Final report
Project ANN 107580
Nanoscale investigation of molecular scaffolding

Participants:
Katalin Németh was replaced by Zsolt Szekrényes in the first year of the project. His expertise is in near-field and luminescence spectroscopy and in SiC nanocrystals. Áron Pekker joined the project in the second year to work on sample preparation and near-field infrared microscopy. Students involved were Bálint Pataki (near-field microscopy), Judit Horváth, Beáta S. Nagy (preparation of hybrid materials), Dániel Datz and Gergely Németh (near-field microscopy and model calculations).

Work plan: The original plan focused on the combination of high-resolution transmission electron microscopy and near-field optical microscopy on molecular scaffolds in order to obtain information with spatial resolution of a few angstroms and energy resolution of a few meV. Both instruments were newly installed in the respective laboratories and their installation and testing took more time than expected. Therefore, the collaborative work consisted mainly of discussions about sample preparation methods and training in each other's methods. Spectroscopy on hybrid structures was performed in Budapest as planned and several types of materials were studied by different spectroscopic methods in both far and near field. Besides carbon nanotube and graphene-based samples, we also extended our studies to boron nitride nanotubes, silicon carbide nanocrystals and nanostructured perovskites and their hybrids with carbon nanotubes. Below, we will first give an overview on the experimental developments, then will summarize the results grouped according to the investigated families of materials. We give the list of publications in the end, in order to be able to refer to them in the text. In case of unpublished work (including unpublished conference posters and theses) we present the results in a more detailed form.

Near-field infrared microscopy and spectroscopy: theory and practice of s-SNOM system

The near-field infrared spectrometer was installed and tested with standard samples. Modeling work started with the light scattering process and calculating the optical conductivity from the phase and amplitude of the scattered light by a simple model for nanotubes [C-2]. It continued with the detailed mechanism of nearfield infrared spectroscopy, using a combined theoretical-experimental approach: extended finite element modeling applied to gold nanospheres on SiO_2 substrate as model systems. The model took into account the special tip-sample interaction due to the finite size and height of nanometer-sized samples and produced excellent agreement with the experiment [T-4]. Then the finite-element calculation was extended from spheres to cylinders, in order to obtain a more realistic model for nanowires [C-4,T-5].

The most important experimental development was the automated control of the wavelength change of the exciting infrared laser, with simultaneous optimization of the pseudoheterodyne detection. This modification made it possible to obtain near-field spectra with 1.5 cm^{-1} spectral resolution. The spectrum of boron nitride nanotubes is shown in Fig. 1. [C-5]. The simple approach to calculate the extinction coefficient from the amplitude A and phase φ of the scattered signal $k = A*\sin\varphi$ agrees with the result of finite-element simulations [T-5].

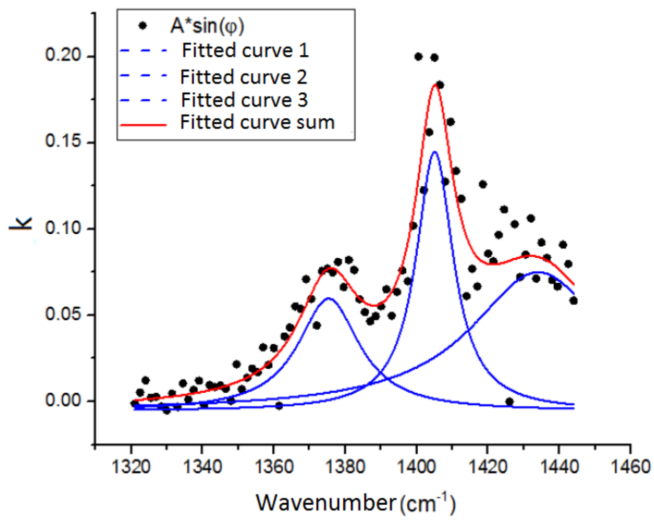

Fig. 1. Extinction coefficient of boron nitride nanotubes determined from nanospectroscopy. The results are in agreement with the literature, but show better spectral resolution [C-5].

Investigation of nanostructures and hybrid systems by near-field microscopy and spectroscopy

We performed a detailed study of carbon nanotubes of different electronic type by far-field spectroscopy and near-field microscopy. We first determined the bundle structure of each type of nanotubes (metallic, semiconducting and mixed) by AFM topography and found that the average bundle diameter is 50 nm. The optical conductivity of the nanotube samples, calculated from wide-range far-field spectra by Kramers-Kronig transformation, showed qualitative agreement with the nanotube type: highest in the metallic tubes, lowest in semiconducting tubes and intermediate in the mixture. The nanotubes were used for transparent conducting coatings and we also determined the conductivity change and stability of various samples [A-1].

Next we studied the nearfield signal of each type of carbon nanotube bundles of 10 nm diameter. Using the above-mentioned extended finite dipole model for cylindrical samples, and the dielectric functions from the far-field measurements as input parameters, we predicted a significant difference in the phase of the scattered signal from the two types of nanotubes. Indeed, in the mixed sample, metallic and semiconducting bundles could be identified based ont the phase contrast with the substrate [A-2].

We studied another intriguing nearfield effect in hybrid systems of carbon nanotubes and graphene with small organic molecules. We have observed earlier that the infrared absorption of small molecules disappears when encapsulated inside carbon nanotubes. We attributed this finding to “active cloaking”, the consequence of mirror dipoles in the polarizable electron system of the nanotube walls, vibrating out of phase with the molecules themselves. The importance of the delocalized π-electrons was proven by the absence of cloaking in boron nitride nanotubes, where the electrons are localized and therefore the polarizability is low. An analogous phenomenon has been found when coating fullerene molecules with graphene: graphene coating decreases the infrared signal from the molecular vibrations. These measurements have been performed at the IR beamline of the synchrotron facility Soleil, where the IR flux was high enough [A-3].

We also studied CVD graphene on copper and silicon and freestanding graphene on a transmission electron microscope grid by near-field infrared spectroscopy, in collaboration with the Nanostructures Department of the Institute of Technical Physics, HAS. On frees tanding graphene the mechanic al vibrations of the graphene sheet prevent high-quality images, therefore we have to try further technical improvements . In graphene sheets on substrates, we could identify grain boundaries not detectable by normal atomic force microscopy (Fig. 2.).

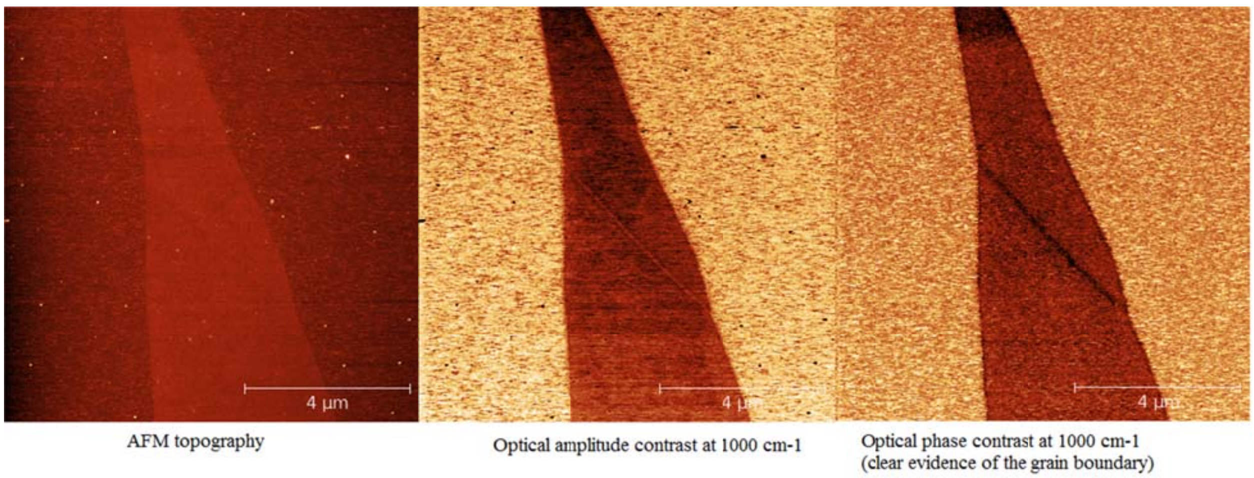

Fig. 2. AFM topography image and optical amplitude and phase contrast of graphene sheet on Si.

We synthetized coronene adsorbed on freestanding graphene layers on transmission electron microscopy (TEM) grids (courtesy of Levente Tapasztó, MFA) and determined its presence by its Raman spectrum. Thermal deposition by sublimation of coronene in vacuum was used to produce the adsorbed molecules. Transmission electron microscopy taken by the Austrian partner showed that the coronene molecules were clustered, instead of covering the surface as a uniform layer (Fig. 3.) We started to build a new evaporator in order to produce more finely resolved monolayers of coronene and other polyaromatic hydrocarbons on graphene, but this process has not been finished by the end of the project.

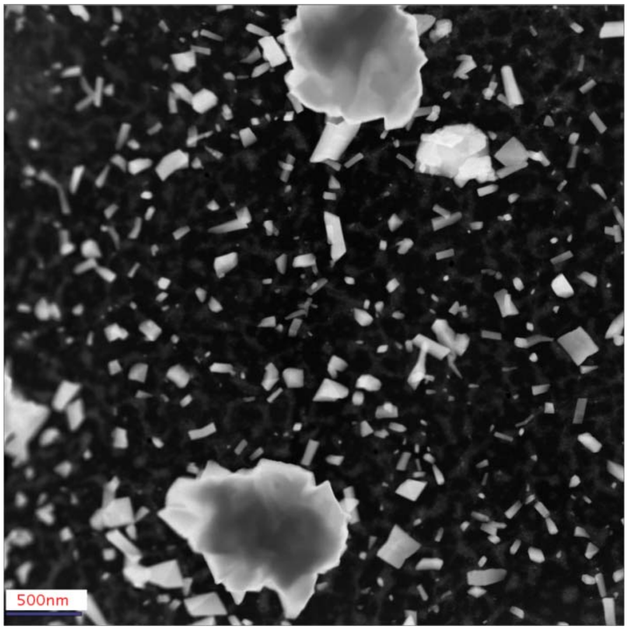

Fig. 3. Transmission electron microscopy image of coronene deposited on TEM grid (Jannik Meyer, University of Vienna)

Other nanostructured inorganic materials

Nanocrystalline SiC is promising as a luminescent bioinert material. Using SiC nanocrystals as scaffolds, surface groups can act as stabilizers, help solubility or induce chemical bonding in a biological environment. We have measured temperature-dependent far-field infrared spectra of these samples and followed some reactions on their surface by another near-field method: infrared attenuated total reflectance (ATR). We identified several surface chemical groups and followed their chemical reactions on SiC nanocrystals. We proved that carboxyl functional groups tend to occupy neighboring sites on the nanocrystal surface, instead of a uniform distribution [A-4]. We followed various oxidation and reduction reactions on carboxyl-coated SiC nanocrystals by infrared ATR spectroscopy, identified the products and related them to photoluminescent properties [A-5].

Another type of biologically relevant scaffold is the polysaccharide dextran used for label-free biosensors. We characterized ultrathin layers of carboxymethylated dextran grafted to Si crystals by ATR-IR spectroscopy to detect the carboxyl groups. ATR, detecting near-field spectra, is uniquely sensitive to such ultrathin films [A-6].

In the case of methylamine lead iodide ($CH_3NH_3PbI_3$) nanowires (prospective candidates for a new family of highly efficient solar cells), we proved by both far- and nearfield infrared spectroscopy that the nanowires have the same infrared spectrum (and therefore the same chemical structure) as the macroscopic material [A-7]. These measurements constitute the first step towards building more complicated scaffold-based structures, e.g. with carbon nanotubes or graphene [S-3].

List of publications resulting from the project:

Articles in international journals:

A-1. H.M. Tóháti, Á. Pekker, B.Á. Pataki, Zs. Szekrényes, K. Kamarás:
Bundle versus network conductivity of carbon nanotubes separated by type
Eur. Phys. J. B **87,** 126-1-6 (2014)

A-2. 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)

A-3. 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)

A-4. Zs. Szekrényes, B. Somogyi, D. Beke, Gy. Károlyházy, I. Balogh, K. Kamarás, A. Gali:
Chemical transformation of carboxyl groups on the surface of silicon carbide quantum dots
J. Phys. Chem. C **118,** 19995-20001 (2014)

A-5. D. Beke, T.Z. Jánosi, B. Somogyi, D.Á. Major, Zs. Szekrényes, J. Erostyák, K. Kamarás, A. Gali: **Identification of luminescence centers in molecular-sized silicon carbide nanocrystals**
J. Phys. Chem. C **120,** 685-691 (2016)

A-6. A. Saftics, S. Kurunczi, Zs. Szekrényes, K. Kamarás, N.Q. Khánh, A. Sulyok, S. Bősze, R. Horvath: **Fabrication and characterization of ultrathin dextran layers: Time dependent nanostructure in aqueous environments revealed by OWLS**
Colloids Surf. B Biointerfaces **146,** 861-870 (2016)

A-7. E. Horváth, M. Spina, Zs. Szekrényes, K. Kamarás, R. Gaal, D. Gachet, L.Forró:
Nanowires of lead-methylamine iodide ($CH_3NH_3PbI_3$) prepared by low-temperature solution processed crystallization
Nano Lett. **14,** 6761-6766 (2014)

Conference presentations:

C-1. K. Kamarás, H.M. Tóháti, G.Klupp, K. Németh, B.Botka, R. Hackl, M.E. Füstös, T.W. Chamberlain, A.N. Khlobystov: **Hybrid materials formed from coronene and carbon nanostructures**
International Winterschool on the Electronic Properties of Novel Materials (IWEPNM 14), Kirchberg, Austria, March 2014, poster

C-2. B.Á. Pataki, H. M. Tóháti[1], Zs. Szekrényes, A. Cernescu, S. Amarie, F. Keilmann, K. Kamarás: **Infrared nano-imaging of conduction electrons in carbon nanotubes separated by type**
International Winterschool on the Electronic Properties of Novel Materials (IWEPNM 14), Kirchberg, Austria, March 2014, poster

C-3. K. Kamarás, B.S. Nagy, H. M. Tóháti, B. Botka, R. Hackl, T.W. Chamberlain, A.N. Khlobystov: **Spectroscopy and microscopy of coronene-carbon nanotube hybrid structures**
American Physical Society March Meeting, San Antonio, TX, USA, March 2015, lecture

C-4. D. Datz, G. Németh, H.M. Tóháti, T. Gál, P. Koppa, Ö. Sepsi, Á. Pekker, K. Kamarás: **Finite element simulation of scattering near-field optical microscopy measurement of carbon nanotubes**
International Winterschool on the Electronic Properties of Novel Materials (IWEPNM 16), Kirchberg, Austria, March 2016, poster

C-5. D. Datz, G. Németh, H.M. Tóháti, T. Gál, Ö. Sepsi, P. Koppa, Á. Pekker, K. Kamarás: **s-SNOM measurements of boron nitride nanotubes**
7th Szeged International Workshop on the Advances in Nanoscience, Szeged, Hungary, October 2016, poster

C-6. G. Németh: **Near-field infrared nanoscopy on different types of carbon nanotube bundles**
7th Szeged International Workshop on the Advances in Nanoscience, Szeged, Hungary, October 2016, lecture

Student theses connected to the project:

T-1. Zsolt Szekrényes: **Study of complex nanostructures by infrared spectroscopy**
PhD, Óbuda University, 2015

T-2. Katalin Németh: **Chemical modification and optical spectroscopy of single-walled carbon nanotubes**
PhD, University of Pannonia, 2016

T-3. Bea Botka: **Optical and Raman spectroscopy of carbon nanotube-based hybrid materials**
PhD, Budapest University of Technology and Economics, 2016

T-4. Gergely Németh: **Investigation of nanostructures by near-field infrared spectroscopy**
MSc, Budapest University of Technology and Economics, 2016

T-5. Dániel Datz: **Near-field infrared nanospectroscopy**
MSc, Eötvös Loránd University, 2016

T-6. Judit Horváth: **Investigation of fulleride anions by infrared spectroscopy**
BSc, Eötvös Loránd University, 2015

Seminars and colloquia:

[S-1] April 24, 2015 - University of Vienna, Katalin Kamarás

[S-2] May 2015 - University of Szeged, Katalin Kamarás

[S-3] December 4, 2015 - Ecole Polytechnique Féderale de Lausanne, Katalin Kamarás

[S-4] April 8, 2016 - Budapest University of Technology and Economics, Katalin Kamarás