Macro, micro and nano-Raman spectroscopy in 2D systems: fundamentals and applications

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Macro-Raman spectroscopy

Pilot plant for mass-scale production of liquid-phase exfoliated graphene from natural graphite
Optical separation of mechanical strain from charge doping in graphene

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Micro-Raman spectroscopy

10μm

1×1 μm² resolution
1μm² ~ 39,000,000 C atoms
Micro- vs. Nano-Raman spectroscopy

Our Nano-Raman spectroscopy on graphene
1024 points
5 sec / point (1h20min)
25×25 nm² resolution

Obs: micro and nano are placed together here for comparison only. They are not on the same sample.
Metrology of defects and local temperature in graphene

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0D & 1D defects – two parameters

Distance among 0D defects
Defect density

Distance among 1D defects
Crystallite sizes

2D Mater. 4, 025039 (2017)
0D & 1D defects – two parameters

2D Mater. 4, 025039 (2017)
Two parameters: (1) Symmetry breaking

Activation of $q \neq 0$ and other symmetry forbidden modes

OBSERVATION OF NEW PEAKS
Two parameters: (1) Symmetry breaking
Two parameters: (2) Phonon confinement

The G band width

\[ \Gamma^A_G(L_a) = \Gamma^A_G(\infty) + C e^{-L_a/\langle \ell_C/2 \rangle} \]

Raman phase diagram (micro)

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Ion bombarded graphene

Heat treated DLC

Mixed defects

Pure point-defects

Pure line-defects

$\frac{A_D}{A_G} \times E_L^4$ (eV)

$\Gamma_G$ (cm$^{-1}$)
Raman phase diagram (micro)

Lucchese-Cançado
*Carbon* 48, 1592 (2010)
*NanoLett* 11, 3190 (2011)

Tuinstra-Cançado
*JCP53* (1970)
*APL88*, 163106 (2006)

Not good for $L_D < 7$ nm

Not good for $L_a < 30$ nm

$\Gamma_G (\text{cm}^{-1})$

$(A_D/A_G)^4 E_l^4$ (eV$^4$)

$L_D^2 (\text{nm}^2) = \frac{(4.3 \pm 1.3) \times 10^3}{E_l^4} \left(\frac{I_D}{I_G}\right)^{-1}$

$E_l^4 \left(\frac{I_D}{I_G}\right)^{-1}$

$L_a(\text{nm}) = \frac{560}{E_l^4} \left(\frac{I_D}{I_G}\right)^{-1}$


VALID FULL RANGE
Characterizing CVD grown graphene from natural gas

Methane with varying level of CO\textsubscript{2}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{graph.png}
\caption{Graph showing the relationship between L\textsubscript{a} (10 nm\textsuperscript{2}) and \sigma (10\textsuperscript{-4} nm\textsuperscript{-2}) for varying levels of CO\textsubscript{2}.

From Alain Pénicaud}
\end{figure}

2D Mater. 4, 025039 (2017)
Raman Spectrum of Defective TMDs (micro)

By Mauricio Terrones

MoS$_2$

Width of 1st order mode and LA band intensity works as $I_D/I_G$ in Graphene

CROSSING THE DIFFRACTION LIMIT (nano) Optical (D band) imaging of a graphene step

Tip Enhanced (nano)Raman Spectroscopy
special resolution beyond the diffraction limit

Conventional microscope

“Near-field” microscope

\[ \Delta x = \frac{0.61 \lambda}{n \sin (\alpha)} \]


Important contributors to TERS development: Zenobi (ETH), Volker (Jena), Novotny (ETH), Kawata (Japan), Hartschuh (Munich), Dong (China) and many others...
Tip up (micro) – Tip down (nano)

IN CARBONO NANOTUBES, FIRST MEASURED BY ACHIM HARTSCHUH, PRL 2003

Cancado et al. PRL 103, 186101 (2009)

Jorio & Cancado
PCCP 14, 15246 (2012)
The problem of TERS on 2D - graphene

10,000 enhancement on a 10,000 smaller area gives basically no spectral enhancement

Beams et al.
PRL 113, 186101 (2014)
Radial polarized excitation field

0D emitter PL image

1 μm
Tip development

Chemical etched Au-tips

NIGHTMARE!

T. W. Johnson et al.
ACS Nano 6, 9168 (2012)

T. L. Vasconcelos et al.,
ACS Nano 9, 6297 (2015)

Cano-Marquez et al.
Scientific Reports, 5:10408 (2015)


PI 1105968-0
BR 1020120333040
Tip up (micro) – Tip down (nano)

Raman on graphene

Average spectral enhancement = 12
(result from this Tuesday!)

Our best result = 62 enhancement
(far-field signal is negligible!)
Tip up (micro) – Tip down (nano)

Raman on transition metal dichalcogenide

Average spectral enhancement = 60  (far-field signal is negligible!)

By Rafael Silva Alencar
Tip up (micro) – Tip down (nano)
Raman on transition metal monochalcogenide

By Rafael Silva Alencar

Average spectral enhancement = 6

GaS

Tip up (micro)

Tip down (nano)
Tip up (micro) – Tip down (nano)

Raman G band on graphene

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**invalid fits**

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**$\omega_G$**

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**$A_G$**

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**$\Gamma_G$**

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**FWHM vs Freq**

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**Histogram (FWHM)**

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**Histogram (Freq)**
Nano-Raman of liquid-phase exfoliated graphene (nanoflakes) deposited on a glass coverslip

Cassiano Rabelo et al., submitted
Nano-Raman of liquid-phase exfoliated graphene (nanoflakes) deposited on a glass coverslip

Spectral Profile

Cassiano Rabelo et al., submitted
Spatially coherent near-field Raman

\[ S(r_0) \propto \int \int \hat{G}^*(r_1) \hat{G}(r_2) \langle \vec{p}(r_1)^* \vec{p}(r_2) \rangle d^3r_1 d^3r_2 \]

\[ = \int \int \langle \hat{\alpha}^*_r \hat{\alpha}_{r_2} \rangle [\hat{G}(r_1) \hat{E}(r_1)]^* \hat{G}(r_2) \hat{E}(r_2) d^3r_1 d^3r_2 \]

Tip approach curves

Phonon coherence length

\[ \ell_C = 30 \text{nm} \]

Beams et al. PRL 113, 186101 (2014); Cancado et al. PRX 4, 031054 (2014)
Calculation for Raman Scattering

\[ S \propto V \left| \hat{e} \cdot \hat{\alpha} \vec{E} \right|^2 \]

Valid for incoherent Raman
Calculation for spatially coherent near-field Raman

\[ S(r_0) \propto \int \int \tilde{G}^*(r_1) \tilde{G}(r_2) \langle \tilde{p}(r_1)^* \tilde{p}(r_2) \rangle d^3r_1 d^3r_2 \]

\[ = \int \int \langle \tilde{\alpha}_{r_1}^* \tilde{\alpha}_{r_2} \rangle \left[ \tilde{G}(r_1) \tilde{E}(r_1) \right]^* \tilde{G}(r_2) \tilde{E}(r_2) d^3r_1 d^3r_2 \]

*Beams et al. PRL 113, 186101 (2014) & Cancado et al. PRX 4, 031054 (2014)*
Calculation for spatially coherent near-field Raman

\[
S(r_0) \propto \int \int \hat{G}^*(r_1) \hat{G}(r_2) \langle \vec{p}(r_1)^* \vec{p}(r_2) \rangle d^3r_1 d^3r_2 \\
= \int \int \langle \hat{\alpha}^*_{r_1} \hat{\alpha}_{r_2} \rangle \left[ \hat{G}(r_1) \vec{E}(r_1) \right]^* \hat{G}(r_2) \vec{E}(r_2) d^3r_1 d^3r_2
\]

\[
\hat{\alpha}^{D,G'}(A_1) = \alpha^{D,G'} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}
\]

\[
\hat{\alpha}^G(E_{2g_1}) = \alpha^G \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}
\]

\[
\hat{\alpha}^G(E_{2g_2}) = \alpha^G \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}
\]
Calculation for spatially coherent near-field Raman

Tip approach curves

Beams et al. PRL 113, 186101 (2014)
Cancado et al. PRX 4, 031054 (2014)
Phonon symmetry dependent spatial coherence

\[ S(r_0) \propto \int \int \hat{G}^*(r_1) \hat{G}(r_2) \langle \tilde{p}(r_1)^* \tilde{p}(r_2) \rangle d^3r_1 d^3r_2 \]

\[ = \int \int \langle \hat{\alpha}_{r_1}^* \hat{\alpha}_{r_2} \rangle \langle \hat{G}(r_1) \bar{E}(r_1) \rangle^* \hat{G}(r_2) \bar{E}(r_2) d^3r_1 d^3r_2 \]

Beams et al. PRL 113, 186101 (2014)
Cancado et al. PRX 4, 031054 (2014)

Coherence length

\[ L_C = 30 \text{ nm} \]
The future of nano-Raman (reaching resolutions better than 1nm)


Ultra high vacuum STM (gap mode)

tetrakis(3,5-ditertiarybutylphenyl)porphyrin (H2TBPP) on Cu(111)
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