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Near-field infrared microscopy of individual single-walled carbon nanotubes and their hybrid systems

Ph.D. dissertation booklet

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Background

Carbon nanotubes possess particularly interesting mechanical, electronic and thermal properties. They have been in the forefront of research during the last decades, together with graphene and later with other low-dimensional materials. Various applications could or already do exploit the advantageous features of carbon nanotubes in the areas of electronics, biological engineering or composite materials.

Owing to the rapid development in selective growth and nanofabrication methods, devices based on individual nanotubes have become possible in the last few years. The characterization of the output of these methods is very important in order to clarify the procedures and understand sample-to-sample differences. Optical methods have been proven to be powerful in uncovering the peculiar properties of carbon nanomaterials. A huge drawback of conventional optical methods is, however, that their spatial resolution is limited by the wavelength of light probing the sample. This limitation prohibits the identification of individual nanoobjects in a closely packed sample. Further, the sensitivity of macroscale optics is also limited by the size of an individual object and the wavelength. These limitations become crucial in the mid-infrared range which is an important wavelength range for material identification.

The only way to overcome the diffraction limited resolution and increase sensitivity in a label-free manner is to utilize optical near-fields. One of these techniques, scattering-type near-field optical microscopy (s-SNOM) is capable of providing optical information with wavelength-independent resolution reaching 20 nm. Despite its commercially availability, it is still a fairly new method with multiple technical difficulties and open questions about its applicability in different research fields. In the Wigner Research Centre for Physics, the laboratory of Katalin Kamarás has a long history in the optical characterization of new materials and recently acquired a new s-SNOM instrument, unique in Hungary. I started my work with s-SNOM during my Master's thesis, getting basic knowledge in the working principle of s-SNOM.

Because of the vastly different contrast mechanism in s-SNOM measurements compared to conventional microscopy, the applicability and the type of information that we acquire from the sample has to be investigated.

Aims

The thesis concentrates on the applicability of s-SNOM to characterize individual single-walled carbon nanotubes and their hybrid systems. The research objects can be separated into two main groups. In the first category I wanted s-SNOM to identify the metallicity of the components of nanotube- based systems.

- Nanotube transistors: The goal here was to study the possibility to use s-SNOM to distinguish between semiconducting and metallic carbon nanotubes in a real device. The reliability and resilience of the s-SNOM signals has to be investigated to routinely use SNOM for device characterization.
- Metallic clusters in carbon nanotubes: nanotubes can serve as nanosized containers where small molecules can be encapsulated and unique chemical reactions can take place. The tracking of the products is very important to gather knowledge about the reactions. The goal here, based on our results in the previous point, was to push s-SNOM to its limits to identify nickel clusters of a few hundred atoms inside a carbon nanotube. We also wanted to modify previously applied dipole models to describe and predict the s-SNOM signals.

The second part of the thesis aims to use s-SNOM not only for material identification but to study exotic nanooptical phenomena. Carbon nanotubes feature Luttinger-liquid plasmon excitations that were shown to have high electromagnetic field confinement and long lifetime. These properties make them perfect candidates to enhance light-matter interactions of the type not studied before.

- My aim was to apply scanning near-field polariton interferometry using s-SNOM to study the interaction of carbon nanotube plasmons and substrate phonons. For this, the dispersion of the plasmon-phonon state has to be measured and analyzed by a coupled harmonic oscillator model.

New scientific results

1. I applied scattering-type scanning near-field optical microscopy to differentiate between carbon nanotubes based on their metallicity. I found that the near-field phase contrast at 960 cm^{-1} unambiguously tells nanotube metallicity. It is in good agreement with the calculations based on the extended finite dipole model modified to describe the cylindrical nanoparticle. [P1]

2. I applied scattering-type scanning near-field infrared microscopy to observe the formation of nickel clusters inside carbon nanotubes. I showed that nano-sized metal clusters can be efficiently detected in near-field phase images. I corroborated the metallic nature of the near-field phase signatures by additional spectroscopic measurements. Studying multiple nanotube bundles I found that the initial filling of the nanotubes was very efficient which is in line with the results from transmission electron microscopy measurements. [P2]

3. I applied a modified version of extended finite dipole model to predict the s-SNOM signature of the small metallic clusters inside carbon nanotube. I found that the experimentally observed phase contrast agrees well with prediction by the modified the model quantitatively. [P2]

4. I performed scanning polariton interferometry in the mid-infrared range for different excitation frequencies and visualized the hybridization between substrate surface phonon polaritons and carbon nanotube Luttinger-liquid plasmons in real space on two different polar dielectric support layers, namely silica and hexagonal boron nitride. I corroborated the hybridization in real space by observing the transparency window in phase contrast and also in momentum space by calculating the dispersion relation of the hybrid modes from the measurements that shows characteristic avoided crossing and mode splitting. [P3]

5. I carried out the analysis of the experimentally measured dispersion relation and phase contrast spectrum of hybridized carbon nanotube plasmons and substrate phonons by applying a classical coupled harmonic oscillator model. I showed that the coupling reaches the ultrastrong regime. I showed that the coupled oscillator model can be used to examine the coupling strength properly even if only direct phase contrast is measured instead of polariton interference fringes. [P3]

6. I showed that the electric field of carbon nanotube plasmons is so strongly confined in the out-of-plane direction that a few nm of separation layer is able to suppress the effect of an underlying phononic substrate. [P3]

Related publications

P1 **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)

P2 **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)

P3 **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)

Other publications

1. C. Abia, C.A. López, J. Gainza, J.E.F.S. Rodrigues, M. M. Ferrer, N. M. Nemes, O. J. Dura, J.L. Martínez, M.T. Fernández Díaz, C. Álvarez-Galván, **G. Németh**, K. Kamarás, F. Fauth, and J. A. Alonso: *The structural evolution, optical gap, and thermoelectric properties of the* $RbPb_2Br_5$ *layered halide, prepared by mechanochemistry.* J. Mater. Chem., 10, 6857-6865, (2022)

2. L. Bereczki, L. A. Fogaca, Zs. Dürvanger, V. Harmat, K. Kamarás, **G. Németh**, B.B. Holló, V. M. Petrusevski, E.B. Bódis, A. Farkas, I. M. Szilágyi, L. Kótai: *Dynamic disorder in the high-temperature polymorph of bis[diammine-silver(i)] sulfate—reasons and consequences of simultaneous ammonia release from two different polymorphs.* J. Coord. Chem., 74, 2144-2162, (2021)

3. D. Datz, **G. Németh**, K.E. Walker, G.A. Rance, Á. Pekker, A.N. Khlobystov, K. Kamarás: *Polaritonic enhancement of near-Field scattering of small molecules encapsulated in boron nitride nanotubes: Chemical reactions in confined spaces.* ACS Appl. Nano Mater., 4, 4335-4339, (2021)

4. L. A. Fogaca, É. Kováts, **G. Németh**, K. Kamarás, K.A. Béres, P. Németh, V. Petrusevski, L. Bereczki, B.B. Holló, I.E. Sajó, Sz. Klébert, A. Farkas, I.M. Szilágyi, L. Kótai: *Solid-phase quasi-intramolecular redox reaction of* $[Ag(NH_3)_2]MnO_4$*: An easy way to prepare pure* $AgMnO_2$. Inorg. Chem., 60, 3749-3760, (2021)

5. **G. Németh**, Á. Pekker: *New design and calibration method for a tunable single-grating spatial heterodyne spectrometer.* Opt. Express, 28, 22720-22731, (2020)

6. D. Datz, **G. Németh**, H. M. Tóháti, Á. Pekker, K. Kamarás: *High-resolution nanospectroscopy of boron nitride nanotubes.* phys. stat. sol. (b), 254, 1700277, (2017)

7. Á. Pekker, **G. Németh**, Á. Botos, H.M. Tóháti, F. Borondics, Z. Osváth, L.P. Biró, K. Walker, A.N. Khlobystov, K. Kamarás: *Cloaking by* π*-electrons in the infrared.* phys. stat. sol. (b), 253, 2457-2460, (2016)

8. **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)