Spectroscopic study of low-dimensional materials

During the three years of the project we have focused on the spectroscopic investigation of low dimensional systems in their pristine and modified form. We have applied various modification strategies in case of the different types of low-dimensional materials (carbon and boron nitride nanotubes, hexagonal boron nitride). In case of nanotubes we utilized the unique one dimensional cavity of the tubes and filled them with small molecules of appropriate size. In addition to the characterization of the filled systems we were able to induce chemical reactions inside the nanotubes and investigate the products.

In case of the boron nitride systems (1D and 2D), we were also interested in the influence of defects on the vibrational and electronic structure of the starting materials.

For the investigation we have used standard far-field spectroscopic techniques like transmission infrared spectroscopy, photoluminescence spectroscopy, and a scattering type scanning nearfield optical microscope (s-SNOM), where the infrared optical response of the samples can be obtained with 20 nm spatial resolution.

We have presented our results at international conferences and published 5 papers in international journals.

Detailed results based on publications and posters:

1. K. E. Walker, G. A. Rance, Á. Pekker, H. M. Tóháti, M. W. Fay, R. W. Lodge, C. T. Stoppiello, K. Kamarás, A. N. Khlobystov: ***Growth of Carbon Nanotubes inside Boron Nitride Nanotubes by Coalescence of Fullerenes: Toward the World's Smallest Coaxial Cable***, Small Methods, 1 (9), 1700184 (2017)

   In collaboration with the group of Andrei Khlobystov at University of Nottingham we investigated fullerene-filled boron nitride nanotubes. The nanotubes were cleaned and opened prior the filling procedure. The filling efficiency was determined by infrared and optical spectroscopy (fig 1 a). By sonicating the filled samples in appropriate solvent we were able to remove the filling molecules demonstrating that in case of boron nitride nanotubes the fullerene-nanotube interaction is weaker than in case of carbon nanotubes.

   The fullerene filled boron nitride nanotube samples were annealed in order to transform the fullerenes into carbon nanotubes inside the boron nitride host. Transmission electron microscopy confirmed the successful formation of boron nitride/carbon nanotube hybrid system (fig 1 b). The formed hybrid nanotube resembles an insulated wire with the carbon nanotube as the conductor and the boron-nitride nanotube as the insulator. We published the results in Small Methods where it was used for the cover illustration.

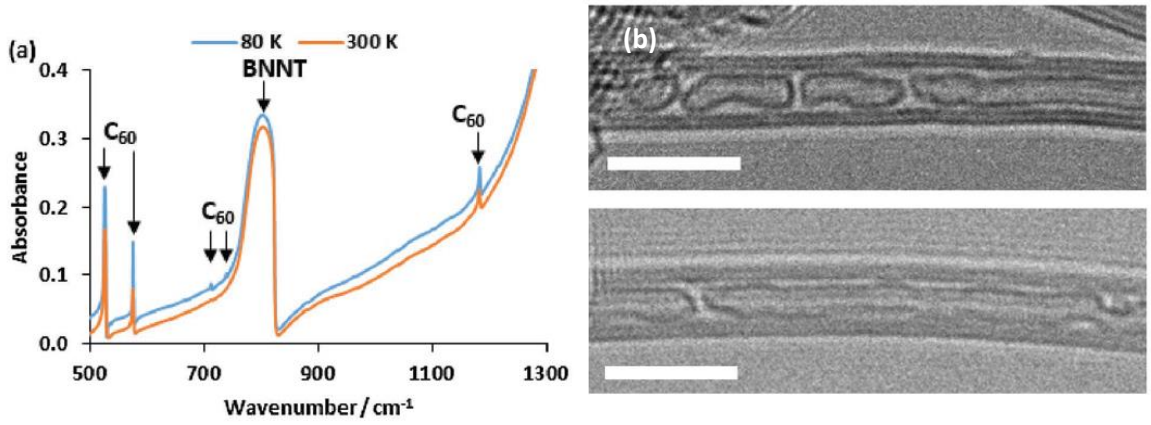

Figure 1. a) infrared spectrum of the C_{60} filled boron nitride nanotube sample showing the characteristic vibrational modes of both the encapsulated fullerene and the boron nitride nanotube host. b) transmission electron microscope image of the fullerene filled boron nitride nanotube after annealing showing short carbon nanotubes inside the boron-nitride host. The scale bar is 5 nm.

2. D. Datz, G. Németh, Hajnalka M. Tóháti, Á Pekker, K. Kamarás: ***High-Resolution Nanospectroscopy of Boron Nitride Nanotubes***, Phys. Status Solidi B, 254 (11), 1700277 (2017)

In continuation of the collaboration with the group of Andrei Khlobystov at University of Nottingham we investigated the starting material of the fullerene-filled boron nitride nanotubes. In order to fill the nanotubes, cleaning and opening procedures had to be applied involving aggressive chemicals. We have investigated the effect of this process on the boron nitride nanotubes by near-field infrared microscopy. Our measurements revealed new infrared vibrational modes in the processed nanotubes samples which can be associated with defect sites along the nanotubes. We were able to map individual nanotubes with 20nm spatial resolution to locate the defects created during the cleaning process (figure 2). The development of an improved cleaning process is underway.

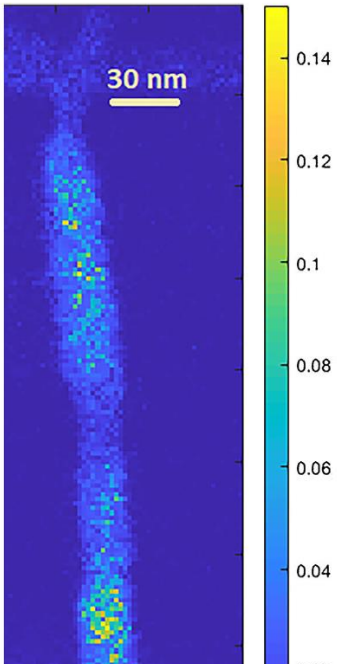

Figure 2 spatial variation of the near-field infrared absorption measured at the frequency of a defect mode.

3. G. Németh, Á Pekker, D. Datz, H. M. Tóháti, K. Kamarás, K. Otsuka, T. Inoue, S. Maruyama: ***Nanoscale characterization of individual horizontally aligned single-walled carbon nanotubes***, Phys. Status Solidi B, 254 (11), 1700433 (2017)

   One of the most challenging tasks in nanotube research is to identify the different electronic types of nanotubes for device fabrication. The implementation of standard spectroscopy techniques at the single-tube level has remained a great task due to small nanotube signal and low spatial resolution. Scattering-type scanning near-field optical microscopy (s-SNOM) yields information on the optical characteristics of the sample with high spatial resolution. We applied this method to characterize individual horizontally aligned single-walled carbon nanotubes (SWCNT). The samples were made by the group of Shigeo Maruyama at The University of Tokyo. Using near-field technique we were able to investigate single nanotube species and differentiate them based on their electrical properties (metallic/semiconducting – Figure 3.). This extremely high sensitivity and high spatial resolution enable the detection of local changes in the electronic properties of carbon nanotubes in case of sidewall functionalization or filling at later stage of the project.

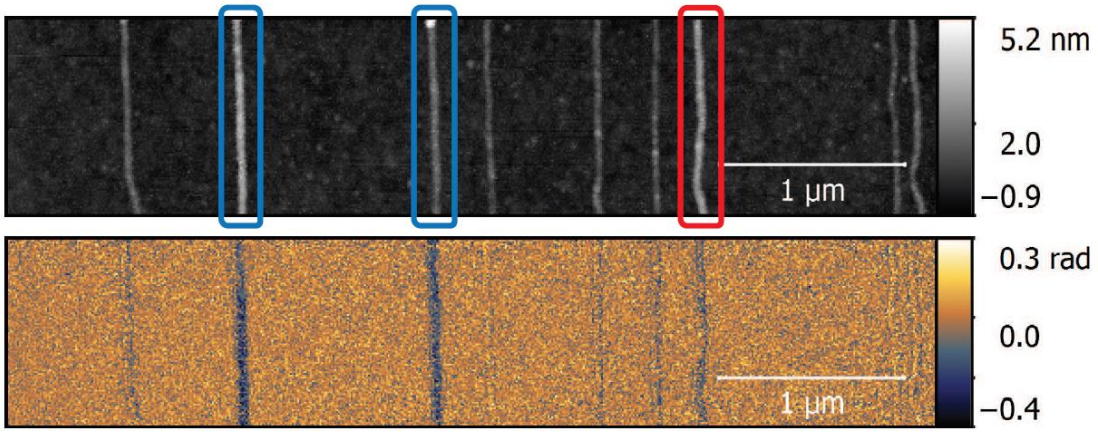

Figure 3 top: AFM topography image of an area containing multiple individual nanotubes, the nanotubes were identified as metallic (blue) and semiconducting (red) using a destructive method (electrical breakdown technique). Bottom: infrared phase map (related to free carrier concentration) of the same area showing strikingly different phase contrast in case of metallic and semiconducting nanotubes.

4. H. M. Tóháti, Á. Pekker, P. Andričević, L. Forró, B. Náfrádi , M. Kollár, E. Horváth, K. Kamarás: ***Optical detection of charge dynamics in CH3NH3PbI3/carbon nanotube composites***, Nanoscale, 9 (45), 17781-17787 (2017)

During the first year we had the opportunity to collaborate with the group of László Forró at Ecole Polytechnique Fédérale de Lausanne on the combination of low dimensional carbon based materials (nanotubes, graphene) with perovskite based solar cell materials. While it was not declared in the workplan this work fits in the topic of this project. We have investigated the light-induced interaction of carbon nanotubes and the perovskite material.

The field of perovskite based solar cells gained remarkable interest in the last few years due to their promising photovoltaic properties. Although the power conversion efficiencies of these cells increased with an unprecedented pace there are still obstacles in the way of commercialization. One of the main challenges is the choice of hole-selective transport material (HTM). Recently carbon nanomaterials emerged as potential HTMs for perovskite based solar cells. However, the investigation of the interface of the two components and the characterization of their interaction is still incomplete. In this paper we presented a spectroscopic study of charge transfer in the methylammonium lead iodide/carbon nanotube composite system. Using mid- and near-infrared spectroscopy we investigated the spectrum of the composite system under dark and illuminated conditions. The optical spectrum of carbon nanotubes is extremely sensitive to charge dynamics and therefore the nanotube part of the composite acts as a strong indicator. The results suggest two charge transfer processes with strikingly different timescale. The fast response is important in sensors while the slow component is relevant in the long term properties and stability in solar cell applications. The results (figure 4.) suggest that separated semiconducting nanotubes are good candidates as hole transporting layers in perovskite based solar cells.

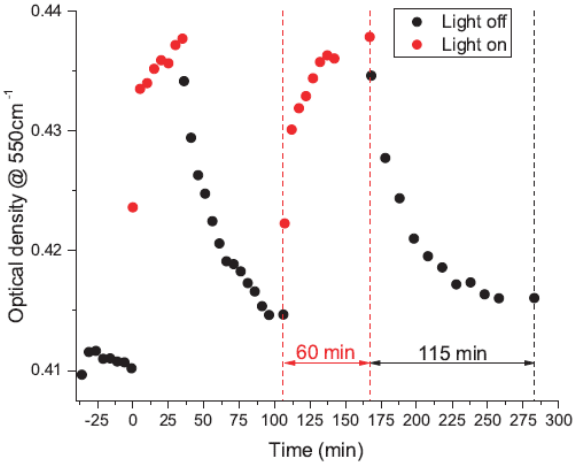

Figure 4 Infrared optical density measured in the free carrier response region. The results suggest effective charge transfer between the perovskite and the nanotube upon illumination.

5. D. Datz, G. Németh, Á. Pekker, K. Kamarás: ***Nano-spectroscopy of phonon-polariton modes in boron nitride nanostructures***, International Winterschool on Electronic Properties of Novel Materials 2018, Kirchberg in Tirol, Austria, Poster (2018)

   The investigation of the defect related phonon modes in boron nitride nanostuctures has multiple importance. In case of nanotubes we need to open the tube ends in order to fill them with small molecules. Opening of the tubes results in defects along the tube wall as well. In order to minimize the unwanted damage we need to optimize the opening process in which the knowledge of the defect distribution along the tube is important. In case of hexagonal boron nitride our goal is to create different defects (adatoms, vacancies, sidegroups) and investigate the resulting defect induced phonon modes and their properties. Using our s-SNOM device it was possible to perform spectroscopic measurements by sweeping the tunable infrared laser with resolution down to 0.5 cm^{-1}. At selected defect mode frequencies defect maps can be generated with 20 nm spatial resolution (figure 5).

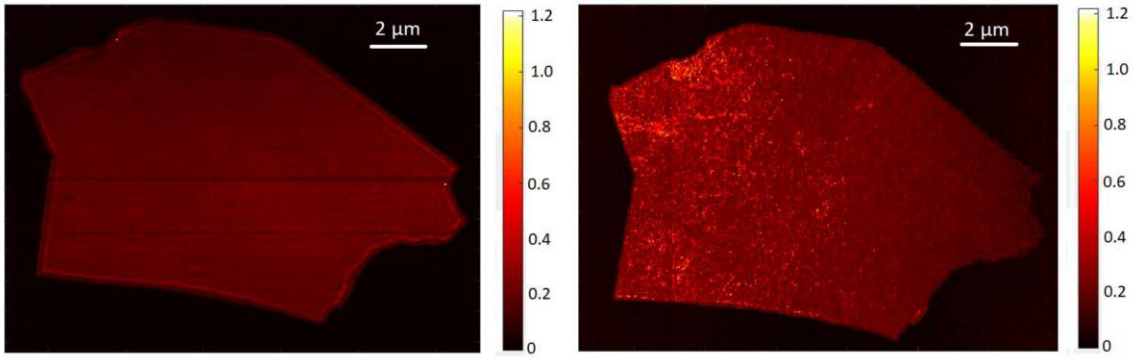

Figure 5 Nearfield optical absorption maps of the same hexagonal boron-nitride flake measured at a defect mode frequrency (1410 cm^{-1}) before (left) and after (right) 30 seconds of air plasma treatment.

6. 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 (59), 34120-34124 (2019)

   Nickel nanoclusters grown inside single-walled carbon nanotubes (SWCNT) were studied by infrared scattering-type scanning near-field optical microscopy (s-SNOM). The nanotubes were filled with Ni(II) acetylacetonate and the molecules were transformed into nickel clusters via annealing. The metal clusters give high local contrast enhancement in near-field phase maps caused by the excitation of free charge carriers. The experimental

results are supported by calculations using the finite dipole model, approximating the clusters with elliptical nanoparticles.
Compared to magnetic force microscopy, s-SNOM appears much more sensitive to detect metal clusters inside carbon nanotubes. We estimate that these clusters contain fewer than 700 Ni atoms.

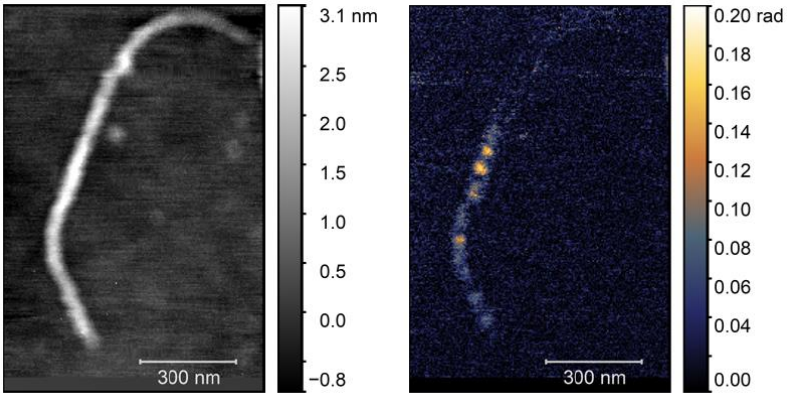

Figure 6 AFM topography (left) and near-field optical response map (right) of a typical carbon nanotube bundle after the annealing process. The bright regions on the right panel originate from higher local free-carrier concentration related to metallic Ni clusters inside the nanotubes.

7. D.Datz, G. Németh, Á. Pekker, K. Kamarás: **Strong interaction between small molecules and boron nitride nanotubes**, 48th International School & Conference on the Physics of Semiconductors, Szczyrk, Poland, Poster (2019)

Low dimensional boron nitride materials, such as hexagonal boron nitride (hBN) and boron nitride nanotubes (BNNT) are becoming increasingly more interesting as an active or passive component of a variety of applications. These applications include supporting insulating components if graphene electronics, components of two dimensional heterostructures, gas sensors, and biological applications. Since BNNTs (and also hBN) are high bandgap, chemically inert materials, with high temperature resistance, another interesting application is to fill them with smaller molecules and use them as nanoreactors. Similar experiments were conducted with carbon nanotubes (CNT) as well, but as opposed to BNNTs, the much smaller or nonexistent bandgap of CNTs makes it challenging to optically probe the small molecules inside the tubes.

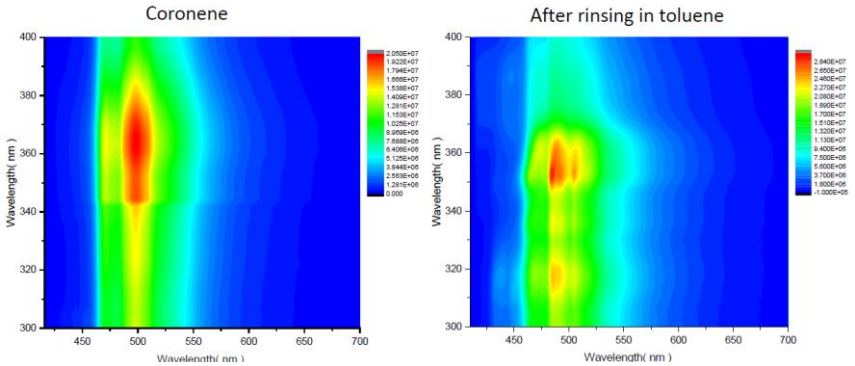

Figure 7 Photoluminescence map of cristallyne coronene (left) and coronene filled boron-nitride nanotubes after washing away the excess coronene from the surface. The spliting of the peak to sidebands indicates strong interaction with the nanotubes.

Coronene filled BNNTs were successfully turned into concentrical CNT@BNNT heteronanotubes, however the exact interactions between the BNNT and the coronene were not discovered. In photoluminescence (PL) studies we have shown that coronene and BNNT show a strong, phonon mediated interaction, when in contact with each other. The characteristic PL peak of coronene split up into multiple peaks (figure 7), with energy difference of the BNNT phonon modes, when the illuminating photon energy is comparable to the excitation energy of localized defects in BNNT. Due to the low Debye-Waller factor of the defect-phonon interaction in BNNT, this suggests a localized exciton mediated energy transfer between the nanotubes and the filler material. This interaction is also present on the surface of hBN.