Near-field optical imaging of single-walled carbon nanotubes

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Acknowledgement

PC Tuebingen:
Mathias Steiner
Hui Qian
Antonio Virgilio Failla

PC Siegen:
Gregor Schulte

Funding: DFG, Cµ Siegen, NSF, FCI
Why High Spatial Resolution Near-field Optics?
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spatial resolution is limited by diffraction $\lambda/2$
Uncertainty relation:
\[\Delta x \cdot \Delta k_x \geq 2\pi\]
\[\Delta k_x = |k| \cdot \sin(\alpha) = \frac{2\pi}{\lambda} \sin(\alpha)\]
\[\Delta x \geq \frac{2\pi}{\Delta k_x} = \frac{\lambda}{\sin(\alpha)}\]
Tip-Enhanced Spectroscopy

Wessel, JOSA B 2, 1538 (1985)

\[ \Delta x > d \quad \text{(diffraction unlimited)} \]
Tip-Enhanced Spectroscopy

laser illuminated metal tip

Theory: (Giant) enhanced electric field confined to tip apex

Mechanism: Lightning rod and antenna effect, plasmon resonances

Novotny et al. PRL 79, 645 (1997)
Tip-Enhanced Spectroscopy

SEM micrograph

diameter = 22 nm

enhanced electric field confined within 20 nm?

..................Optical imaging with 20 nm resolution?!

..................Signal enhancement !?
Tip-Enhanced Spectroscopy

The tip has to be very close to the sample.

- Enhanced electric field close to the very end of the tip.
- Raster-scanning the sample and point-wise detection of the sample response.
Experimental Setup

Confocal microscope + Tip-sample distance control

a sharp metal tip is held at constant height (~2nm) above the sample using a tuning-fork feedback mechanism

K. Karrai et al., APL 66, 1842 (1995)

Optical Images and Spectra

Topography of the sample
Near-field Raman Imaging of SWCNTs

Raman image (G’ band)

only SWCNT detected in optical image
optical contrast with 25 nm resolution

Topography

chemically specific
enhanced field confined to tip

Hartschuh et al.
PRL 90, 95503 (2003)

NT06, Nagano 20.06.2006
Achim Hartschuh, Nano-Optics München
Near-field Raman Imaging of a SWCNT

Raman image (G band) 2 x 1 μm$^2$

Topography

$d\approx1.2$ nm
Near-field Raman Spectroscopy

Raman image (G band)

Topography image

height: 0 - 1.9 nm

RBM at 199 cm\(^{-1}\)
diam = 1.2 nm
structure \((n,m)\approx(14,2)\)
metallic SWCNT

Experiment

Exp. parameters:

~3 nm steps between spectra exposure time per spectrum = 100 ms

intensity of the RBM
Resolution enhancement

Farfield

Near-field

A

B

no tip  same area  with tip

500 nm
Signal Enhancement

![Graph: Raman shift vs. photon counts]
Signal Enhancement

\[ \text{tip-enhanced signal} > \text{signal} \times 2500 \]

_Hartschuh et al. Phil. Trans. R. Soc. Lond A, 362 (2004)_
Distance Dependence

Enhanced Raman scattering signal

tip-enhancement is near-field effect => tip has to be close to sample
Simultaneous Raman and PL Spectroscopy

Excitation at 633 nm ⇒ Emission and Raman signals are spectrally isolated
Near-field optical imaging of SWCNTs

- Farfield Photoluminescence
- Topography
- Raman (G-band)
- Photoluminescence

length of emissive segment \( \approx 70 \) nm

- changes in chirality \((n,m)\)?
- coupling to substrate?
Localized PL-Emission on Glass

Emission spatially confined to within 10 – 20 nm

⇒ Localized excited states
Bound excitons?

• role of defects?
• substrate?
Near-field optical imaging of SWCNTs

Simultaneous near-field Raman and PL imaging
⇒ PL extended along nanotube

SWCNTs in SDS on mica
Near-field PL-Spectroscopy

⇒ Emission energy can vary on the nanoscale

Near-field PL-Spectroscopy

Origin of emission energy variations:

- Huge exciton binding energies $E_{\text{bind}} = 400$-1000 meV
  
- Electron density is confined to plane of rolled sheet.
  $\Rightarrow$ Dielectric screening determined by environment.

\[ E_b \propto \frac{1}{\varepsilon^\alpha} \]

$\Rightarrow$ Emission energy sensitive to dielectric environment

$\Rightarrow$ Changes in local dielectric environment expected to modulate emission energy.
Tip-enhanced Microscopy

⇒ Spatial resolution < 15 nm
⇒ Signal amplification

⇒ Tip as nanoscale „light source“
Signal Enhancement

**Raman scattering**

Enhancement of incident field and scattered field

\[ S_{\text{enhanced}} \sim (E_{\text{local}} / E_0)^2 \]

- local field at tip
- field without tip

**Photoluminescence**

PL depends on \( k_{\text{ex}}, k_{\text{radiative}}, k_{\text{non-radiative}} \)

- \( k_{\text{ex}} \): enhanced excitation field
  \[ S_{\text{enhanced}} \sim (E_{\text{local}} / E_0)^2 = f^2 \]
- \( k_{\text{rad}} \): Purcell-effect
  \[ Q = \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{nonrad}}} \]
  - \( Q \) is increased (\( Q \approx 10^{-3} \))
  - cycling rate is increased
- \( k_{\text{nonrad}} \): energy transfer to metal quenching of PL

PL Enhancement depends on \( Q \)!
Signal Enhancement

**Raman enhancement**

- Far-field Raman \(\sim 2000\) counts/s
- Near-field Raman \(\sim 4000\) counts/s
- Raman-enhancement \(\sim 6000 / 2000 = 3\)

**PL enhancement**

- No far-field PL \(< 200\) counts/s
- Near-field PL \(\sim 17000\) counts/s
- PL-enhancement \(> 17000 / 200 = 85\)

\[ S_{\text{enhanced}} \sim f^4 \]

\[ S_{\text{enhanced}} \sim f^2 \]

⇒ PL quantum yield must be increased by tip (SEF)
Signal Enhancement

(Very first data)

⇒ PL quenching for very small distances
⇒ optimum distance for PL enhancement
Near-field Interactions

**Uncertainty relation:**
Diffraction limit for propagating waves:

\[ \Delta x \cdot \Delta k_x \geq 2\pi \]
\[ |k| = \frac{2\pi}{\lambda} \approx 0.01\text{nm}^{-1} \]

\[ \pi \frac{\Delta k}{\Delta x} \approx 10.01\text{nm} \]
\[ \Delta k \approx \frac{2\pi}{5-10\text{nm}} \approx 1\text{nm}^{-1} \]

⇒ k-vectors of tip enhanced fields extend through BZ!
⇒ selection rules for optical transitions?
Summary

High-resolution optical microscopy of carbon nanotubes using a sharp laser-illuminated metal tip

- PL and Raman spectroscopy and imaging
- Spatial resolution < 15 nm
- Signal enhancement

Results

- Resolved RBM variations (IMJ) on the nanoscale
- Non-uniform emission energies that result from local variations of dielectric environment
- Strongly confined emission signals $\Rightarrow$ bound excitons?
- PL-Quantum yield can be enhanced
Outlook

**Optimize Technique**
- Higher spatial resolution < 5 nm?
- Higher enhancement

**Nanotubes**
- Role of structural defects: Correlation between Raman and PL data
- Role of local dielectric environment…
- Enhancement of PL quantum yield

**Near-field interactions**
- Mechanisms for signal enhancement?
- Selection rules?
Thank you!