Spectroscopic study of chemically modified low-dimensional materials

Detailed results

During the four years of the project we have focused on the spectroscopic investigation of low dimensional systems in their pristine and modified form. The results can be categorized based on the dimensionality of the investigated material:

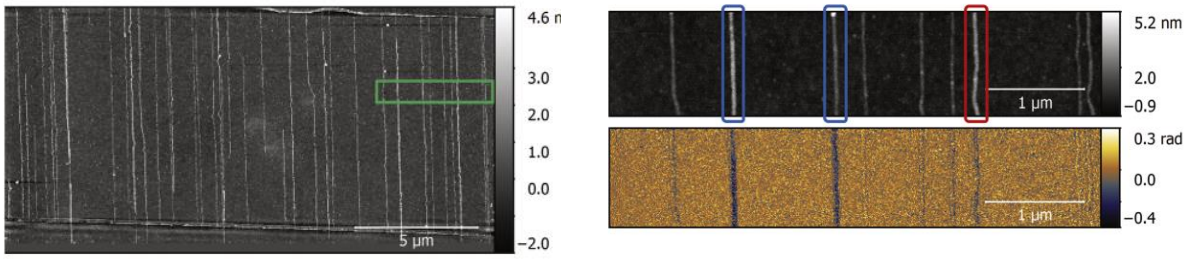
1. One dimensional materials like carbon of boron-nitride nanotubes (CNT, BNNT) were investigated by conventional far field spectroscopic techniques and a scattering type near-field infrared microscope (SNOM), which is capable of providing infrared spectral information with 20nm spatial resolution. We were interested in the filling of the nanometer sized cavity of the nanotubes with sufficiently small molecules. We have also induced chemical reactions between the encapsulated molecules either by heath or light. We have also investigated the plasmonic properties of these materials such as enhanced near-field scattering by surface plasmon-polaritons in BNNTs or the excitation of Luttinger plasmon phonon polaritons in CNTs.
2. Two dimensional materials: within this topic we were in collaboration with other research groups and published jointly high impact papers concerning the catalytic properties of transition metal chalcogenides and the quantum spin hall insulator properties of an exotic layered material.
3. Three dimensional materials. This was an outlook to the topic of perovskite based solar cell materials. Besides the fascinating electro-optical properties, we were also interested in the combination of low-dimensional carbon based materials (nanotubes, graphene) and the perovskites.

Due to the pandemic we had less opportunity to present the results at conferences, the few occasions were online meetings. We have published 13 papers in international journals related to the topic of the project (see bibliography at the end of the document).

A brief summary of selected publications:

1.) Nanoscale Characterization of Individual Horizontally Aligned Single-Walled Carbon Nanotubes [1]

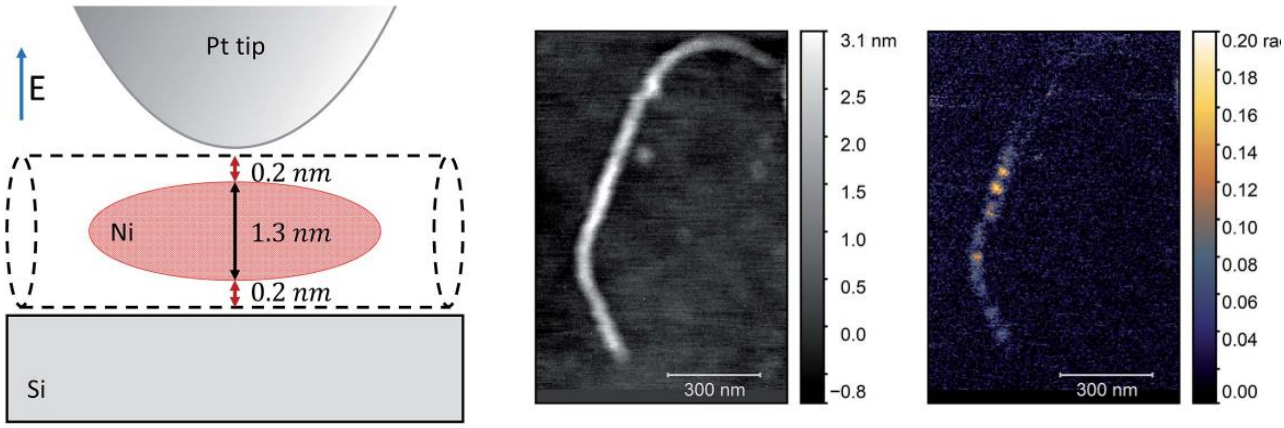
We have investigated individually grown single walled carbon nanotubes with our SNOM setup. We were able to distinguish between metallic and semiconducting species based on the difference in the phase of the scattered near-field light.



1. Figure Left: scanning electron microscope image of the sample showing the individually grown nanotubes. Right top: atomic force microscopy (AFM) image of the green region highlighted on the right image. Blue box indicates metallic, red box indicates semiconducting nanotubes. Right bottom: SNOM phase image of the same region. Metallic nanotubes show visible phase contrast compared to the substrate (Si) while in case of semiconducting nanotubes the phase contrast is negligible.

2.) Near-field infrared microscopy of nanometer-sized nickel clusters inside single-walled carbon nanotubes [2]

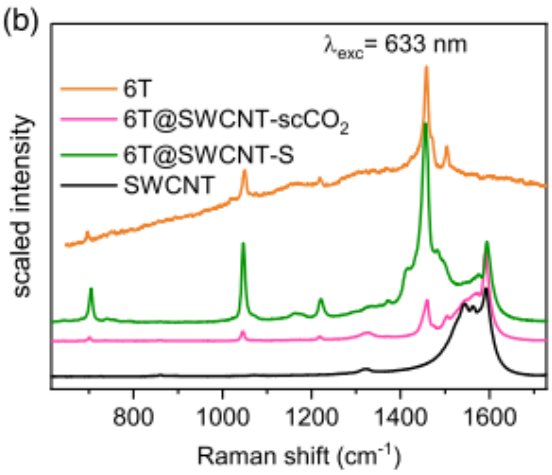
Single walled carbon nanotubes were filled with Ni(II) acetylacetonate (NiACAC). Annealing the samples at 700°C transformed the molecules into metallic Ni clusters. The presence of the Ni clusters was detected by SNOM microscopy showing a remarkable detection limit of about 700 Ni atoms.



2. Figure Left: schematic representation of the measurement geometry. The SNOM method employs a metallic tip illuminated with infrared laser. The resulted scattered light is collected and analyzed. Middle: AFM topography of a selected nanotube. Right: near-field phase image showing high contrast regions along the nanotube indicating the presence of encapsulated Ni clusters.

3.) Encapsulation of Sexithiophene Molecules in Single-Walled Carbon Nanotubes Using Supercritical CO2 at Low Temperature [3]

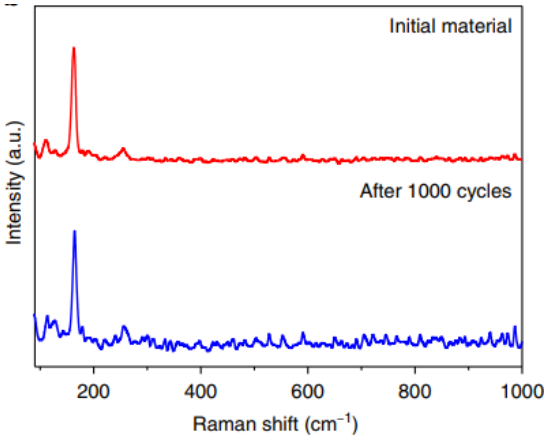
Carbon nanotubes are ideal nanoreactors for encapsulated small molecules. We showed that sexithiophene (6T) can be successfully encapsulated into carbon nanotubes using low-temperature nanoextraction from supercritical CO_2. This filling method prevents the formation of insoluble longer oligomers on the outer surface of the carbon nanotubes.



3. Figure Raman spectra of 6T, empty nanotube (SWCNT), filled nanotube using high temperature sublimation (6T@SWCNT-S) and filled nanotube using supercritical CO_2 method (6T@SWCNT-scCO2). The spectra indicate high filling ratio for the low temperature method as well.

4.) The rapid electrochemical activation of MoTe2 for the hydrogen evolution reaction [6]

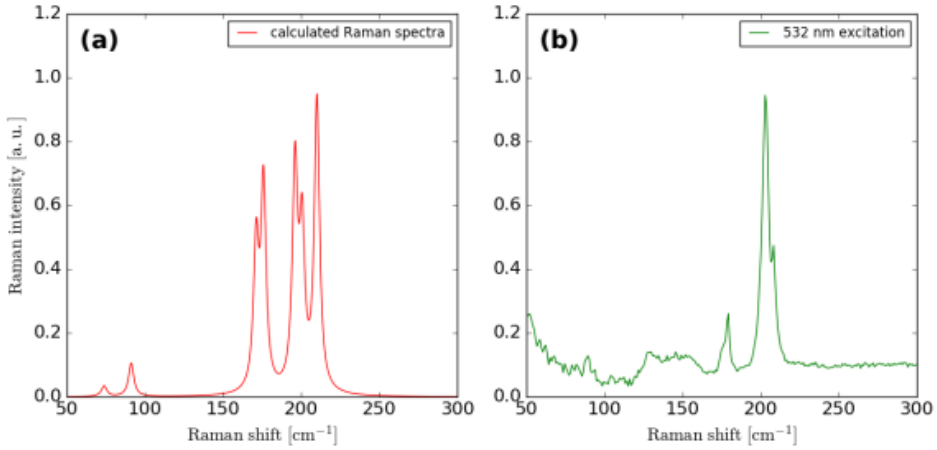
Transition metal chalcogenides show considerable promise as catalysts for electrochemical generation of hydrogen. In this publication we have investigated the catalytic performance of metallic 1T'-MoTe2. Our contribution to the project was the spectroscopic confirmation of the stability of the material under numerous test cycles.



4. Figure Wide-range Raman spectra of nanocrystalline 1T'-MoTe2 measured before (top) and after 1000 cycles (bottom). The material remains unchanged; hence we can eliminate any structural changes.

5.) Signature of Large-Gap Quantum Spin Hall State in the Layered Mineral Jacutingaite [7]

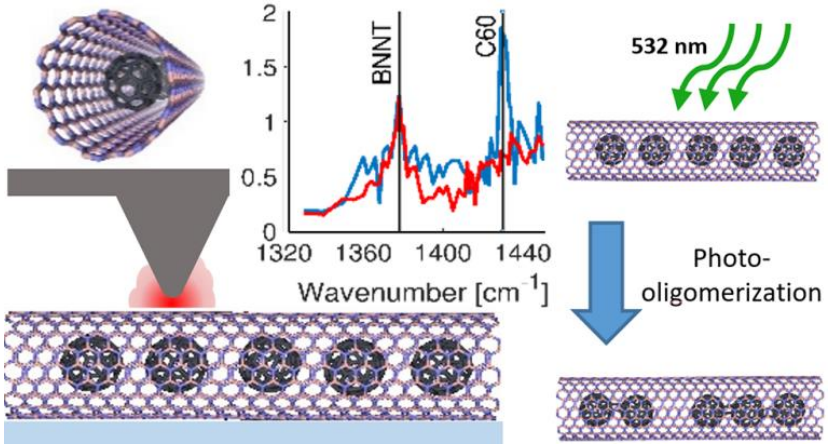
Jacutingaite is a quantum spin Hall (QSH) insulator, promising for applications like low power electronics, quantum computing. A major challenge is the identification of large gap QSH materials, which would enable room temperature dissipationless transport in their edge states. Jacutingaite is stable in air, and we demonstrate exfoliation down to at least two layers and show that it can be integrated into heterostructures with other two-dimensional materials. This adds a topological insulator to the 2D quantum material library. We have contributed to the project by the Raman spectroscopic investigation of the synthetically produced sample.



5. Figure Raman spectrum of jacutingaite. (a) Calculated Raman spectrum of Pt2HgSe3. (b) Measured Raman spectrum of Pt2HgSe3. Laser power was 1.5 mW

6.) Polaritonic Enhancement of Near-Field Scattering of Small Molecules Encapsulated in Boron Nitride Nanotubes: Chemical Reactions in Confined Spaces [10]

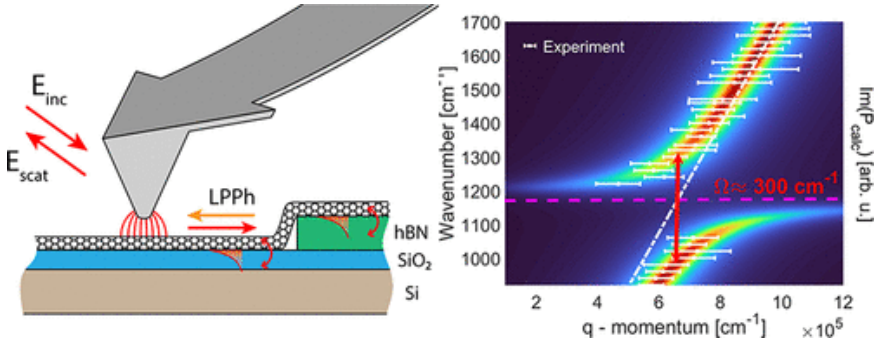
We showed that phonon polaritons of boron nitride nanotubes (BNNTs) enhance the near-field vibrational spectra of molecules in close proximity to the surface. By encapsulating C_{60} fullerene in BNNTs, we reached a sensitivity level of a few hundred molecules. Furthermore, we showed by the photopolymerization of C60 that products of chemical reactions inside the tubes can be identified, so long as their vibrational signatures lie in the reststrahlen band of the BNNT.



6. Figure Schematic of the measurement concept. The near-field infrared spectrum indicates the presence of C60 molecules inside the nanotubes. After laser irradiation appearance of characteristic peaks indicate the photo-polimerization of the molecules inside the nanotube.

7.) Direct Visualization of Ultrastrong Coupling between Luttinger-Liquid Plasmons and Phonon Polaritons [11]

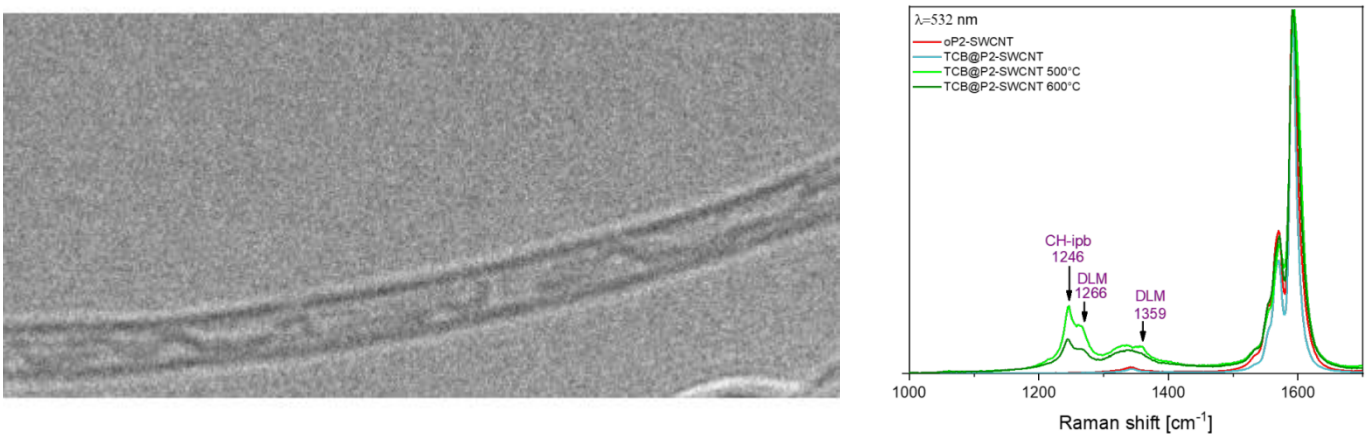
One-dimensional Luttinger-liquid plasmons in metallic carbon nanotubes are long-lived excitations with extreme electromagnetic field confinement. We applied near-field polariton interferometry to examine the interaction between propagating Luttinger-liquid plasmons in individual carbon nanotubes and surface phonon polaritons of silica and hexagonal boron nitride. The extracted dispersion shows pronounced mode splitting, indicating the ultrastrong coupling with both native silica and hBN phonons



7. Figure Measurement schematics, and the extracted dispersion relation.

8.) Molecular Encapsulation from the Liquid Phase and Graphene Nanoribbon Growth in Carbon Nanotubes [12]

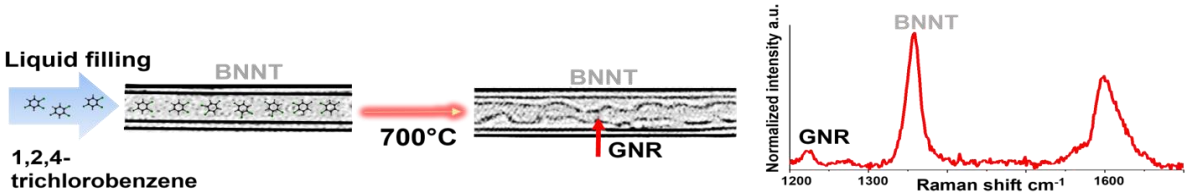
We have grown graphene nanoribbons inside carbon nanotubes by encapsulation of 1,2,4-trichlorobenzene from the liquid phase and subsequent annealing. This procedure resulted in graphene nanoribbons several tens of nanometers long. The presence of nanoribbons was proven by Raman spectra both on macroscopic samples and on the nanoscale by tip-enhanced Raman scattering and high-resolution transmission electron microscopic images.



8. Figure Left: Transmission microscope image of graphene nanoribbon grown inside a carbon nanotube. Right: Raman spectra showing the emergence of nanoribbon related peaks at certain annealing temperatures.

9.) Encapsulation of the Graphene Nanoribbon Precursor 1,2,4-trichlorobenzene in Boron Nitride Nanotubes at Room Temperature [13]

We prepared graphene nanoribbons inside boron nitride nanotubes by liquid phase encapsulation and subsequent annealing of 1,2,4-trichlorobenzene. The product was imaged with high resolution transmission electron microscopy, and characterized by optical absorption and Raman spectroscopy. The observed structures twist under the electron beam and the characteristic features of nanoribbons appear in the Raman spectra.



9. Figure Schematic of the experiment. High resolution transmission electon microscope image showing ribbon like structure inside the BNNT. After annealing the Raman spectum shows additional peaks associated with graphene nanoribbons.

Bibliography

(1) Németh, G.; Datz, D.; Tóháti, H. M.; Pekker, Á.; Otsuka, K.; Inoue, T.; Maruyama, S.; Kamarás, K. Nanoscale Characterization of Individual Horizontally Aligned Single-Walled Carbon Nanotubes. *Physica Status Solidi (b)* **2017**, *254* (11), 1700433. https://doi.org/10.1002/pssb.201700433.

(2) Németh, G.; Datz, D.; Pekker, Á.; Saito, T.; Domanov, O.; Shiozawa, H.; Lenk, S.; Pécz, B.; Koppa, P.; Kamarás, K. Near-Field Infrared Microscopy of Nanometer-Sized Nickel Clusters inside Single-Walled Carbon Nanotubes. *RSC Adv.* **2019**, *9* (59), 34120–34124. https://doi.org/10.1039/C9RA07089C.

(3) Cadena, A.; Botka, B.; Székely, E.; Kamarás, K. Encapsulation of Sexithiophene Molecules in Single-Walled Carbon Nanotubes Using Supercritical CO_2 at Low Temperature. *Phys. Status Solidi B* **2020**, *257* (12), 2000314. https://doi.org/10.1002/pssb.202000314.

(4) Németh, G.; Pekker, Á. New Design and Calibration Method for a Tunable Single-Grating Spatial Heterodyne Spectrometer. *Opt. Express* **2020**, *28* (15), 22720. https://doi.org/10.1364/OE.395569.

(5) Bortel, G.; Kováts, É.; Földes, D.; Jakab, E.; Durkó, G.; Pekker, S. Recognition-Control and Host–Guest Interactions in High-Symmetry Cocrystals of Fullerenes with Cubane and Mesitylene. *Crystal Growth & Design* **2020**, *20* (6), 4169–4175. https://doi.org/10.1021/acs.cgd.0c00440.

(6) McGlynn, J. C.; Dankwort, T.; Kienle, L.; Bandeira, N. A. G.; Fraser, J. P.; Gibson, E. K.; Cascallana-Matías, I.; Kamarás, K.; Symes, M. D.; Miras, H. N.; Ganin, A. Y. The Rapid Electrochemical Activation of MoTe2 for the Hydrogen Evolution Reaction. *Nat Commun* **2019**, *10* (1), 4916. https://doi.org/10.1038/s41467-019-12831-0.

(7) Kandrai, K.; Vancsó, P.; Kukucska, G.; Koltai, J.; Baranka, G.; Ákos Hoffmann; Áron Pekker; Kamarás, K.; Horváth, Z. E.; Vymazalová, A.; Tapasztó, L.; Nemes-Incze, P. Signature of Large-Gap Quantum Spin Hall State in the Layered Mineral Jacutingaite. *Nano Lett.* **2020**, *20* (7), 5207–5213. https://doi.org/10.1021/acs.nanolett.0c01499.

(8) Cadena, A.; Botka, B.; Kamarás, K. Organic Molecules Encapsulated in Single-Walled Carbon Nanotubes. *Oxford Open Materials Science* **2020**, *1* (1), itab009. https://doi.org/10.1093/oxfmat/itab009.

(9) Özeren, M. D.; Botka, B.; Pekker, Á.; Kamarás, K. The Role of Potassium in the Segregation of $MAPb(Br_{0.6}I_{0.4})_3$ Mixed-Halide Perovskite in Different Environments. *Phys. Status Solidi RRL* **2020**, *14* (12), 2000335. https://doi.org/10.1002/pssr.202000335.

(10) Datz, D.; Németh, G.; Walker, K. E.; Rance, G. A.; Pekker, Á.; Khlobystov, A. N.; Kamarás, K. Polaritonic Enhancement of Near-Field Scattering of Small Molecules Encapsulated in Boron Nitride Nanotubes: Chemical Reactions in Confined Spaces. *ACS Appl. Nano Mater.* **2021**, *4* (5), 4335–4339. https://doi.org/10.1021/acsanm.1c00064.

(11) Németh, G.; Otsuka, K.; Datz, D.; Pekker, Á.; Maruyama, S.; Borondics, F.; Kamarás, K. Direct Visualization of Ultrastrong Coupling between Luttinger-Liquid Plasmons and Phonon Polaritons. *Nano Lett.* **2022**, *22* (8), 3495–3502. https://doi.org/10.1021/acs.nanolett.1c04807.

(12) Cadena, A.; Botka, B.; Pekker, Á.; Tschannen, C. D.; Novotny, L.; Khlobystov, A. N.; Kamarás, K. Molecular Encapsulation from the Liquid Phase and Graphene Nanoribbon Growth in Carbon Nanotubes. *The Journal of Physical Chemistry Letters* **2022** (submitted: 2022.06.30. accepted: 2022.09.28.)

(13) Cadena, A.; Pekker, Á.; Botka, B.; Dodony, E.; Fogarassy, Z.; Pécz, B.; Kamarás, K. Encapsulation of the Graphene Nanoribbon Precursor 1,2,4-trichlorobenzene in Boron Nitride Nanotubes at Room Temperature. *Physica Status Solidi Rapid Research Ltrs* **2022**, pssr.202200284. https://doi.org/10.1002/pssr.202200284.