# Experimental and numerical investigations of the near-field scattering of boron nitride based nanomaterials

PhD thesis booklet


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**Budapest**

**2023**

# Motivation

With the emergence of graphene and related structures, the interest in low-dimensional nanostructures has skyrocketed. Investigating the electronic, optical and thermal properties of the different morphologies of graphene, transition metal dichalcogenides and boron nitride materials became the focal point of research for applications in electronics, ceramics and biological engineering.

Within these low-dimensional materials, boron nitride nanostructures take a special position, owing to their unusual and advantageous mechanical and optical properties, such as high thermal and chemical stability. Boron nitride materials are structural analogues of their carbon counterparts; wurtzite boron nitride has diamond-like structure, hexagonal boron nitride has a graphite-like structure, and both fullerenes-like balls and nanotubes can be synthetized. Unlike the carbon structures, boron nitride materials possess a large bandgap. This large bandgap makes these materials especially attractive as insulators in nano-electronic systems, and also makes boron nitride materials transparent in a wide spectrum of visible and infrared illumination. Optical measurement methods are proven to be powerful techniques in probing the interesting properties of boron nitride nanostructures. However, conventional optics is limited in its spatial resolution; the wave nature of light limits the achievable resolution to about half of the wavelength. This limitation is the diffraction limit.

Overcoming the diffraction limit is possible in multiple ways. Here I introduce an efficient, non-destructive, marker-free method that harnesses the enhancing effects of optical near fields. Scattering-type scanning near-field microscopy (s-SNOM) is able to provide optical information with a spatial resolution of 20 nm, independent of the exciting wavelength. It employs metal coated atomic force microscope (AFM) probes as nano-antennas to create enhanced optical near-field confined to the nano-sized volume at the vicinity of its apex. The near-field interaction between the probe and the sample modifies the scattered light from the probe which can be detected by an infrared detector in the far field. Despite becoming more mainstream and also commercially available, operating the equipment and understanding the interaction mechanisms is a challenge.

To better understand the contrast mechanisms in near-field microscopy, a number of numerical models were constructed. The simplest of these models uses the quasi-static limit to simplify the scattering problem. This method works well for non-resonant or weakly resonant materials, but produces inaccuracies for strongly resonant samples. For these materials (such as silicon carbide or boron nitride) a more extended electrodynamic model has to be taken into account, that considers the scattering mechanism of the entire tip length and the consequently emerging retardation effects.

While working on my PhD project at the Wigner Research Centre for Physics, I had the opportunity to understand both the measurement technical aspects as well as the model creation aspects of near-field spectroscopy while working predominantly on boron nitride nanotubes.

# Methods

In this thesis, I demonstrate the nanoscale sensitivity and spatial resolution of the scattering-type scanning near-field optical microscopy technique with measurements on boron nitride nanotubes (BNNT). The first part of the thesis focuses on the filling process of the nanotubes. To prepare them for filling, the raw, as-synthetized nanotube sample has to be purified of contaminants and the nanotubes have to have their caps opened. The cleaning and opening process introduces defects into the structure of the nanotubes. By near-field microscopy, I detect the defects of an individual nanotube. Measuring the spectrum also reveals additional peaks beside the characteristic boron nitride nanotube phonon peaks that I attribute to modified scattering of the introduced defects. Analyzing the defects introduced during the cleaning and opening steps can lead to an optimized filling procedure that also helps the further near-field characterization of the nanotubes.

Filling fullerenes inside the boron nitride nanotubes is carried out by sublimating solid $C_{60}$ powder in vacuum ($10^{-5}$ torr) and elevated temperatures (600 °C) in the presence of BNNT powder. Filled BNNTs are deposited onto silicon surface for near-field characterization. Near-field maps and spectra clearly reveals the encapsulated

$C_{60}$ molecules. The number of detected molecules this way is approximated to be below 200. By coupling visible laser illumination (532 nm) into the near-field system, I induced chemical reactions between the $C_{60}$ molecules encapsulated inside the BNNTs. The photopolymer products (mainly dimers and trimers) are also detectable by near-field microscopy and spectroscopy, but only in the Reststrahlen band of the nanotube's phonon excitation. This implies the active role of the dielectric properties of the nanotube in enhancing the scattering of the encapsulated molecules.

In the previous results, I demonstrated the exceptional sensitivity of the near-field measurement technique and showed the enhancing interaction between molecular vibrations and the phonon modes of BNNTs. To better understand the scattering properties of strongly resonant materials with momentum-dependent reflection coefficient, numerical models beyond the quasi-static approximation are needed. I present a fully electrodynamic, numerical model based on spherical multipole expansion that is able to calculate the scattering properties of multiple scatterers in arbitrary orientation in the vicinity of a (possibly layered) interface. I use this model to calculate the near-field spectra of BNNTs and show the phonon polariton interference in hexagonal boron nitride materials.

# New scientific results

1. By near-field infrared measurements of boron nitride nanotubes of less than 10 nanometers in diameter, I found that the peak of the characteristic transverse optical phonon mode is measurable over the entire length of the nanotube, while other peaks show strong positional dependence. I assigned the position-dependent peaks to the defects of the nanotube. By mapping these peaks, I visualized the defect structure of a single, small diameter nanotube, demonstrating the ability of near-field microscopy in the detection of truly nanometer sized scatterers. [P1]

2. I carried out hyperspectral, near-field mapping of $C_{60}$ molecules encapsulated in boron nitride nanotubes. For the first time, I detected fullerene vibrations in boron nitride nanotubes with infrared near-field microscopy. [P2]

3. By focusing a visible laser beam on the nanotube, I induced a photochemical reaction between the fullerene molecules encapsulated in boron nitride nanotubes. I was able to detect dimer- and trimer-related peaks in the near-field infrared spectrum. I showed that the boron nitride nanotube plays an active role in the enhancement of the near-field signal. My results indicate the exceptional sensitivity of the measurement technique, being able to detect the signal of just a few hundred molecules. [P2]

4. I applied a generalized Mie's scattering theory for numeric near-field calculations in full electrodynamic treatment. I showed that this numeric method is suitable for near-field calculations of multiple scattering centers in arbitrary configurations. For the first time with this method, I calculated the near-field spectrum and spatial characteristics of particles on hexagonal boron nitride sheets. I calculated the near-field spectrum of both unfilled and filled boron nitride nanotubes. The results show good qualitative agreement with the measurements. [P3]

# Related publications

P1 D. Datz, G. Németh, H. M. Tóháti, Á. Pekker, and K. Kamarás: *High-Resolution Nanospectroscopy of Boron Nitride Nanotubes*. physica status solidi (b), 254, 11, 1700277, (2017)

P2 D. Datz, G. Németh, K. E. Walker, G. Rance, Á. Pekker, A. N. Khlobystov and K. Kamarás: *Polaritonic enhancement of near-field scattering of small molecules encapsulated in boron nitride nanotubes: chemical reactions in confined spaces*. ACS Applied Nano Materials, 4, 5, 4335–4339, (2021)

P3 D. Datz, G. Németh, Á. Pekker, and K. Kamarás: *Generalized Mie theory for full wave numerical calculations of scattering near-field optical microscopy with arbitrary geometries*. Ready for submission

# Other publications

1. G. Németh, **D. Datz**, H. M. Tóháti, Á. Pekker, K. Kamarás: *Scattering near-field optical microscopy on metallic and semiconducting carbon nanotube bundles in the infrared.* phys. stat. sol. (b), 253, 2413-2416, (2016)

2. G. Németh, **D. Datz**, H. M. Tóháti, Á. Pekker, K. Otsuka, T. Inoue, S. Maruyama, and K. Kamarás: *Nanoscale characterization of Individual Horizontally Aligned Single-Walled Carbon Nanotubes.* phys. stat. sol. (b), 254, 11, 1700433, (2017)

3. G. Németh, **D. Datz**, Á. Pekker, T. Saito, O. Domanov, H. Shiozawa, S. Lenk, B. Pécz, P. Koppa, K. Kamarás: *Near-Field Infrared Microscopy of Nanometer-Sized Nickel Clusters inside Single-Walled Carbon Nanotubes.* RSC Advances, 9, 34120-34124, (2019)

4. K. G. Simić, I. Đorđević, G. Janjić, **D. Datz**, T. Tóth-Katona, and N. Trišović: *On the photophysical properties of a liquid crystal dimer based on 4-nitrostilbene: A combined experimental and theoretical study.* Journal of Molecular Liquids, 339, 116969, (2021)

5. G. Németh, K. Otsuka, **D. Datz**, Á. Pekker, S. Maruyama, F. Borondics, K. Kamarás: *Direct Visualization of Ultrastrong Coupling between Luttinger-Liquid Plasmons and Phonon Polaritons* Nano Letters, 8, 3495–3502, (2022)