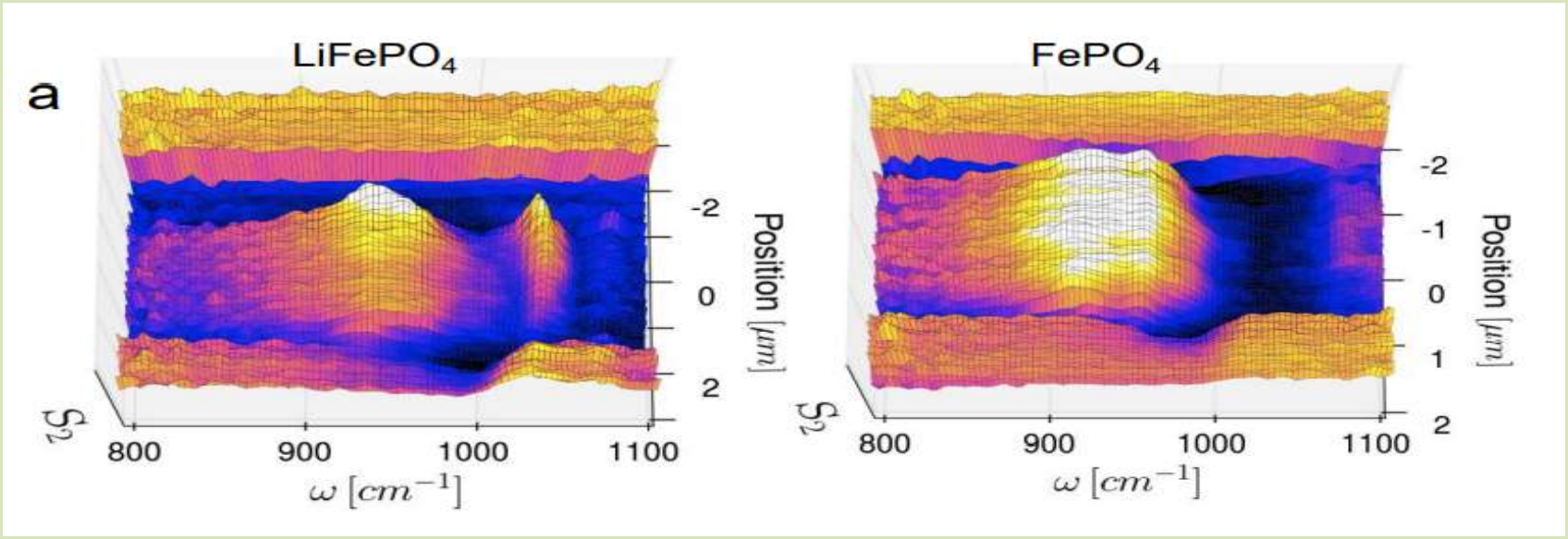


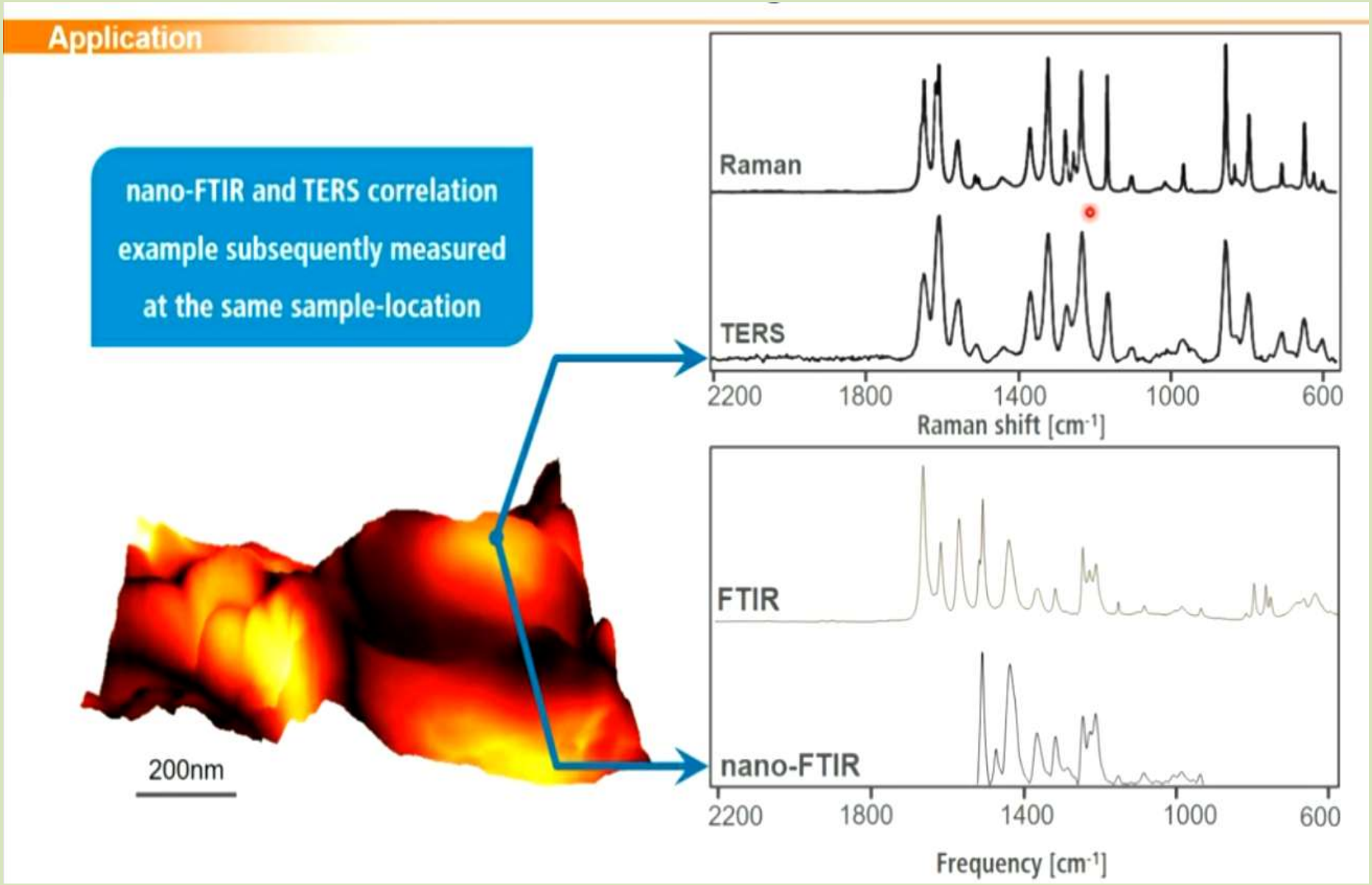
AFM topography and corresponding infrared near-field amplitude images acquired at 1087, 1042 and 962 cm^{-1} for $LiFePO_4$, $Li_{0.5}FePO_4$ and $FePO_4$ crystals

Příklad IR-SNOM: IR Near-Field Spectroscopy and Imaging of Single Li_xFePO_4 Microcrystals





Kombinace FTIR (SNOM) a Raman (TERS)



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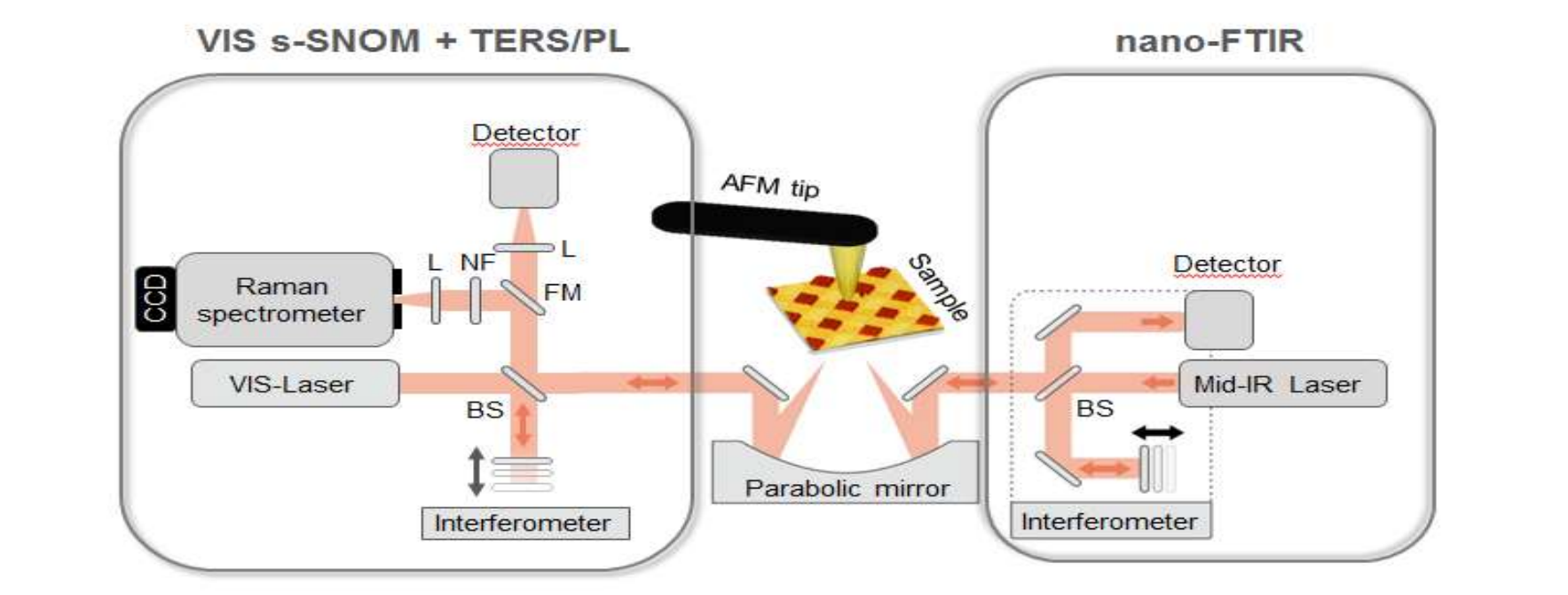

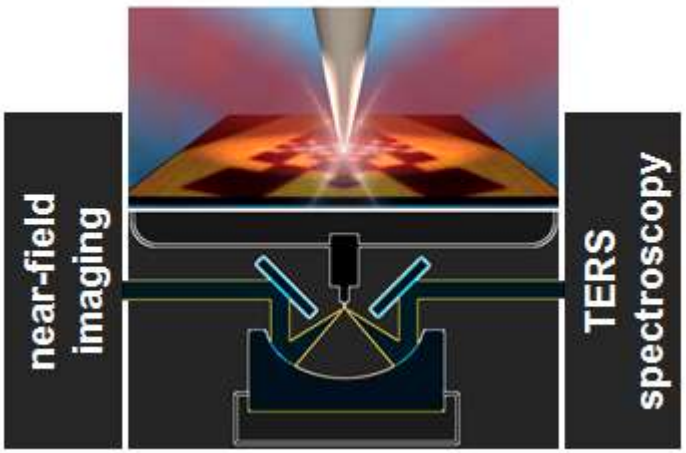

correlative TERS and nano-FTIR

spectroscopy mode

using patented dual beam-path design

IR-neaSCOPE +TERs

Exclusive

•Same spot for nano-FTIR and nano-Raman/PL spectroscopy
using modular design and multi-port access to the AFM-tip,

•Maximum TERS signal even with standard AFM probes
by simple alignment using strong elastic light scattering from the tip,

•Single user interface for all measurement modes
optimized for storing and organizing multidimensional correlative data.

Děkuji za pozornost!

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