## Investigating the surface transfer doping of organic molecules on diamond

Principal Investigators:

Prof. Rafi Kalish - Physics, Technion Prof. Loh Kina Ping - Chemistry, NUS Start Year ► 2007

The proposed work is to investigate the "transfer doping" that H terminated diamond surfaces undergo as a result of exposure to specific "tailor made" organic molecules with high electron affinity.

The work is driven by the, by now, well studied and well established fact that two dimensional p-type surface conductivity on nominally undoped diamond is induced following surface hydrogenation of diamond and exposure to some specific molecules ( $H_2O$   $C_{60}$ ). These have been explained by an electrochemical model in which the reduction of hydrated protons in an aqueous surface layer gives rise to a hole accumulation layer in the diamond. This is the so-called surface transfer doping, where the adsorbate induces charge transfer from diamond.

The present work is to study the surface transfer doping effects induced by specific organic molecules with high electron affinity including a class of interesting molecules such as P4-TCNQ,  $C_{60}$  etc. This charge transfer across the organic – diamond interface has not been investigated despite its fundamental importance and relevance to photovoltaics and to bio-sensing. Surface transfer doping thus appears to be the mechanism behind a variety of surface electronic phenomena which, when controlled, may become a valuable tool for engineering micrometer- and nano-meter-scale electronic devices.

This study requires the manufacturing of H terminated diamond surfaces, their exposure to selected molecular species, the study of the electrical properties of the so produced surfaces at the various stages and the investigation of these as for their electron-emission properties.

The work at NUS has been proceeding well, though at a slower pace then expected. Following preliminary experiments in which Prof. Kalish took part in experiments with Prof Loh's team during his one week visit to NUS (Oct 2008) it turned out that in order to be able to perform the required transfer doping in a well controlled manner, both diamond surface hydrogenation, exposure to the selected molecular species, as well as the preliminary electrical evaluations are best all performed *in situ* with no exposure to atmosphere. This has required substantial technical modifications to the glove box and other sample handling systems as well as the installment of an in situ electrical evaluation system.

The work at the Technion has concentrated, so far, on detailed electrical evaluations of H terminated diamond surfaces using Hall effect measurements at different temperatures.

These experiments, which are ongoing, were started during the visit of Mr. Yu Lin, a graduate student of Prof. Loh, to the Technion. At the Technion preliminary Hall effect measurements on P4 PNQ and C60 exposed diamond surfaces, were carried out. In light of the technological systems modifications required both on the NUS and the Technion sides the project has been extended without any increase in the budget for another 6 months.

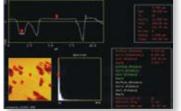
Two graduate students are involved in this research: Mr. Torjman (an MSc student of Prof. Kalish) and Mr. Yu Lin (a PhD student of Prof. Loh).

Slide 1 Microscope image of C(100)



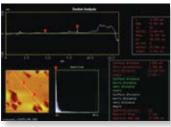
Macroscopic pits and scratches. On both sides of diamond.





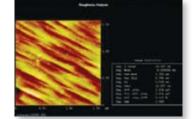
10um x 10um scan area shows numerous pits of 150nm depth and area of a few microns.

Slide 4 Dropcastof F4TCNQ



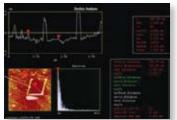
10 um x 10 um scan area

Slide 3 Zoomed in on flat area



In an imaged area of 2.5 um2, the flat surface roughness  $$\rm Rms{=}~0.8\ nm.$  Not very flat.

Slide 5 Dropcast of F4TCNQ



Nano droplets of F4TCNQ across the flat diamond region.Scratched area

### High Power Supercapacitors Based on New Nano Structured Carbon

#### **Principal Investigators:**

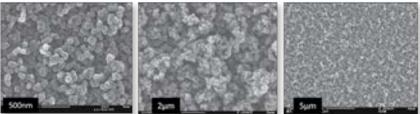
Prof. Yair Ein-Eli - Materials Engineering, Technion Prof. Yeshayahu Shay Lifshitz - Materials Engineering, Technion Prof. Lu Li - Mechanical Engineering, NUS Start Year ► 2007

The project aimed at studying and developing high performance supercapacitors by synthesis of novel porous carbon films with an extremely high surface area and which should provide high capacity and hence high power storage.

Novel porous pure carbon films with a unique fractal structure of agglomerates of basic units of carbon nanospheres (3-5 nm in diameter) were prepared on metallic substrates and used as electrodes for ultracapacitors. The high measured electrochemical capacitance of lab scale ultracaps devices made of the developed novel porous carbon electrodes is expected to increase significantly by modifying the electrolyte and the parameters controlling the carbon deposition.

#### Results obtained so far:

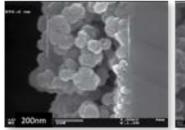
Porous carbon films were prepared on metallic electrodes. These special films have a fractal structure of agglomerates of carbon spheres which can be observed from the micron scale down to nanoscale (nanospheres of 3-5 nm). Their density is ~0.5g/cm<sup>3</sup> and their surface area increases with thickness to reach a value of 170 m<sup>2</sup>/gr (for 1 micron thick films). The measured electrochemical capacitance of lab scale cells made of porous carbon electrodes immersed in aqueous solution increases linearly with thickness to reach 3.3mF/cm<sup>2</sup> for 1 micron thick films. This value is expected to be significantly increased by increasing the thickness and by switching the electrolyte to a non-aqueous one.

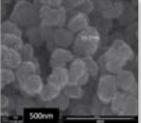


HRSEM image of the porous carbon (mag. X 50,000)

HRSEM image of the porous carbon (mag. X 10,000)







Cross section-HRSEM top view
Figure 1: HRSEM images of porous homogeneous carbon films.

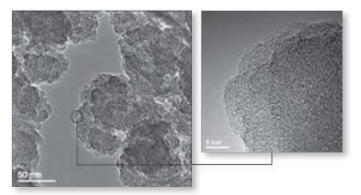


Figure 2: TEM image of carbon spheres indicating each sphere is made of smaller nanospheres (left) having a diameter of ~3-5 nm (right).

## Investigations into Berry phase and its utilization in spintronic, optical and possible quantum computing applications

Start Year ► 2007

Principal Investigators:

Dr. Eyal Buks - Electrical Engineering, Technion Dr. Mansoor Jalil - Electrical & Computer Engineering, NUS

The scientific goal of this research is to study geometrical phases in several mesoscopic systems.

In this project, we aim to study the Berry-phase effect in the presence of spin-orbit interactions. These originate from electric fields in the lattice reference frame being Lorentz transformed to a magnetic field in the reference frame of the moving electron. It has been predicted that a geometrical (Berry) Phase that an electron acquires due to this SO interaction may affect the conductance of mesoscopic structures such as the Aharonov-Casher rings. It turns out that the realization of the ideal conditions, which are required for a clear smoking-gun experimental demonstration of these effects, is highly challenging. Here, we propose to study novel configurations for the observation and investigation of a geometrical phase originating from SO interaction. Rather than considering and assuming ideal conditions, we will focus on a careful analysis of realistic device parameters and non-ideal conditions (e.g. non-adiabbaticity, interband mixing) in order to develop a feasible experimental configuration. The theoretical interest lies in understanding the additional contributions from nonuniform (chiral) spin texture or electric magnetic field configurations, and the effects of introducing symmetry-breaking, interfaces, and hybrid segments. The study of Berry phase is also extended to two-dimensional magnetic conductors in the presence of Rashba/Dresselhaus spin-orbit effects. Our recent studies have shown that Berry phase not only affects the electron dynamics, but also that of local magnetic moments. This has many implications in spintronic devices: Berry phase can potentially be applied for spin transfer switching, spin microwave excitations and controlled domain wall motion.

#### Results obtained so far by the Technion group:

The system under investigation is a superconducting stripline resonator (SSR), which is integrated with a superconducting interference device (SQUID). The SQUID loop contains two nanobridges that serve as weak links. The flux-dependent inductance of the SQUID allows tuning the resonance frequencies of the SSR. Moreover, the large nonlinear inductance of the SQUID, which also can be tuned by the external flux, gives rise to strong nonlinear response of the SSR. We have developed a theoretical model to describe the system. In that model we employ an adiabatic approximation to eliminate the relatively fast degrees of freedom of the SQUID. The resulting effective Hamiltonian contains a geometrical vector potential, which gives rise to Berry's phase accumulated during cyclic evolution of the SSR degrees of freedom. Our preliminary results are summarized in a draft that has been recently submitted for publication. In the theoretical section of that draft we kept only the lowest order term in the adiabatic expansion. In our current work we include the first order terms in the adiabatic expansion in order to study corrections due to non-adiabaticity.

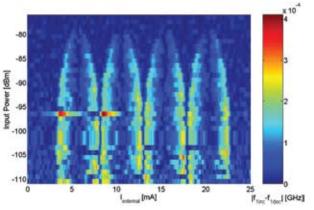
One student took part in the research.

#### Publications:

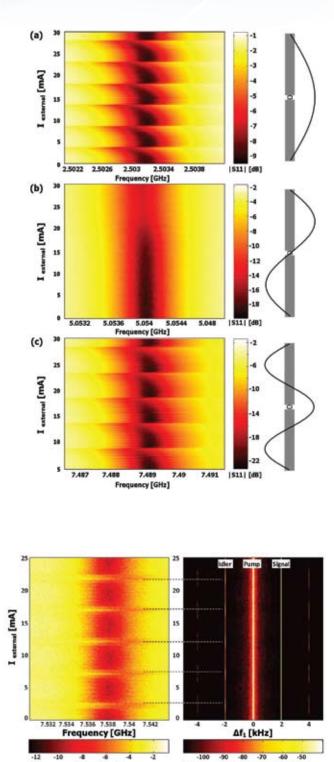
[1] Intermode Dephasing in a Superconducting Stripline Resonator

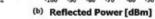
Oren Suchoi, Baleegh Abdo, Eran Segev, Oleg Shtempluck, Miles Blencowe and Eyal Buks, submitted for publication, arXiv:0901:3110

[2] Intermode Dephasing in a Superconducting Stripline Resonator - Supplementary Information Oren Suchoi, Baleegh Abdo, Eran Segev, Oleg Shtempluck, Miles Blencowe and Eyal Buks, submitted for publication, arXiv:0901:3133



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(a)

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## Utilization of quantum dots for tracking human embryonic stem cells-derived cardiomyocytes transplanted into the infracted myocardium in rats

Start Year ► 2008

Principal Investigators:

Prof. Ofer Binah - Medicine, Technion Prof. Itskovitz-Eldor Joseph - Medicine, Technion Prof. Yonina Eldar - Electrical Engineering, Technion

The past decade has seen rapid advances in the use of embryonic and adult stem cells for tissue regeneration and repair in the heart. These cells may have the potential to differentiate into mature cardiac cells or promote native repair through angiogenesis, recruitment of host stem cells, or induction of myocytes into the cell cycle. However, supporting studies are not without controversy; most have been unable to adequately track delivered stem cells with sufficient resolution in large animals. The ability to account for exogenous stem cells after delivery to animal models is important not only for determining the overall efficacy of intended treatments but also to rule out potentially dangerous side effects. Thus, it becomes increasingly important to develop optimal tracking methods to identify delivered cells in vivo. Traditional tracking agents such as green fluorescent protein (GFP) or fluorescent dyes fail to illuminate delivered cells above high levels of autofluorescence in the heart. Secondary staining as used to detect LacZ or amplify GFP generates false positives and would also involve painstaking efforts to identify the exogenous cells in hundreds of tissue sections. More recently, cells have been labeled with inorganic particles for detection by magnetic resonance imaging (MRI) or positron emission tomography (PET), but these imaging approaches can resolve no fewer than thousands of cells.

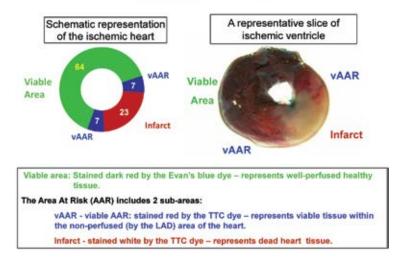
Since none of the existing tracking techniques offers the ability to unambiguously identify delivered cells in vivo with single-cell resolution using relatively high-throughput approaches (i.e., no secondary staining), in this long-term project we will utilize intracellular quantum dots (QDs) to trace hESC-CM administered to the infracted myocardium in the rat model of acute coronary syndrome (ACS). This novel nanotechnology-based procedure will enable us to accurately trace the transplanted hESC-CM into the infracted myocardium, and thus to correlate between the amount/distribution/location of the transplanted cells, and the improvement of the cardiac function as determined echocardiographically as well as by means of the Milar-Tip catheter. In brief, QDs are highly fluorescent semiconductor nanoparticles that possess unique optical properties. Hence, the on-going project is based on Prof. Ira Cohen's (a P.I on this application, Stony Brook, NY) recent studies demonstrating that single QD-human mesenechimal stem cells (hMSCs) can be easily identified in histologic sections to determine their location for at least 8 weeks following delivery in vivo. Furthermore, Cohen's group has utilized this approach to present for the first time a complete three-dimensional reconstruction of an in vivo stem cell "node."

Our specific goals are: (1) To develop the technological means to efficiently load hESC-CM with QDs. (2) To generate confocal images of the transplanted hESC-CM QDs. (3) To reconstruct the 3-D locations of the transplanted QDs-hESC-CM in the transplanted infracted (and control) myocardium. (4) To correlate between the amount and distribution of the QDs-hESC-CM with the improvement of function of the infracted myocardium.

#### Results obtained thus far:

Most of our efforts have been devoted to establishing the experimental model of myocardial infarction in rats, which is a critical prerequisite for the progression of the QD project. As can be seen in Fig. 1, we have successfully mastered the surgical technique of inducing myocardial infarction (MI) in rats, and have learned to quantify the area at risk and the infarct size. Importantly, to correlate the histological data to cardiac function, in collaboration with Prof. Dan Adam, we are monitoring by means of advances US techniques, the ventricular function. As can be seen in Fig. 2, 20 minutes and 24 hrs after LAD occlusion, ventricular function was severely depressed. Now that the surgical model and the experimental and analytical tools are functional, we will move forward to developing the QD tracking methods in the experimental animals.

#### TTC staining definitions: 24 hr post-LAD occlusion



**Figure 1**: The induction of myocardial infarction in rats by occlusion of the left anterior descending (LAD) artery and the quantitative analysis of the viable area, area at risk and the infarct size.

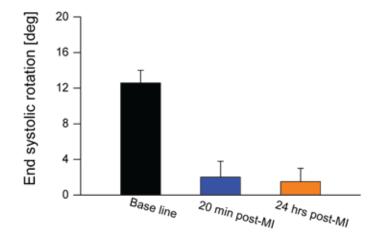


Figure 2: The reduction of ventricular function by LAD occlusion (induction of MI in the I/R model), represented by the echocardiographic measurement of "End systolic rotation".

## Nano-structure and local mechanical characteristics of natural bio-composites

Start Year ► 2008

Principal Investigators:

Prof. Emil Zolotoyabko - Materials Engineering, Technio Dr. Doron Shilo - Mechanical Engineering, Technion

The scientific goal of this research is to investigate the structural aspects of the organic/inorganic interactions and their effect on mechanical characteristics in natural bio-composites

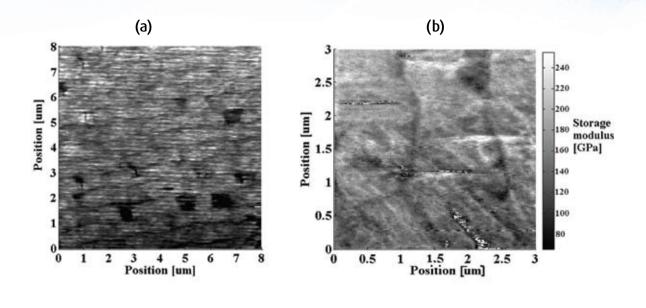
This research proposal is aimed at clarifying the mysterious routes developed in nature for producing nano-composites with extraordinary characteristics. The research program is focused on investigating the structural organization within individual crystallites containing occluded organic macromolecules and the effect of these macromolecules on local mechanical characteristics. For these purposes we plan to apply high-resolution electron microscopy ("TITAN" FEG-TEM) and newly developed technique - nano-scale mapping of elastic modules, to biogenic crystallites (calcite, aragonite, and vaterite polymorphs of calcium carbonate) extracted from mollusk shells and other organisms.

#### Results obtained so far:

We started to investigate the aragonitic nacre layer of specific shells having well defined interfaces between ceramic phase and organic substance. Nacre, also known as mother-of-pearl, is a hard biological composite found in many shells belonging to different families. Nacre is composed of a "brick-and-mortar" microstructure containing of about 95 wt% of calcium carbonate (ceramic mineral phase) and about 5 wt% of the protein-rich organic substance. The mineral is very brittle and unsuitable as a structural material. Amazingly, nacre can still sustain significant inelastic deformation and exhibit toughness being 2-3 orders of magnitude higher than that of calcium carbonate. The superior properties of nacre attract a great deal of attention focusing on clarifying the mechanisms responsible for its increased toughness. Several recent comprehensive works indicate that the high toughness is a result of a large crack process zone induced by sliding of interfaces. The properties of the mineral/organic material interface are a key issue, as they should allow sliding yet exhibit high slide resistance.

In this joint research we study the mechanical, morphological and structural characteristics of the mineral/organic interface using several techniques. The mechanical characteristics have been studied by means of a new nanoscale modulus mapping method, which allows us to map the 2D-distribution of the mechanical properties in these materials. Freshly cleaved and polished nacre specimens, taken from aragonitic shells of Perna canaliculus (green mussel), served as samples in this research. The maps of elastic modulus revealed clear separation between the ceramic lamellae and inter-lamellar organic substance (see Figure 1).

Comparison of the obtained results with finite element simulations allows us to evaluate the elastic modulus of the inter-lamellar organic material. Moreover, comparison with scanning electron microscopy images revealed an interesting and unexpected feature. While the physical thickness of the organic layers is 20-50 nm, the mechanical characteristics exhibit gradual changes across the interfaces in the range 100- 200 nm. We explain this phenomenon as a result of penetration of organic molecules inside ceramic lamellae, in concentrations which gradually decrease with the distance from the organic/mineral interface. This finding also explains the presence of the anisotropic deformations in biogenic aragonite measured by us by using high-resolution x-ray and neutron diffraction techniques.



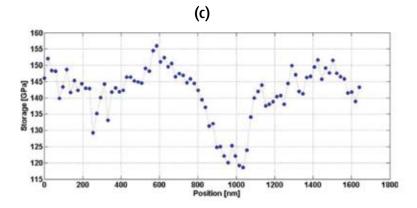


Figure 1: Storage elastic modulus maps showing: (a) the microstructure of ceramic tablets separated by thin organic layers and (b) a zoom-in on few ceramic/organic interfaces which allows their characterization with a 10 nm lateral resolution. A profile of the storage elastic modulus across an individual interface is shown in (c).

## Bright quantum dot based semiconductor sources for single and entangled photons on demand

Start Year ► 2008

Principal Investigators:

Prof. David Gershoni - Physics and The Solid State Institute, Technion Prof. Gad Bahir - Electrical Engineering and The Microelectronics Research Center, Technion

This proposal outlines a research program at the forefront of science and technology, which is based on semiconductor materials. These materials form the basis of modern electronics, communication, data storage and computing technologies, which shape our civilization. These technologies are currently based on precise control and manipulation of electric charge transport in semiconductors and the ability to use semiconductors for efficient generation and detection of light.

Our proposal aims to advance these technologies by improving the ability to control the spin state of single and of few charge carriers confined in semiconductor quantum dots, while drastically increasing the efficiency by which single photons emitted from these nanostructures, are harvested and utilized. We propose to embed these quantum dots in three dimensional, semiconductor microcavities, which strongly confine photons and enhance their interaction with the quantum dots' confined carriers. This interaction and the control over the spin state will be used in order to efficiently generate single photons with control over their internal degree of freedom – their polarization states.

The scientific goal of our research program is to develop the technology and physical understanding of light-matter interaction within semiconductors in the single-electron single-photon limit. Its technological goal is a demonstration of an efficient prototype semiconductor based light source, capable of producing polarization entangled, single photon pairs on demand. Such a device is an essential ingredient of any scheme for future quantum information processing technologies.

In this NEVET proposal we suggest to combine the expertise and know-how of two leading researchers in the Technion. Professor Bahir, formerly the director of the microelectronic center in the Technion has the campus's deepest knowledge in microelectronic processing and fabrication. His expertise is a corner stone for the development of the device that we outline below.

Professor Gershoni, was the first, world-wide, to demonstrate entanglement between the polarization states of two photons emitted sequentially from a microcavity embedded, single semiconductor quantum dot. He posses the knowledge and laboratory equipment to perform the measurements and demonstrations outlined in detail below.

Both PIs have tradition of collaborative successful research. In particular, Alon Vardi one of the 2 PhD students which will explore the ideas discussed in this proposal was mutually mentored by both PIs towards his master degree.

For this research effort they will join forces in order to develop within a year or so a semiconductor quantum dots based device. The device will be embedded within a three dimensional optical microcavity, providing full control over the magnitude and direction of an externally applied electric field. This control over both the magnitude and the direction of the applied field is required in order to force degeneracy on various optical transitions between confined carriers' energy levels.

We strongly believe that the device that we propose is highly interesting scientifically, and at the same time, it has huge potential for future applications. One such application, namely generating entangled photon pairs 'on demand', is the specific goal that we will strive to achieve.

Studies of electronic and photonic systems of lower dimensionality are currently at the forefront of research in solid-state physics. Its potential importance is both fundamental and applied. On the one hand, our research should contribute to the understanding of the physics of one and many charge carriers and electron-hole pairs, interacting with radiation in restricted geometries in the limit where both electron and photon energies are discrete. On the other hand, it should affect the design and engineering of future applications and devices such as single electron and photon devices and devices for quantum information processing and computing. These applications and the limits of light-wave technology are very actively pursued in many laboratories around the world. Therefore, success in our proposal will result in a significant impact on this forefront field of science and technology.

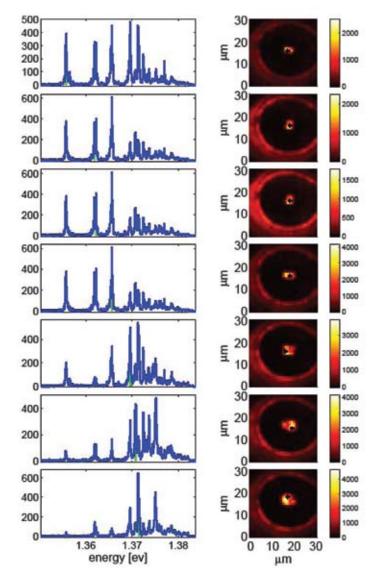
#### Preliminary results:

Below we briefly present preliminary, yet unpublished results pertaining to the research proposal.

In the below figure we present selective wavelength images of an oxidized aperture pillar, excited by a HeNe laser. The images present the photoluminescence emission intensity (expressed by the color bar to the right), as a function of the position of the confocal microscope objective above the pillar. Each image is obtained at different emission energy as given by the green area imposed on the spectrum to the left of each image. The spectrum to the left is obtained from the position marked by the + sign on the image. The upper-most image is obtained by a low spatial resolution scan of 30 by 30 micrometers at the same energy as the higher resolution image beneath it. Most of the light is emitted through the central aperture. Yet at this high excitation intensity, which support many different microcavity modes, leaky modes are observed from the pillar edges.

From this pillar maximal single photon emission rate of 0.5 MHz was measured, when a single quantum dot emission line was temperature tuned to resonate with the lowest energy cavity mode. This is an order of magnitude brighter from the emission rate we previously reported on when we demonstrated the first quantum dot based entangled light source. For correlation measurements this means two order of magnitudes better statistics!

Two PhD students took part in this research: Alon Vardi and Yaron Kodriano.



**Fig. 6**: Selective wavelength images of an oxidized aperture pillar. The spectra (left panels) are obtained from the brightest position indicated by the + signs on the images. The green areas on the spectra, indicate the spectral domains used for generating the images. The upper-most image is obtained at the same wavelength as the one beneath it. It covers a larger area so that the whole pillar is observed. The sample was excited by ~1mWatt HeNe laser at ambient temperature of 20K

## Improved PV Cells using Sol-Gel Technology and Nanocrystals Absorbers

Start Year ► 2008

Principal Investigators:

Prof. Gideon. S. Grader - Chemical Engineering, Technic Prof. Nir Tessler - Electrical Engineering, Technion Prof. Efrat Lifshitz - Chemistry, Technion

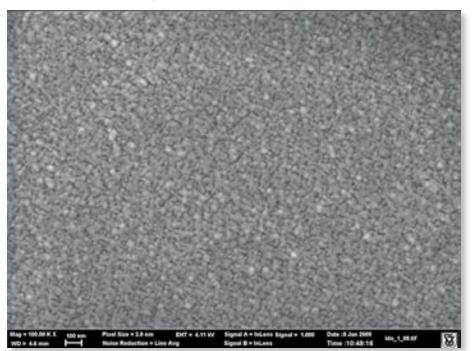
The scientific goal of this research was to develop state of the art TCO layers based on doped Zinc Oxide using the sol-gel method with a secondary goal of lowering the processing temperature. The ultimate objective of this project is to apply the TCO films in real PV devices and demonstrate high quality performance.

To reach the full potential of photovoltaic (PV) technology, the cost performance of PV devices must be improved. Production of thinlayer PV enables the reduction of substrate costs, materials usage and processing expense. This is a joint project of three Technion groups in order to produce novel PV cells based on nanotechnology. Sol-Gel method is being used to synthesize Al doped ZnObased transparent conductive layers in Grader's lab. Nanocrystals absorbing over a wide spectral range and matched to the TCO and potentially conjugated polymer matrix are developed in Lifshiz's lab. Nano structuring of the TCO through imprinting and final device fabrication are developed in Tessler's lab. The significance of this joint project will be in the form of state of the art PV cells with potentially improved performance at a reduced cost.

#### Results obtained so far:

Aluminum doped ZnO TCO layers were produced using the sol-gel method. The influence of different processing parameters and working conditions was examined. 200 nm thick TCO layers with excellent transparency (~90%), with relatively low resistivity  $(10^{-2} \Omega \cdot cm)$  were successfully produced.

However the results so far were not reproducible from run to run. Some difficulties were encountered in the stability of the solutions prepared for the deposition. In addition there were difficulties getting consistent measurements of the resistivity that were partly related to the instrument at the central lab. The solution stability has been solved lately, and the instrument to make the measurements was identified and ordered. We are currently waiting for its arrival in our lab.



Surface and profile images of AI doped ZnO TCO layer produced in Grader's lab

Figure 1: Top image of the surface of an Al-doped (1 mol% Al) ZnO film (bar=100 nm).

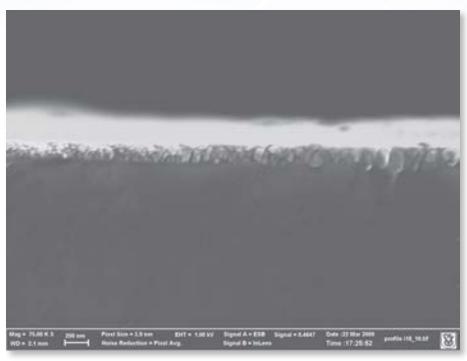


Figure 2: Cross sectional view of the a ~150 nm thick, Al-doped ZnO film on a glass substrate (bar=200 nm).

## Morphology, Atomistic Structure and Functionality of Nano-Holes

Start Year ► 2008

Principal Investigators:

Prof. Wayne D. Kaplan - Materials Engineering, Technion Dr. Nurit Ashkenasy - Materials Engineering, Ben-Gurion University

The formation of nanometric holes in membranes, either as single holes or as an array, is an important task for current research with applications ranging from filtration [1], to nano- and molecular- electronics [2] and biosensing [3]. In addition, nanometric sized holes in thin crystalline films provide a unique environment for the study of ordering at geometrically confined solid-liquid interfaces. Previous studies dedicated to the investigation of ordering phenomena at solid-liquid interfaces have shown that ordering in the liquid adjacent to the solid surface occurs [4]. The ordering takes the form of layering of the liquid adjacent to the solid, and by in-plane order within the liquid layers.

The aim of the current research is to develop a controlled method to form nanometric sized holes in thin films using transmission electron microscopy (TEM), and to characterize the surface of the holes to determine the formation mechanism. In addition, experiments are being conducted to evaluate the degree of order in liquids confined within the nanometric sized holes.

Nanometric sized holes were formed in three different materials: single-crystal Si, single-crystal  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> (sapphire), and amorphous Si<sub>3</sub>N<sub>4</sub>. The holes were 'drilled' using the Titan TEM. The metal was melted in the TEM during in-situ experiments, and the ordering phenomenon was studied as a function of the confinement volume and shape both in-situ and ex-situ.

Prior to introducing the metal liquid, a method to form nanometric holes must be established, and a detailed understanding of the shape and composition of nanometric holes is required. In the current research the nanometric holes are created using a converged electron beam in scanning TEM (STEM) mode. Figure 1(a) demonstrates our ability to control the size of the nanometric holes, which may vary from 4 to 40nm in diameter. Figure 1(b) presents an image of a reconstructed electron wave of a single nanometric hole drilled in crystalline Si. No damage to the crystalline Si adjacent to the hole was introduced during hole formation. The amorphous sub-nanometric layer detected at the Si edges was identified as silicon oxide by electron energy loss spectroscopy (EELS), resulting from oxidation due to the finite partial pressure of oxygen in the microscope column.

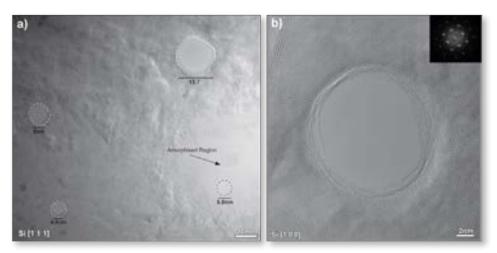


Figure 1: (a) HRTEM micrograph of a number of holes of different sizes drilled in the TEM. (b) Complex- valued wave function reconstructed from a defocus series of a nanometric hole in Si.

The three-dimensional shape of the nanometric holes was found to depend on the thickness of the Si crystal and the size of the hole; an hour-glass shape was formed for holes with a smaller diameter created in relatively thick Si layers, while holes with a larger diameter or holes drilled in thinner regions formed a truncated conical shape. A model to explain the final shape has been developed, which includes both atom knock-in damage by the incident electrons, and thermal activation. Holes in amorphous  $Si_3N_4$  have also been formed, and transferred to N. Ashkenazy (BGU) for ion transport experiments.

In order to investigate faceting and reconstruction of Si holes, in-situ heating experiments were conducted. As presented in Figure 2, full equilibration of nanometric holes was achieved, and a sharp edge at the hole in Si was obtained at 580°C. High resolution micrographs of the sharp Si edge will enable us to obtain information regarding Si surface reconstruction below the upper surface layers.

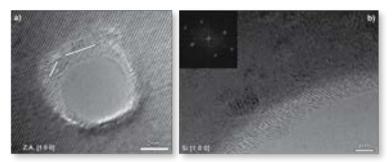


Figure 2: TEM micrographs of (a) equilibrated hole in crystalline Si acquired at 660°C, and (b) sharp edge of a hole in crystalline Si acquired at 580°C.

Alumina is a widely used ceramic material. The fact that the stoichiometry of alumina does not change in the presence of oxygen makes it convenient material for in-situ experiments. Moreover, at elevated temperatures and under the electron beam, the preferential knock-on damage of oxygen results in the formation of liquid Al drops on the Al<sub>2</sub>O<sub>3</sub> surface, providing a readily-made solid-liquid interface. Figure 3 presents an example of a semi-confined Al-Al<sub>2</sub>O<sub>3</sub> solid-liquid interface. Due to use of the aberration corrected TEM at the Technion, the contrast perturbations in the liquid can be directly assigned to density perturbations, i.e. ordering in the liquid. Quantification of the degree of ordering in liquid Al will enable the comparison of in-plane ordering and layering at a planar solid-liquid interface with confined interfaces.

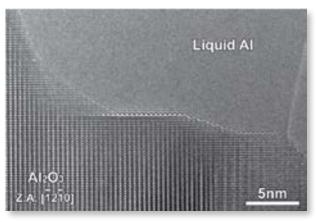


Figure 3: Cs-corrected HRTEM micrograph of Al-Al\_2O\_3 solid-liquid interface acquired at 750°C.

One PhD student, Miri Drozdov took part in this research.

- 1. J. P. Fu, P. Mao and J. Y. Han, Nanofilter array chip for fast gel-free biomolecule separation, Appl. Phys. Lett. 87[26]: 263902, 2005.
- 2. D. Krapf , M. W. Wu, R. M. M. Smeets , H. W. Zandbergen, C. Dekker, and S. G. Lemay, Fabrication and characterization of nanopore-based electrodes with radii down to 2 nm, Nano Lett. 6[1]:105-109, 2006
- 3. C. Dekker, Solid state Nanopores, Nat Nanotechnol. 2[4]:209-215, 2007.
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## Nano-scale optoelectronic characterization of hybrid photovoltaic materials

Start Year ► 2008

**Principal Investigators:** 

Prof. Gitti L. Frey - Materials Engineering, Technion Dr. Iris Visoly-Fisher - Chemistry and IKI, Ben-Gurion University

Research scientific goal was to study the local opto-electronic processes and correlate them with the nano-scale structural features of an organic-inorganic hybrid film for photovoltaic solar energy conversion devices. Specifically, we apply conductive probe AFM for the characterization of MEH-PPV-incorporated mesoscopically-ordered cubic titania to study: 1. the connectivity of charge-transporting domains across the hybrid film, 2. photo-induced charge transport and recombination mechanisms in each charge-transporting phase within the hybrid material, as compared to such mechanisms in macro-phase separated MEH-PPV and titania blends. 3. local short circuit current mapping, compared to the device overall short circuit current, and 4. the effect of the interfacial chemical composition on the above properties.

Hybrid organic-inorganic donor-acceptor systems have been suggested as low-cost, stable alternatives for solar energy conversion. Efficient charge generation and transport in such systems requires an organic-inorganic phase separation on a sub 20 nm length scale, and continuity and of each phase through the film. A new methodology was developed at the Frey lab for self-organization of such conjugated polymer-titania networks for photovoltaic applications. Here we use Nano-scale scanning probe methods, such as photoconductive AFM microscopy, to provide nano-scale level understanding of the physicochemical processes governing charge generation and transport in the novel nano-scale assembled hybrids. Correlation of the local optoelectronic processes with the multiscale structural ordering and macroscopic device performance will provide directives towards fabrication of high efficiency photovoltaic devices.

#### Results obtained so far:

We have obtained a nano-scale topographical images of the hybrid film surface, verifying the ordered pore structure previously seen using SEM (Fig. 1). While SEM required calcination of the sample, AFM imaging was performed with no special preparation, confirming the calcination has not modified the general structure. The pores in the structure appear smaller in the pristine sample compared to the calcined one, probably due to TiO2 crystallization at elevated temperatures. High resolution imaging displayed the AFM's ability to image and measure the properties of a single structural feature with a diameter of ca. 15 nm (Fig. 2). Current imaging has shown an expected barrier for charge transport in the dark, with the TiO<sub>2</sub> matrix showing larger currents than the MEH-PPV (Fig. 3). It should be noted that, at this stage, the Nevet year is only half-way through. The research continues in the directions set by its goals: High resolution current- and photocurrent mapping is performed at different bias to compare to macroscopic current-voltage characteristics of the device. Comparison of hybrid films of various configurations (with/ without MEH-PPV, with SiO<sub>2</sub> replacing the total structure to the other total structure to the dark of the device.

TiO<sub>2</sub>) will point to the role of each phase in the hybrid in photocurrent generation. The result will lead to further optimization of the hybrid materials towards low cost, high efficiency energy conversion devices.

Shany Neyshtadt, Ph.D student, took part in this research.

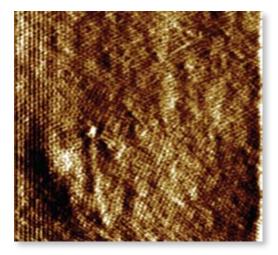


Figure 1: AFM topography image (contact mode, deflection signal) of the surface of a hybrid (TiO\_2/P123 surfactant/MEHPPV) film deposited on ITO/PEDOT. Image size:  $1\mu m \times 1\mu m$ .

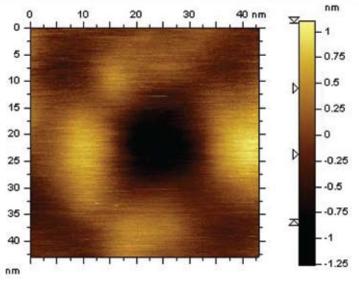


Figure 2: High-resolution AFM topography image ("tapping" mode) of the surface of a hybrid (TiO\_/P123 surfactant/MEHPPV) film deposited on ITO/PEDOT, showing a single pore. Image size: 47nm x 47nm. The color scale shows the height values.

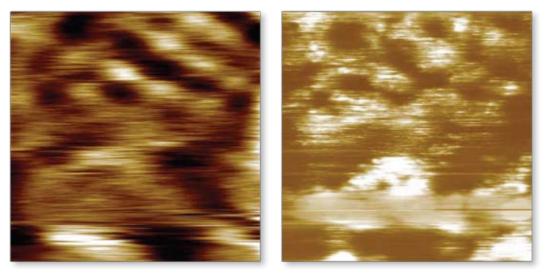


Figure 3: AFM topography (left) and current (right) mapping of the surface of a hybrid (TiO<sub>2</sub>/P123 surfactant/MEHPPV) film deposited on ITO/PEDOT, showing a correlation between the nano-scale features and the electronic properties. Image size: 100nm x 100nm, applied bias: 2 V.

## In-situ Removal of Phenylethanol from Yeast Fermentation Using Hydrophobic Nano-capsules

Start Year ► 2008

Principal Investigators:

Dr. Ayelet Fishman - Biotechnology and Food Engineering, Technion Prof. Shlomo Margel - Chemistry, Bar-Ilan University

The scientific goal of this research is to develop a biotechnology-based process for the production of a flavor and fragrance compound, phenylethanol, from yeast cells, employing continuous extraction of the product into hydrophobic nano-capsules.

Phenylethanol (PEA) is an aromatic alcohol with a rose-like odor which is widely used in the cosmetic and food industries. It is currently produced via chemical routes from benzene or styrene generating toxic wastes to the environment. Various yeast strains are capable of producing PEA from L-phenylalanine in a growth associated manner under controlled conditions. The drawback of this method is the inhibition of cell growth by the accumulating product. We propose to limit the contact between PEA and the growing cells by in situ extraction into hydrophobic micro or nano-capsules. At the end of the fermentation, the nano-capsules will be separated from the broth and dissolved to liberate the product. By now we have shown that the yeast cells can grow and produce PEA in the presence of micro-capsules and surfactants. Additionally, it seems that the beads incorporate PEA but the use of them for increasing the yield has yet to be shown.

#### Results obtained so far:

The project is in its mid stages and therefore initial results have been obtained so far.

The team in the Technion includes PI Fishman and the MSc student Yigal Achmon. They are working on improvement of the biocatalyst for the process. Two approaches are being evaluated in parallel. One is further improvement of the natural yeast strain Saccharomyces cerevisiae Ye-612, which has been isolated from nature and has stress-resistance properties. The expectation is that by exposing the strain to increasing concentrations of PEA, the tolerance to this compound will increase and the new yeast strain will be able to withstand higher PEA quantities. Another route that is being investigated is the cloning of the three genes from the Ehrlich pathway (in the yeast) into an Escherichia coli strain for overproduction. The expectation is that E. coli cells will be able to produce larger quantities of PEA due to overexpression of the specific enzymes. By now, the three genes have been expressed separately in E. coli, each showing expression and activity. Expression has been checked by using SDS-PAGE analysis whereas activity has been measured using colorimetric methods. Currently, we are trying to express all three genes jointly.

The team in Bar-Ilan University includes PI Margel and a PhD student Jenny Goldstein. They are developing the micro- and nanocapsules and evaluating their ability to absorb PEA. Both polystyrene (PS) and polymethylmethacrylate (PMMA) beads were tested with different surfactants which aid in the incorporation of the product, PEA, into the beads. Initial studies showed that the yeast cells can tolerate all of the components of the system, i.e. the surfactants and beads (Figure 1). The growth rate is unaffected and the PEA production is similar.

To investigate the absorption of PEA into the hydrophobic beads, beads were immersed in PEA solutions with various surfactants, and the residual PEA in the medium was measured using high performance liquid chromatography (Figure 2), while the bead diameter was measured under the microscope (Figure 3). The decrease in PEA concentration in the medium coupled with the increase in bead diameter, indicate that PEA is most likely incorporated into the beads.

We are now further optimizing the conditions in order to test whether the use of beads in the fermentation actually facilitates the increase in product yield under stress conditions.

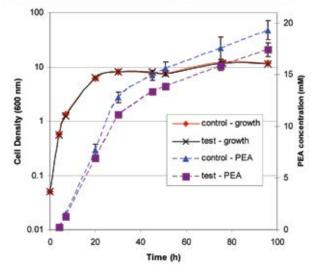


Figure 1: Growth and PEA production of yeast strain Ye-612. The test reaction contained PS beads (2% v/v) and Tween 80 (2.5%). PEA concentration was calculated from HPLC measurements.

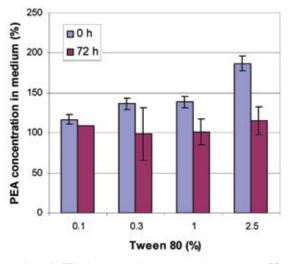


Figure 2: PEA absorption following 72 h of incubation into PS microcapsules containing different concentrations of Tween 80. PEA concentration was calculated from HPLC measurements

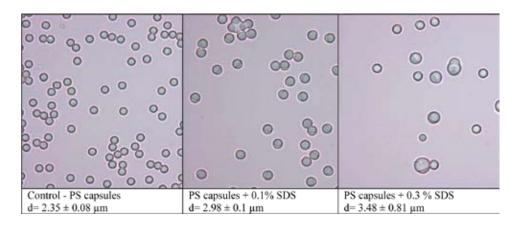


Figure 3: PS capsules incubated with surfactant (SDS) and PEA for 72 h. The average diameter is indicated below each figure. The increase in diameter is an indication of the incorporation of PEA into the beads.

## Active waveguides with embedded gain elements in nano-optical 2D photonic crystal structures

Start Year ► 2008

Principal Investigators:

Prof. Baruch Fischer - Electrical Engineering, Technion Prof. Michael Rosenblu - Physics, Bar-Ilan University

The scientific goal of this research is developing special nano-photonics waveguide structures that includes active (gain) elements.

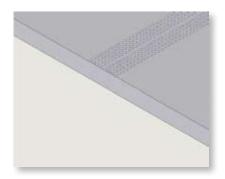
We study 1 and 2D nano-photonics waveguide structures for the visible, near IR spectral region by two methods: (1) Using a Focused lon Beam (FIB) machine (in the BIU Nano-Center/Rosenbluh lab) and very high resolution e<sup>-</sup> beam lithography apparatus (also in the in the BIU Nano-Center); (2) UV induced gratings in glass (at Technion), fabricating structures in fibers and 2-D waveguides. The focus is periodic structures with a large aspect ratio and active waveguide structures that include gain elements with erbium doped and semiconductor or metallic nano-clusters glasses. Those structures can provide new guided wave photonic circuits, and new measuring methods.

Results obtained so far:

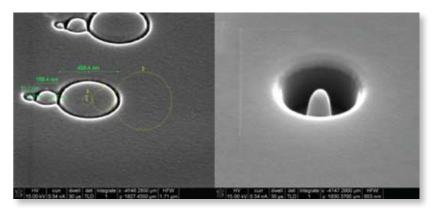
Fabrication of grating structures at the tip of a fiber and coupling of light into it. We are in the process of further developing it to a tiny Fabry-Perot etalon by two gratings set at the fiber tip, and then to make it "active" by fabricating the structure in an erbium-doped fiber tip. The active element is expected to be a very sensitive device that can develop to be a new measuring method. Research continuation:

We have very interesting follow up ideas for new methods of super resolution measuring technique.

One student took part in this research.



**Fig. 1**: Typical waveguide structure design showing a 3 micrometer thick glass substrate, either free standing or bonded to a high index material, with 400 nm holes 'drilled' through the glass, and spaced by 700 nm center to center. Light can be coupled into the structure either from the polished end face or via a prism coupler on the top surface.



**Fig. 2**: Circles and holes made in a gold film on a silicon substrate, demonstrating the resolution that can be obtained with the FIB. In the lower figure a gold pillar was left standing inside the hole while in the upper figure adjacent circles with nominally 15 nm gaps were milled. Although it is not visible in the picture the depth of the straight cut was more than 3 times the cut width yielding an aspect ratio greater than 3.

## Shot noise measurements in short high T<sub>c</sub> superconductors

**Principal Investigators:** 

Associate Prof. Michael Reznikov - Physics, Technion Associate Prof. Aviad Frydman - Physics, Bar-Ilan University Start Year ► 2008

The Scientific Goal of this research is to test existence of preformed Cooper pairs in High-T<sub>c</sub> superconductors.

We study noise generated by the current through a short high temperature superconductors (HTSC). The ultimate goal is to try to check possible existence of bound pairs (analogues to the Cooper pairs in BCS superconductors) above  $T_c$ , which should manifest themselves as the shot noise doubling. Since shot noise is intrinsically nonequilibriunm phenomenon, one needs to create a strongly nonequilibrium energy distribution of the carriers, otherwise the noise would reduce to the thermal one at elevated temperature, out of which quasiparticle charge cannot be extracted. Since the typical length over which electrons exchange energy with the lattice is short (of the order of nanometers in HTSC) such an experiment requires cutting edge nanotechnology for success. Our preliminary results on BCS superconductors in the vicinity of  $T_c$  will assist in revealing possible mechanisms of excess noise other then shot noise, such as paraconductivity and phase slips. Our experimental techniques are expected to provide useful and unique information towards the long-time quest of understanding high  $T_c$  superconductivity and, in particular, the origin of the pseudogap and possible pairing mechanisms.

#### Results obtained so far:

We managed to build and test the experimental setup suitable for the high-sensitivity noise measurements for low (a few Ohms) impedance samples. The setup is calibrated against external signal, and against thermal noise; these calibrations reasonably agree with each other.

We better understood the requirements for the samples to make the shot noise visible. In particular, it happens that quality of the contacts (gold contacts to LASCO in our case) is very important for the experiment. The reason for this is that the contact region size should be effectively added do the sample length. This size is inversely proportional to the square root of the contact resistance; the contact resistance of the order of 10<sup>-8</sup> Ohm cm<sup>2</sup> is required to put the contact length into 100 nm range.

One master student and one post-doc took part in the research.

The research did not lead to external funding. It is, however partially funded by the BSF grant devoted to more widely formulated goal of studying nonequilibrium fluctuations in superconductors.

The research continues. We are currently making new samples, and hope to finish the project by the end of the year.

During the research we used e-beam writing facilities at the Technion, and growth and etching facilities available in the laboratory of Prof. Gad Koren at the Technion

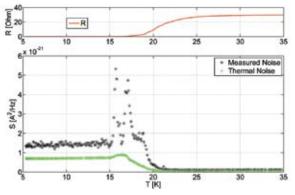


Fig.1. Top Panel: Resistance of YBCO (8% Sr) 100 nm long sample as a function of the temperature. Bottom panel: noise generated by  $150\mu$ A current, compared to the thermal noise. The large noise due to the superconducting fluctuations well below the transition temperature is clearly visible.



Fig.2. The 57 nm cut through the gold sample contacts, which defines the sample length.

## Novel and High Performance Side-polished Photonic Crystal Fiber based Surface Plasmonic Resonance Sensors

Start Year ► 2008

**Principal Investigators:** 

Prof. Yehuda Leviatan - Electrical Engineering, Technion Associate Prof. Shum Ping - School of EEE, NTU

Optical fiber based surface plasmonic resonance (SPR) senor offers miniaturization, high degree of integration and remote sensing capabilities and furthermore reduces the cost. In the optical fiber setup, one can not change the incident angle, so broadband light sources are always adopted. If the SPR coupling occurs, a sharp dip in the output spectrum could be detected and be used to calculate the refractive index of the analyte. But for the single mode fiber (SMF), there are some problems. First, the field intensity at the SPR interface is very weak, so the dip in the spectrum is not deep enough to improve sensitivity. Second, the phase matching between plasmon and fundamental waveguide mode is typically hard to realize. Because the fact that the effective refractive index of a core guided mode is close to the refractive index of the core material, which is typically larger than 1.45 due to practical material limitations. But the effective refractive index of a plasmon is close to the refractive index of the ambient medium which is typically air  $n_a = 1$  (gas sensing) or water  $n_a = 1.3$  (biological sensing). Thus, large discrepancy in the effective indices makes phase matching between the two modes hard to achieve.

In order to overcome the first problem, and achieve improved coupling efficiency and sensing resolution, the use of a side polished fiber, in which the metal coating is closer to the mode-field center, can be a good solution. For the second problem, the use of photonic crystal fiber (PCF) is a good option. Because PCFs have the advantage of higher degree of design freedom, we could optimize the parameters of the PCF and then reduce its effective refractive index to the level of ambient medium used. In PCFs, even though the effective refractive index of a propagating mode is smaller than that of the waveguide cladding, the light also could guide in the fiber. Then the fundamental Gaussian-like leaky core mode can be phase matched with a SPR wave at any desired wavelength of operation. In this work, we thus plan to combine side polishing and PCF design methodology to achieve side-polished photonic crystal fiber based surface plasmon resonator sensors.

The theoretical modeling of the proposed side-polished PCF based SPR sensors will be carried out using a software package based on the source model technique (SMT) developed at the Technion, while the NTU group will work on the fabrication and characterization. The SMT is a fully vectorial method that can be used to determine the modes of a cylindrical structure of a piecewise-homogeneous cross section. The sources radiate in a homogeneous medium with the same material parameters as those of the region they enclose in the PCF cross section. Their fields, therefore, have well-known analytic expressions. The SMT analysis approach has been proven to be an efficient technique for mode calculations in cylindrical dielectric structures that have a piecewise-homogeneous, yet otherwise arbitrary, cross-section, thus allowing modeling of PCFs with arbitrary shaped inclusions/holes. Permittivity models for silica and noble metals are included in the software. High index contrasts, metals, and dispersive media can be handled. The input can be defined either by the Matlab code or as a binary image of the cross-section.

The fabrication of side-polished fiber will be carried out using the polishing machine in NTU. The side-polished fiber will then be coated with a thin-film and a layer of gold with a thickness of ~20nm. Together with the full sets of calibrated ambient index oils, the broadband super continuum light source and the high resolution optical spectrum analyzer, we will be able to characterize the refractive index sensitivity as using the side polished fiber based SPR devices. The temperature performance in the range from 30-100 degrees will be characterized in a temperature chamber.

#### Results obtained so far:

PCF structures with metal coated air holes that can be infiltrated with different materials such as gas, liquid, and polymers have been proposed recently for sensing applications. In this work a novel sensor consisting of selectively coated air holes has been explored. It was found that the selective coating enhances the phase matching between the plasmonic mode and the core-guided mode. Good sensitivity as high as 10-6 in terms of refractive index units (RIU) has been achieved. Compared with the fully-coated structure, the selectively-coated sensor design demonstrates resonance of narrower spectral width, which provides better sensing resolution. Moreover, the resonance is of deeper depth and therefore greatly improves the sensing performance in terms of signal-to-noise ratio.

### Coupled CNT-TiO, systems for photocatalysis

Principal Investigators:

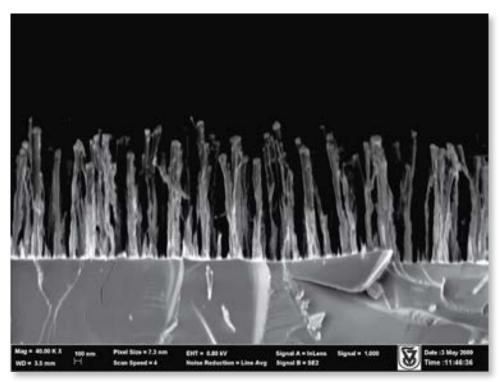
Prof. Yachin Cohen - Chemical Engineering, Technion Assoc. Prof. Yaron Paz - Chemical Engineering, Technion Assoc. Prof. Tan Cher Ming - School of Electrical & Electronic Engineering, NTU Start Year ► 2008

The objective of this project is to explore the possibility of using composite structures made of carbon nanotubes and titanium dioxide to photodegrade contaminants under visible light conditions. High photoefficiency is expected due to the coupling between CNTs and titanium dioxide that will improve charge separation as well as mass transfer of contaminants. A specific goal related to this objective is the study of light induced electron transport between carbon nanotubes and nanoparticles of titanium dioxide.

"Forests" of vertical carbon nanotubes (CNTs) attached to silicon wafer were grown at NTU, using a nickel nanoparticles as catalysts. The distance between the carbon nanotubes in the "forests" is controllable to allow for attaching single particles of titanium dioxide on top. Samples are being shipped to the Technion where characterization (see Figure), surface treatment and photocatalytic measurements are done. A current sensing Atomic Force Microscopy accessory for in-situ measurements of light induced I-V curves to be measured from a single vertical CNT attached to a single nanoparticle of TiO<sub>2</sub> is currently under construction. The effect of chemical treatments of the CNT's on their adeherence to TiO<sub>2</sub> is understudy. Once optimal adherence is achieved, photocatalytic measurements with an experimental set-up that was constructed for photocatalytic measurements under visible light will measure the effect of coupling between the two components on the effectiveness of phocatalytic degradation of pollutants in air and water.

The manpower for this project is based on a PhD researcher, working on this project on a part- time level, plus a graduate student from NTU who stayed at our laboratory for several months. Measures to recruit another graduate student from the Technion are underway.

A proposal which has partial overlap with this project was submitted to the Israeli Science Foundation and was approved for funding. The project is still underway, and in fact we expect to obtain the most significant results within the next few months. Only a few weeks ago we were visited by the NTU partner, to discuss the project and its implications. Although it is too early to present publications, we are quite confident with the prospects of this program, based on what we have at the moment.



**Figure 1**: A micrograph showing vertically aligned multi-walled carbon nanotubes fabricated using Plasma enhanced chemical vapour deposition technique. The CNTs were grown on Si wafers using Ni catalyst which could be observed at the tips of the CNTs. The diameter ranges from 60-80 nm, with an average length of 1.9 μm.

## Integration of self-assembling multi-enzymatic hydrogels and carbon nanotube arrays for advanced bioelectrode fabrication.

Start Year ► 2008

Principal Investigators:

Prof. Yoav Eichen - Chemistry, Technion Dr. Yuval Yaish - Electrical Engineering, Technion Prof. Tay Beng Kang - EEE, NTU

The main objective of this joint research proposal is the development and characterization of novel and highly efficient bioelectrodes created from self-assembling multi-functional enzymatic hydrogels incorporated into nanostructured carbon nanotube-based templates.

The main deliverable of this proposal will be the first demonstration of the integration of self-assembling enzymatic proteinaceous hydrogels into novel ordered CNT arrays for electron transfer. The CNT array will be composed of pattern CNT forests using pregrowth catalyst sites or post-growth etching processes.

#### Results obtained so far:

The Technion group focused on two main aspects of this proposal. The first is covalent attachment of proteins to CNT. This attachment is based on peptide chemistry in which amine end group creates covalent bond with carboxylic acid group that exist on the NTs surface. Results of typical attachments that we performed are shown in figure 1. The second task was focused on three dimensional CNT growths. In the beginning we study how to grow CNT forests on hard substrates. We examine three different substrates (Silicon dioxide, Alumina, and Sapphire) and two kinds of catalysts (Nickel and Iron). Various growth conditions were examined and CNT forests were obtained. Figure 2 depicts catalyst deposition on top of three different substrates, and figure 3 presents growth results. It turns out that Ni functions as a better catalyst for forest growth although well aligned CNT are still missing. Currently, we optimize growth conditions in order to obtain well align carbon nanotube forests.

Three students took part in the research: Eichen and Yaish group: Hadar Nir, Yael Pascal, Orit Even-Zur

#### Facilities used during the research:

This research combines material and device studies which require extensive usage of microscopy and fabrication equipment. We took advantage of various novel infrastructures that were purchased recently at the Technion. For imaging we utilized HRSEM, TEM, STEM, and AFM. Fabrication was done in the Technion clean room, and extensive use has been made of the new FIB, stepper, and e-beam lithography tool.

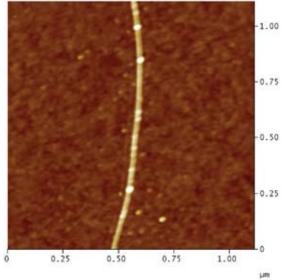
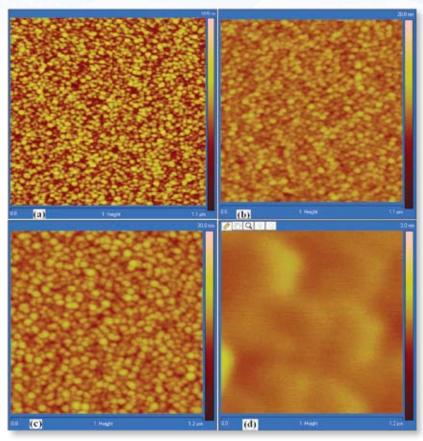
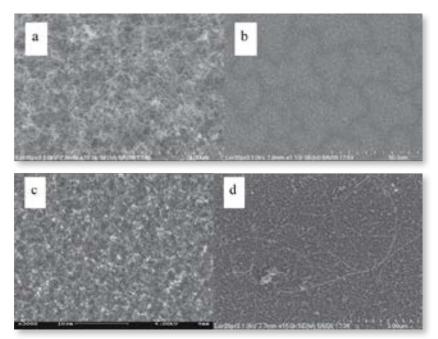


Fig. 1: chemical bonding of NutraAvidin toCNT



**Fig. 2**: AFM Images of: (a) Sputtering product layer (multicrystalline  $Al_2O_3$ ); (b) Deposited Fe layer (~2-3nm) on  $Al_2O_3$ ; (c) Deposited Ni layer (~2-3nm) on  $Al_2O_3$ ; (d) Deposited Ni on Sapphire (0001)



**Fig. 3**: SEM Images of: (a) Si/ SiO<sub>2</sub> (500 nm)/ Al<sub>2</sub>O<sub>3</sub> with Ni catalyst; (b) Si/ SiO<sub>2</sub> (500 nm)/ Al<sub>2</sub>O<sub>3</sub> with Ni catalyst; (c) Sapphire (0001) with Ni as catalyst; (d) Si/ SiO<sub>2</sub> (500 nm)/ Al<sub>2</sub>O<sub>3</sub> with Fe catalyst

# Approved Proposals



## Picking Up the Pieces: A Nano-scale Approach for Proteome-wide Analysis of 20S Substrates

**Principal Investigators:** 

Dr. Michal Sharon - Biological Chemistry, Weizmann Dr. Ester Segal - Biotechnology and Food Engineering, Technion Dr. Liiliana Fruk - Universitaet Karlsruhe Centre for Functional Nanostructure Start Year ► 2009

The long term objective of this proposal is to develop a method for the characterization of the 20S-substrate proteome by using a multifunctional nanostructured SiO<sub>2</sub> scaffold. We propose to design and construct a biosensor-based microaffinity purification method to recover peptide fragments for downstream proteomics analysis.

#### Specific research aims:

- 1. Construction of porous Si/SiO<sub>2</sub> nanostructured scaffolds (Segal). Porous Si (PSi) scaffolds are synthesized by anodic electrochemical etch of single-crystal Si. The porosity and the average pore diameter can be easily tuned by adjusting the electrochemical preparation conditions. Thus, etching conditions will be adjusted to fabricate pores small enough to exclude out proteins (only small peptides will be able to infiltrate into the PSi film). The resulting freshly etched PSi sample is then thermally oxidized at 800°C to create porous SiO<sub>2</sub> matrix. The purpose of the oxidation process is to improve the chemical stability of the PSi layer, and allow the use of the wide repertoire of silica surface chemistry.
- 2. Modification of the porous SiO<sub>2</sub> scaffolds with linkers that enable reversible attachment of proteasome moieties. We will focus on development of a double bond-containing bifunctional linker, which can be attached to the photosensitizer and proteasome. Several mild approaches for protein attachment will be investigated such as maleimide-cystein interaction or amide coupling through surface lysine groups. Although porphyrin derivatives have been widely used, we will also explore recently described ability of small semiconductor nanoparticles (quantum dots, QD) to produce superoxide radical in presence of light to enable linker cleavage. In a second approach, DNA will be used as a structural template to immobilize the proteasome through DNA directed immobilization. Different DNA labeling strategies will be tested including the use of bifunctional linkers. Such DNA-templated surfaces can be easily regenerated using mild DNA melting conditions to remove proteasome from the surface.
- 3. Design of sensing schemes for monitoring the optical changes in the reflectivity spectrum of the proteasomelinked porous SiO<sub>2</sub> platforms during different protein degradation processes (Segal, Fruk and Sharon). Briefly, the reflectivity spectrum of the porous film consists of a series of interference fringes that result from Fabry-Pérot interference at the top and bottom of the hybrid layer and the Bruggeman effective medium theory is used to relate porosity to refractive index. Changes in porosity result when molecules are admitted to the internal surface area of the porous scaffold/sensor matrix. This increases the optical thickness, causing a red shift in the light reflected from the sensor. A unique advantage of the PSi is that the optical response varies linearly with pore filling. Herein, this property will be exploited for quantitative analysis purposes.
- 4. Development of methods for retrieving/recovering peptide fragments from the porous scaffold for downstream proteomics analysis (Segal, Fruk and Sharon). The proteasome moieties will be removed from the biosensor surface, followed by dissolution of the SiO<sub>2</sub> nanostructure to allow collection of the entrapped peptides.
- Mass spectrometry (MS) proteomic analysis of products (Sharon). MS and tandem MS approaches will be applied for peptide sequencing followed by database search and protein identification. The set of identified proteins will reflect the specific pool of protein degraded by the 20S UID.

#### Expected outcome:

The proposed project presents a multidisciplinary approach for studying a very important cellular mechanism of protein degradation, which could shed light on the governing principles of 20S UID and its role in maintaining cellular homeostasis. It is noteworthy that the approach developed here for proteasome study can be applied to on the whole cell extract in search for substrates (substrate screening) as well as different isoforms of the proteasome (function screening) once the immobilization chemistry is established. The use of porous SiO<sub>2</sub> materials as a screening platform could enable high throughput analysis of substrate degradation and open new possibilities for biosensing of other classes of proteases (enzymes where reaction products could be captured and screened by MS). This proposal is built upon the PIs complementary expertise, in the fields of biologically oriented chemical synthesis and DNA based nanotechnology (LF), nanomaterials science and sensors/biosensors (ES), and biochemistry and mass spectrometry of the proteasome system (MS).

## Nano Oxide Perovskites with Enhanced Surface Exchange Kinetics

Start Year ► 2009

**Principal Investigators:** 

Dr. Yoed Tsur - Chemical Engineering, Technion Prof. Igor Lubomirsky - Department of Materials and Interfaces, Weizmann Prof. Ellen Ivers-Tiffée - Institute for Materials in Electrical Engineering, Karlsruhe Prof. Claus Feldmann - Institute of Inorganic Chemistry, Karlsruhe

Oxygen-ion and mixed ionic-electronic conducting perovskites are of great scientific and practical interest for a number of applications ranging from sensors and separation membranes to fuel cells' electrodes. Operation of all these devices is strongly dependent on the surface exchange kinetics and oxygen diffusion coefficient. Both these parameters are a function of the grain size because it affects (a) the effective surface area and (b) surface activity due to changes in defects distribution driven by the space charge effects at the grain boundaries. These effects are especially important for micro-devices utilizing µm-thick films with 10-100 nm sized grains. Properties of such films are distinctively different from those of the corresponding bulk materials. In addition, incorporation of such films into practically useful devices poses a considerable problem because of necessity to control grain growth and mechanical properties. Therefore, finding ways to control the surface kinetics for oxygen reduction/incorporation by controlling the grain size and the properties of the grain boundaries is of utmost importance.

#### Proposed research:

The proposed research is aimed to study technologically important members of the oxide perovskites family to gain control over their chemical and physical properties and explore the ways of incorporating these materials in practical micro-devices. The primary attention will be given to the lanthanum strontium cobalt ferrites (LSCF) family of mixed ionic electronic conductors (MIEC) with high ionic transference number. These materials are being considered for cathodes and separation membranes. The following issues will be addressed:

- 1. Synthesis of nano-sized powders with controlled size, composition and surface properties. This will be done by combustion synthesis at Tsur's lab and by liquid phase synthesis at Feldmann's lab.
- 2. Investigation of the grain-size dependent properties of the powders by various techniques (i.e., size analysis, surface area by B.E.T., phase transformations by DSC and XRD, SEM and TEM imaging, etc.) both at the Technion and CFN.
- 3. Deposition of thin films on a suitable oxygen electrolyte (e.g., gadolinia doped ceria- GDC) will be done at CFN.
- 4. Investigation of the mechanical properties of the films and utilizing this knowledge for micro-machining of the films into selfsupported structures for device prototypes will be performed in the WIS by Lubomirsky's group.
- 5. Measurements of surface exchange kinetics will be carried out at the lvers-Tiffée lab. This will be done by various techniques including impedance spectroscopy (IS).
- 6. The analysis of the IS measurements will be performed in parallel at Ivers-Tiffée's and Tsur's labs, by two different analysis techniques. This would also serve to countercheck two novel analysis techniques for IS results based on evolutionary programming (Technion) and the distribution on relaxation times (CFN) both recently developed and published.

#### Expected outcome and long-term collaboration:

Although restricted to one year time period, the proposed research is expected to achieve two important goals.

Firstly, it will explore the pathway for controlling the surface exchange kinetics of LSCF and thereby serve as a foundation for further research. Secondly, as it is clear from the list of tasks given above and the list of the fields of expertise given below, there is a strong synergism combined with some overlap in research interests between the groups. Therefore, the groups participating regard it as a vehicle for further collaboration.

## Multiple Frequency Dynamics of Hybrid Scanning Probes for Simultaneous Imaging and Force Detection

**Principal Investigators:** 

Prof. Oded Gottlieb - Mechanical Engineering, Technion Dr. Hendrik Hölscher - Institut für Mikrostrukturtechnik (IMT), Forschungszentrum Karlsruh Start Year ► 2009

The atomic force microscope (AFM) has become a standard instrument in nano-analysis with regards to the rapid and uncomplicated imaging of surfaces at the micro- and nanometer scales. The highest lateral resolution that can be obtained in AFM sampling is via dynamic mode operation, where the cantilever oscillates near a target sample surface. If one uses the amplitude change as the control signal, it is possible to measure the sample topography with high vertical and lateral resolution. Other techniques have also been developed to obtain information about tip-sample interactions. For example, the resonant frequency of the cantilever can be measured as a function of the tip-sample separation, from which the tip-sample interaction force can be obtained [Hölscher et al., Phys. Rev. B 61, 12678 (2000)]. However, these additional measurements can only be performed through a subsequent characterization after scanning of surface topography.

Recently, Sahin et al. [Nature Nanotechnology 2, 507 (2007)] introduced an approach using specific cantilevers where the normal and torsional oscillation of the cantilever are employed for imaging and spectroscopy, respectively. In this approach the surface structure is obtained from the normal vibration scanned, whereas the tip-sample interaction is measured through a Fourier analysis of the torsional cantilever oscillation. However, due to the specific design of the cantilevers the resonance frequency of the torsional oscillation is only slightly lower than the as that of the third normal mode. Unfortunately, this fact limits the resolution of this approach. In their theoretical analysis Solares and Chawla [Meas. Sci. Technol. 19, 055502 (2008)] proposed that this limitation might be overcome with an AFM method based on dual frequency modulation using two cantilevers in series. In this way the tip–sample interaction as well as the topography of the entire sample can be measured within a single surface scan.

Cantilevers enabling such measurements are currently developed in the group of at the IMT of the Forschungszentrum Karlsruhe. While first experimental results prove that the basic concept works, it also turnes out that the dynamics of these paddle cantilevers cannot be analyzed by a simple lumped mass model. Therefore, it is the aim of this collaboration to go beyond this first and simple approach. The idea is to develop a continuum model and to analyze the paddle AFM cantilever response analytically and numerically in both weakly and strongly nonlinear domains, respectively. This approach has been successfully demonstrated by application of multiple-scale asymptotics to both the continuum problem [Wolf and Gottlieb, J. Appl. Physics 91, 4701 (2002)] and to a reduced low-order system [Hornstein and Gottlieb, Nonlin. Dyn. 54, 93 (2008)]. Based on this analysis we propose to develop a fast and convenient analysis method for the paddle cantilevers. The theoretical work in Haifa will be accompanied by experiments in Karlsruhe [Hölscher, Appl. Phys. Lett. 89, 123109 (2006); Hölscher and Schwarz, Int. J. Non-Linear Mech. 42, 608 (2007)]. The analysis method will be implemented into a user-programmable AFM system (Labview Electronics of Nanonics) and measurements will be taken out on thin films of block-copolymers in collaboration with Prof. Thomas Schimmel from the University of Karlsruhe (CFN). We choose such films because they contain two types of materials in an almost flat geometry which makes them the perfect test-sample for our method.

#### Expected Outcome:

The novelty of the proposed research is twofold. First, the proposed research program is unique as it consistently incorporates derivation and analysis of a quasi-continuum based theoretical dynamical system [PI Gottlieb], its implementation into a workable design scheme which enables simultaneous imaging and spectroscopy and verification via controlled experiments of block-copolymers which exhibit spatial complexity [PI Hölscher]. Second, this work will enable application of novel research tools for additional surfaces which exhibit irregular spatial complexity.

## Radiative electron-plasmon interaction in nanometrically modified metal films

Start Year ► 2009

Principal Investigators:

Prof. Dr. Dagmar Gerthsen - Laboratory for Electron Microscopy, Karlsruhe
 Prof. Gary Hodes - Materials and Interfaces, Weizmann
 Dr. Hagai Cohen - Department of Chemical Research Support, Weizmann
 Prof. Tsofar Maniv Schulich - Chemistry, Technion

Manipulation of light-beams with metallic nano-optic devices (e.g. lenses, mirrors, etc...) has recently become a very active field following the discovery of extraordinary transmission of electromagnetic (EM) waves through sub-wavelength apertures in thin noble metal films, e.g. gold and silver. The basic physical mechanism behind these remarkable observations concerns the breakdown of translational symmetry along sub-wavelength scales, which dramatically enhances the coupling between far-field photons and near-field plasma modes propagating along these surfaces.

A powerful technique for generating and detecting surface plasmons (SP) in nanostructures is provided by very fast (relativistic) electron beams (e-beams), with typical lateral resolution on an atomic scale, available in scanning transmission electron microscopes (STEM). We have recently shown, by means of a quantum mechanical model, that radiation excitation of surface-palsmon-polariton (SPP) modes by the e-beam propagating inside vacuum tunnels can take place in such an experiment directly from the vacuum far-field zone. Furthermore, our calculations suggest that this excitation should enhance dramatically by coating the films with materials of higher dielectric constant.

Several questions motivate our research: (1) the fundamental understanding of the electron-plasmon coupling under nanoscale object modifications; (2 the similarity and differences between the use of e-beams and that of photons under the same modifications; (3) the effect of surface treatments (and in particular, dielectric coatings and self assembly of molecular layers) on the coupling above; (4) potential applications of our systems.

Samples will be prepared both in Germany and Israel, starting with hole arrays in gold and silver. In a second stage, coating of the metal films by semiconducting layers with high refractive index, e.g. PbS or PbSe, will be attempted in order to test our prediction of giant enhancement of the SPP signal. These semiconductor layers will be deposited by solution deposition at close to room temperature, thereby minimizing damage and stress to the metal layers. Coating with organic selfassembled monolayers will be explored in a third stage. XPS will be used as the main means for sample characterization (Weizmann).

Optionally, the samples will be studied by optical transmission as well. EELS will be conducted both in Germany and at the Technion. In the theoretical work (Technion) we plan to extend our QM model to situations similar to those investigated experimentally, e.g. by calculating the EEL signal of a relativistic focused e-beam propagating inside a long slit in a silver or gold film. In particular, the influence of neighboring parallel slits (or periodic arrays, i.e. in photonic crystals), as well as the effect of a coated dielectric layer, on the EEL spectrum will be investigated.

Two postdocs/assistant scientists will be employed in Israel: one for the theory and one for the experimental work. A graduate student will carry out high-resolution EELS spectroscopy in Karlsruhe using a monochromated FEI Titan transmission electron microscopy. Focused-ion-beam milling will be used to pattern thin films consisting of different materials.

#### Expected outcome:

We will first look for experimental confirmation of the e-beam SPP radiativecoupling phenomenon. A more detailed understanding of the role of nanoscale patterning in these metal films will be attempted. The impact of dielectric and molecular layer coatings is another intriguing issue, already known in optical measurements, but still unexplored with e-beams. We shall also look for new conditions where the far-field coupling is expected to further enhance (e.g. by coating with high dielectric layers), aiming at future practical applications.

## Microscopic Sources of Nonlinearities in Superconducting Resonators

Principal Investigators: Prof. Dr. Alexey Ustinov - Physikalisches Institut, Karlsruhe Prof. Eyal Buks - Electrical Engineering, Technion Start Year ► 2009

Nonlinearity strongly affects the microwave properties of superconducting devices. However, in many cases the underlying mechanisms have not been conclusively determined, though experiments pointed towards micro- and nano-scale defects. Recent progress in using superconducting resonators for quantum data processing made the need to achieve a better understanding of these effects and their possible applications very relevant. The proposed research aims at revealing the underlying mechanisms responsible for nonlinearity in superconducting thin film resonators made of NbN. Recent study of such resonators by the Technion group reported intriguing nonlinear properties including high intermodulation gain, noise squeezing, and self-modulation. However, a comprehensive explanation of the observed effects is still lacking. Here we propose to employ a unique spatially resolved characterization method developed by the Karlsruhe group to provide further insights. This may help not only to identify the underlying mechanisms responsible for nonlinearity but also to develop methods to control these effects and to exploit them for novel applications as e.g. ultra-sensitive parametric amplifiers.

The main objectives of the proposed collaboration:

1. Reveal the microscopic origins of nonlinear effects in NbN stripline resonators;

2. Study possible ways of controlling nonlinear behavior of superconducting thin films.

We will use LTLSM technique that is available at Karlsruhe to perform spatially-resolved imaging of the nonlinear response at microwave frequencies of NbN resonators fabricated by the Technion group. The LTLSM technique is based on scanning a sample with a laser beam with simultaneous recording of the variation in the transmitted or reflected microwave power that arises due to the change in the dissipative losses within the illuminated spot. By applying two microwave signals f1 and f2 we can perform measurements of spatially resolved intermodulation response in superconducting devices.

#### Expected outcome:

The results of the proposed studies will be significant for applications of superconductors in communication systems and quantum information processing.

## Biomimetic hydrogels decorated with chromatic polydiacetylene nanoparticles for studying 3D cell motility

Start Year ► 2009

**Principal Investigators:** 

Prof. Dror Seliktar - Biomedical Engineering, Technion
 Prof. Raz Jelinek - Department of Chemistry and the Ilse Katz Institute for Nanotechnology
 Ben-Gurion University

Cell mobility plays a crucial role in many of the most basic biological processes, including tissue development, tissue healing, and disease progression. Most eukaryotic cells are able to generate motile forces that allow them to migrate inside 3D tissues with ease and efficiency. In vitro, cells are readily able to migrate on various tissue substrates (in 2D) and within 3D matrices that can support their migratory requirements (i.e. proteolysis, cell adhesion, etc.). Despite the importance of cell migration, the in vitro and in vivo mechanisms of motility are still poorly understood. In vivo models of cell migration are complicated by a plethora of other cellular events occurring simultaneously, which limit efforts to expand on the mechanistic understandings of the migration processes. Much of what is known about cell motility is, in fact, derived from 2D in vitro models which generally represent suboptimal systems for studying cell migration. Until recently, there have been few 3D matrices available for studying cell migration; most 3D culture matrices that can support cell growth do not allow for the precise control of the material's physical properties for specifying the experimental environment.

The Seliktar group has recently introduced a unique biomaterial hydrogel matrix that may be used for this purpose. The matrix is based on a protein-polymer conjugate that can be cross-linked into a hydrogel in the presence of cells and tissues (i.e. PEG-fibrinogen hydrogel). The proposed research aims to create a novel platform for in situ visualization and documentation of cell mobility through incorporation of chromatic polydiacetylene (PDA) nanoparticles (NPs) within these hydrogel matrices. The PDA NPs, developed and studied extensively in the Jelinek laboratory, undergo dramatic color and fluorescence transformation induced by external biological stimuli, including physical pressures exerted by cells, and molecules secreted through cell metabolism. Accordingly, when embedded in the novel cell-seeded hydrogels, the particles could facilitate real-time in situ illumination of cellular trajectories and allow investigation of parameters affecting cell motility, including cell-mediated proteolysis of the 3D matrix, local cell-adhesion, and localized remodeling of the protein polymer backbone of the hydrogel.

#### Research Objectives and Significance:

Understanding cell mobility in constrained 3D environments is essential due to its significance in a variety of normal physiological processes as well as pathological conditions such as cancer and embryonic malformations.

The proposed research aims to develop an innovative platform for studying cell motility in a hydrogel milieu by creating composite polydiacetylene (PDA)/hydrogel assemblies in the presence of 3D cell cultures. The research will be designed to synthesize the new biomimetic constructs and examine their applicability for in situ visualization of molecular events associated with cell motility. Successful realization of the proposed research would be beneficial from both scientific/biomedical standpoints as well as for the technological potential of the platform as a vehicle for analysis of cell migration.

The specific aims of the research are:

- 1. To prepare biocompatible hydrogels having different compositions, which additionally incorporate the PDA NPs.
- 2. To incorporate smooth muscle cells (SMCs) and fibroblasts into the new PDA/hydrogel constructs and evaluate their survival and motility.
- 3. To apply time-lapse fluorescence microscopy with the biomimetic constructs in order to follow cell mobility by observing the in situ fluorescence changes of the PDA NPs relative to the cellular morphogenesis and motility activity within the hydrogel.

## Actin polymerization and force generation on soft interfaces

**Principal Investigators:** 

Dr. Anne Bernheim - Chemical Engineering, Ben-Gurion University Dr. Kinneret Keren - Physics, Technion Start Year ► 2009

The cytoskeleton is comprised of an active network of filamentous proteins which gives the cell its mechanical resistance and plays important roles in many cellular processes. The ability of the cytoskeleton to execute a diversity of tasks depends on its ability to self-organize and to constantly remodel itself. Many vital cellular processes, such as cell motility and division, involve cytoskeletal dynamics close to soft surfaces, particularly, fluid membranes.

The mechanisms governing cytoskeletal self-organization and dynamics near such surfaces are still largely unexplored. In this project we propose to develop synthetic physical model systems to study actin polymerization and force generation on such soft interfaces in a simplified and controlled environment, detached from the complexity of the living cell. Microfluidic devices will be developed to generate surfaces of well defined shapes. We plan to study the effect of curvature, surface tension, as well as the type and composition of the motility machinery on the forces generated and their subsequent effect on surface deformations.

#### Research Objectives:

We propose an integrated experimental project using artificial model systems to deepen our understanding of the fundamental physical and biological principles governing cytoskeletal organization and force generation on fluid interfaces. The experimental model systems consist of a fluid interface (supplemented with actin nucleators) and a motility medium. We will quantitatively explore the dynamics of actin polymerization and force generation on these soft interfaces and test how they depend on biophysical parameters, the identity of the actin nucleator and the biochemical composition of the motility medium.

Specifically, the project will address the following topics and goals:

(i) Explore the impact of surface curvature on actin polymerization and force generation.

We will explore the role of surface curvature on the forces generated and on the extent of actin polymerization for different actin nucleators. We will compare the effect of convex versus concave surfaces on actin self-organization.

(ii) Study the influence of the type and surface density of actin nucleators.

We will explore the dependence of actin self-organization on the type and surface density of nucleators of actin filaments, which are confined to the fluid interface. Two types of nucleators will be used: (i) those that promote actin branching and (ii) those that induce unbranched filaments, and are known to generate very different types of structures in cells.

(iii) Investigate the role of surface tension on force generation and interface deformability.

An additional biophysical parameter which can be modified is the surface tension. Experimentally this will be manipulated by adding various combinations of surface-active agents including lipids and surfactants.

## Synthesis and magnetic properties of Au-Fe nanoonions and core-shell nanoparticles

Start Year ► 2009

Principal Investigators:

Prof. E. Rabkin - Materials Engineering, Technion Dr. R. Shneck - Materials Engineering, Ben-Gurion University

Composite Fe-Au nanoparticles will be synthesized by de-wetting of thin Fe-Au bilayer sputter deposited on sapphire substrate. The nanoparticles consisting of ferromagnetic Fe core and passivating outer Au shell will be produced by direct dewetting, while layered nano-onions will be produced in the course of precipitation reaction in the homogeneous Fe-Au nanoparticles formed during high temperature homogenization heat treatment. In the latter case, the times and temperatures of the thermal treatments will be determined employing thermodynamic modeling of Fe-Au nanoparticles.

#### Project Objectives and Significance:

The objective of this project is the synthesis and characterization of composite Fe-Au nanoparticles. To this end, thin (3-5 nm in thickness of each layer) Fe-Au bilayers will be deposited on sapphire substrate and annealed in the temperature range 200-400 C. Since the wetting of sapphire by metals is poor, and the wettability in metal/metal systems is good, we expect that the bilayer will break down into individual nanoparticles that preserve the layers sequence, i.e. the inner region of the nanoparticle will consist of Fe, while the outer shell will consist of Au. In parallel, we will heat the bilayer to the temperature above the solubility limit of Fe-Au system (to be determined in the modeling part of this project). We expect that the homogenization of the bilayer and its breakdown into individual nanoparticles will occur simultaneously during this high-temperature treatment. Afterwards, the assembly of nanoparticles will be annealed at lower temperatures (to be determined in thermodynamic modeling) at which thin Fe lamella or shells can precipitate from homogeneous Fe-Au alloy either by the mechanism of discontinuous precipitation or as Widmanstätten platelets exhibit face centered cubic (fcc) atomic structure rather than body centered cubic (bcc) structure typical for bulk Fe below 910 C. This fcc Fe may exhibit saturation magnetization exceeding that of bcc Fe. We also expect that discontinuous precipitation will occur in a way ensuring that the surface of a nanoparticle will be covered by a thin layer of Au-rich phase, since the surface energy of Au is lower than that of Fe. The shape, size and magnetic state of obtained nanoparticles will be characterized by atomic and magnetic force microscopies (AFM and MFM), while their microstructure and composition will be characterized by transmission electron microscopy (TEM).

The significance of the project is in the fact that we propose an alternative to the traditional organometallic synthesis route of metallic nanoparticles. Our method is based on intrinsic, atomistic properties of the Fe-Au system and may result in nanoparticles with much higher degree of structural perfection. We should emphasize that our project is exploratory in nature and is aimed at checking the feasibility of the proposed synthesis route. It is not suitable for producing mass quantities of nanoparticles. If proven to be successful, the method can be modified for producing the large quantities of nanoparticles, for example by employing nanoporous thermally stable polymer templates.

## Single-photon emitters by controlled selective crystal growth of nanostructures on InP substrates

**Principal Investigators:** 

Prof. Daniel H. Rich - Physics, Ben-Gurion University Prof. Dan Ritter - Electrical Engineering, Technion Start Year ► 2009

The goal of this project is to realize single-photon (5 1.5~3m) emitters using single InGaAs quantum dots (QDs). Such a single-photon source has the potential for enabling many new applications in the field of long range quantum information technology. The QDs will be fabricated by growing InP/InGaAs/InP layers selectively on

nanometer scale openings in thin dielectric layers deposited on InP substrates, using metal-organic molecular beam epitaxy. This approach for the fabrication of the QDs is radically different from the widely explored self assembly method. It aims at producing fully controlled QD structures, without the statistical size distribution characteristic of the self assembly approach. Previous experiments at Technion revealed that the growth of nmscale structures is feasible, but their characterization by optical methods, is very complex. In this proposal, we suggest to simultaneously probe the optical and structural properties of the nanostructures by spatially and temporally resolved cathodoluminescence (CL). The information obtained from the CL experiments will make it possible to better understand how to control the position and composition of single nanostructures.

#### Objectives and Expected Significance of the Research:

The fundamental goals for this project are to control the size and position of InGaAs QDs in an InP matrix, and to evaluate their structural and optical properties. By controlling and monitoring the exact position of the quantum dots, we will significantly enhance the flexibility during investigations and the ability to manipulate individual nanostructures. An approach that utilizes pre-patterned InP substrates allows for the creation of different growth regions and conditions that favor the formation of InGaAs nanostructures. Important results during the timeframe of the project are the observation of emission lines from single InGaAs QDs on top of the InP pre-patterned substrates, excited either optically or by an electron beam.

## Magnetic Nanoparticles with Designed Surfaces for Polymer Film Nanocomposites: Advanced Materials Through Control of Interfaces

Start Year ► 2009

Principal Investigators:

Prof. S. Margel - Chemistry Department , Bar-Ilan University Prof. Wayne D. Kaplan - Materials Engineering, Technion Prof. Michael S. Silverstein - Materials Engineering, Technion

Nanoparticles often have unique electrical, chemical, mechanical or magnetic properties. Magnetic nanoparticles, which can exhibit ferromagnetic single domain behavior, superparamagnetism, and granular giant magnetoresistance, are of interest for many advanced technology applications. A few percent nanoparticles added to a polymer matrix can have profound and synergistic effects on the thermal, mechanical, barrier, dielectric, magnetic, electrical, and optical properties, but surface modification is essential to prevent agglomeration and enhance adhesion. The objectives of this research are to develop innovative magnetic nanocomposites; to characterize their structures and properties; and to understand the parameters that affect the structures and properties. These objectives will be achieved by synthesizing and characterizing the magnetic nanoparticles, developing nanocomposites, attaining previously unachievable descriptions of the interfaces, and characterizing the nanocomposite properties.

#### Research objectives and significance:

The objectives of this research are to develop innovative magnetic nanocomposites (nanoparticles with designed surfaces in polymer films); to characterize their structures and properties; and to understand how the structures and properties of these novel nanocomposites are influenced by the nature of the nanoparticles, the nature of the nanoparticle surfaces, the processing technique, and the interfaces within the nanocomposites. These objectives will be achieved by: (1) synthesizing and characterizing magnetic nanoparticles composed of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with narrow size distributions (between 5 and 100 nm) and with designed surfaces, hydrophilic, hydrophobic or polar, that are compatible with the polymeric matrices; (2) developing nanocomposite films using amorphous polymers, semi-crystalline polymers, and multiphase polymeric systems and using various processing techniques; (3) attaining previously unachievable descriptions of the nanoparticle/polymer interfaces using the unique state-of-the-art TEM capabilities at the Technion; (4) characterizing the mechanical, thermal, and magnetic properties of the nanocomposites.

### Nano-Scale Oxide Coatings for Membranes

Principal Investigators: Prof. Raphael Semiat - Chemical Engineering, Technion Prof. Carlos Dosoretz - Civil and Environmental Engineering, Technior Prof. Haim Sukenik - Chemistry Department. Bar-Ilan University Start Year ► 2009

Coating polyimide-based membranes for water purification with an ultra-thin (10-20 nm) overlayer of titania should make them more resistant to biofouling and allow them to last longer and function more efficiently. The proposed research couples the extensive experience of the Semiat and Dosoretz laboratories with membranes for water filtration with a process that has been developed in the Sukenik laboratory for liquid phase deposition of oxides to create uniform, compliant, oxide films. This methodology has been used to provide adherent overlayers on a variety of flat substrates ranging from semiconductors to glass and metal to polymers.

The research proposed herein will extend this effort to the coating of three dimensional matrices and will work towards using this mild, inexpensive, methodology to coat the pores and all exposed surfaces of polyimide membranes for water filtration. The coating chemistry will be developed in the Sukenik laboratory and the Semiat/ Dosoretz laboratory will investigate the effectiveness of this coating in terms of a detailed analysis of the structure of the modified membranes (before and after oxide treatment) and in terms of the ability of the surface oxide to prevent biofilm formation while maintaining proper membrane function. While neither of our laboratories has explored this approach to enhancing the performance of filtration membranes, there is adequate experience in both laboratories for us to be confident that the one-year framework of this project will allow us to evaluate this approach and for us to acquire sufficient preliminary results to enable the submission of a proposal for research support to external agencies.

#### Research Goals and their Importance:

The goal of this project is to develop the ability to apply a uniform, compliant coating of titania on all exposed surfaces (including the interiors of all pores) of polyimide-based membranes. The multilayer structure of the coated membranes will then be examined as will their resistance to biofilm formation. The filtration efficiency of the membranes after coating will also be assessed.

Micro and ultra filtration membranes are usually used in an environment that contains bacteria, whether for effluent purification or in membranes bioreactors for wastewater treatment. Any improvement to this process, whether by increasing the time between membrane cleaning or by reducing the cost of the cleaning would lead to important improvements in the treatment of wastewater. As it is virtually impossible to keep a typical industrial system completely sterile, microorganisms waiting for nutrients will always be present on surfaces. Biofilms will always develop, even after the most stringent feedwater pretreatment. An integrated antifouling strategy will not aim to kill all organisms in a system but to keep them below a threshold of interference. Since once developed, biofilms are almost impossible to combat without stopping the system, the most common anti-biofouling strategy practiced today is a preventive biocidal protocol. This alone is not enough to prevent biofouling since most existing polymers for dense membrane separations are not resistant to oxidizing biocides and the continuous supply of non-oxidizing biocides is prohibitive in water and wastewater membrane treatment.

Biofouling remains an unsolved problem because very little is understood about the fundamental nature of the growth processes. Since biofilms are almost impossible to eradicate once developed the most efficient means to combat biofouling in membranes is to avoid or control their formation. Thus, development of new membranes with reliable antibacterial properties, particularly if it can improve the durability and long term efficiency of the membranes using an easy-to-apply and inexpensive coating process, is still a challenge to be accomplished for the widespread application of membranes technologies in water treatment. The widespread application of membrane separation technologies requires the development of antibacterial surfaces which will minimize the application of biocides.

## Nanostructuring of PEG-Fibrinogen Polymeric Scaffolds

Start Year ► 2009

**Principal Investigators:** 

Prof. Dror Seliktar - Biomedical Engineering, Technion Prof. Havazelet Bianco - Chemical Engineering, Technion

Recent studies have shown that nanostructuring of scaffolds for tissue engineering has a major impact on their interactions with cells. The underlying hypothesis of the current investigation is that nanostructuring of hydrogel scaffolds could potentially provide an additional means to control both the physical properties of the material and the subsequent interaction between the material and the cells. We propose to utilize the self-assembly ability of biocompatible amphiphilic block-copolymers (Pluronic<sup>®</sup>) for preparing PEG-Fibrinogen (PF) hydrogels with distinct nanostructures. The overall objective of this study is to develop a methodology for creating nanostructures in the PF hydrogels and to understand the structure-property relationship associated with these nanostructures in cell culture applications. Experimental work will include small angle x-ray scattering and cryo-transmission electron microscopy experiments aimed at the characterization of the nanostructure. The mechanical properties of the nanostructured hydrogels will be investigated using stress-sweep rheological testing, and in vitro cellular assays will be used to asses the ability of the cells to form extensions and become spindled within the 3-D hydrogel culture environment.

#### Research Objective:

The underlying hypothesis of the current investigation is that nanostructuring of a PF scaffold could potentially provide an additional means to control both the physical properties of the material and the subsequent interaction between the material and the cells. We propose to utilize the self-assembly ability of biocompatible amphiphilic block-copolymers of poly(ethylene oxide)/poly(propylene oxide) (Pluronic<sup>®</sup>) for preparing PF hydrogels with distinct nanostructures. The overall objective of this study is to create nanostructures in PF hydrogels and understand the structure-property relationship associated with these nanostructures in cell culture applications. Specifically, we attempted to gain additional control over the material properties of the scaffold using nanostructuring, without changing their compatibility for 3-D cell culturing.

# Nano injectors to individual cells and their application to the study of cell communication during differentiation

Principal Investigators:

of. Lior Gepstein - Physicles, rechnicition of. Lior Gepstein - Physiology and Biophysics. The Bruce Rappaport Faculty of Medicine Start Year ► 2009

The proposed research program comprises two parts. The first half aims at developing a nanoinjecting system for an easy, repeated delivery of molecular cargos over a prolonged period of time into vital cells. The second half of the program utilizes this platform for studying cell communication and signaling pathways during differentiation.

#### Research plan:

a. Fabrication of the nano-injector platform. The needles fabricated on top of a silicon-on-insulator (SOI) wafer are defined by electron beam lithography and etched into the silicon by deep reactive ion etching. Fluid is fed through ducts and reservoirs etched into the back side of the wafer. Injection is induced by a short pulse applied to a piezoelectric crystal glued to the back-side sealing of the reservoir. Cells are grown on the wafer's surface with the needled penetrating the cell membrane. Surface chemistry will be used to promote membrane penetration and membrane sealing against the needle's base.

b. Studying signaling pathways and cell communication during differentiation. To this end we plan to combine the human embryonic stem cell (hESC) differentiating system and the aforementioned nanoinjector technology to study the molecular mechanism involved in early differentiation and cell-lineage fate-decisions. Our plan is to use the suggested technology as a mean to allow single cell post-transcriptional gene silencing through selective siRNA application. This will allow discrimination between the paracrine and autocrine effects of pivotal growth factors (such as Wnts, TGF-beta, BMP, Activin) during early cell-lineage fate decisions. Additional studies involving the nanoinjector technology will include: development of a unique strategy for fate-mapping of specific progenitor cells (by tagging of a single-cell within the differentiation by generation of "artificial gap junctions" between cells, and development of novel methods that do not involve viral vectors to generate induced pluripotent stem cells (iPS).

## Nanoporous Responsive-Hydrogels Containing Magnetic Nanoparticles

Start Year ► 2009

Principal Investigators:

Dr. Ester Segal - Biotechnology and Food Engineering, Technion Prof. Michael Silverstein - Materials Engineering, Technion

Hydrogels are three-dimensional cross-linked polymer networks capable of undergoing a reversible volume change in response to environmental stimuli. Such reversible volume changes make hydrogels excellent candidate materials for sensing, drug delivery, and microfluidics. The swelling rate is inversely proportional to the square of the characteristic dimension of the hydrogel. To reduce the response time to a usable level, it is therefore necessary to reduce the gel size dramatically. To answer this challenge, we suggest to synthesize highly porous hydrogel nanocomposites containing super paramagnetic nanoparticles. Iron oxide (Fe3O4) nanoparticles will be incorporated in the synthesis scheme of N-isopropylacrylamide (NIPAM) through polymerization in the continuous phase of high internal phase emulsions (HIPE)). Application of high frequency alternating magnetic fields (AMF) will be used to generate heat in the magnetic particles and actuate the volume phase transition of the thermoresponsive poly(NIPAM) nanocomposite. The detailed effects of the synthesis conditions and AMF on the volumetric change during the phase transition of the nanocomposites will be investigated. An externally actuated (temperature triggered) device will be fabricated.

#### Objectives:

The objectives of the research are to synthesize nanoporous responsive hydrogel polyHIPE containing magnetic nanoparticles, to investigate the ability of such polyHIPE to undergo a phase transition using nanoparticle-generated heating, and to develop a self-heat-generation polymerization mechanism.

## Self-excited Oscillations in NanoOptoMechanical Systems

Principal Investigators: Prof. Eyal Buks - Electrical Engineering, Technion Prof. Oded Gottlieb - Mechanical Engineering, Techn Start Year ► 2009

Optical schemes are widely employed for displacement detection and actuation of micro and nano scale mechanical devices. Recent studies have found that the coupling between the optical field and the measured mechanical device may result in strong back reaction effects. Here we propose to study both experimentally and theoretically such back reaction effects and particularly focus on the region where the coupled system reaches instability, and consequently self-excited oscillations occur. The combined experimental and theoretical efforts will aim at reaching a quantitative understanding of such effects, and on developing novel low power actuators, and mechanical sensors that exploit such instabilities for achieving ultra high sensitivity.

#### Objectives and Significance of Research:

In the present proposed research we will focus on studying both theoretically and experimentally self-excited oscillations in NOMS. Our general aim is to investigate the complex nonlinear dynamics of self-excited phenomena in NOMS and to provide a quantitative comparison between a deduced quasi-continuum theory and a controlled set of experiments. The specific goals of this research proposal are: i) to manufacture a self-excited NOMS with controllable and measurable coupling of the thermal and elastic fields; ii) to derive a theoretical nonlinear quasi-continuum initial-boundary-value (IBVP) problem for the system; iii) to perform a set of controlled calibration experiments (free and forced vibration) to enable estimation of the nano-mechanical properties required for the theoretical model and to examine their parametric dependency; iv) to validate the theoretical model via solution of the self-excited dynamical system incorporating the measured parameter set using both asymptotic multiple-scales and numerical methods for weak and strong nonlinearities respectively; v) to derive the system bifurcation structure and examine thresholds of complex aperiodic response to enable a quantitative comparison of theoretical and experimental results. The results of our research may open the way towards a novel class of mechanical sensors that exploit such dynamical metastabilities for ultra sensitive detection of small forces.

### Analysis of streaming potential phenomena

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Electrokinetic phenomena associated with the relative motion of electrolyte solutions within electric double layers (EDL) adjacent to charged surfaces constitute the enabling platform in many advanced applications of nano-fluidics to nanotechnology (the labon-a-chip concept). An important feature of these phenomena is that the transport processes taking place within the EDL (whose characteristic scale is the nano Debye length) have global effects and their resolution is therefore essential. The mathematics and physics of electrokinetics are, however, complicated by the nonlinear coupling of the dynamic and electro-diffusive aspects of the problem. Numerical simulations may not be straightforward owing to large disparity of the scales involved.

We propose to carry out a fundamental theoretical research aimed at clarifying the global mechanisms associated with the EDL by means of asymptotic analysis and numerical simulations in the prevailing singular limit of a thin EDL. We consider the sedimentation-potential problem as a prototypical electrokinetic scenario, focusing upon the important case of dominant convection which has so far not been analyzed in a consistent rigorous manner.

The proposed research considers the class of electrokinetic problems where a relative motion between fluid in the diffuse part of the EDL and the adjacent charged solid surface is generated by the action of a mechanical external agency acting on either the fluid (e.g. pressure-driven flows in channels) or the solid (e.g. gravitational or centrifugal forces on sedimenting particles). The relative motion thus induced creates electric fields (e.g. the Dorn effect) which in general act to increase resistance to the relative fluid motion. This is relevant to applications concerned with geophysical two-phase flows through fine porous media (e.g. oil recovery and water seepage through porous rock formations) and in the accurate measurement of zeta potential. From the fundamental aspect we aim at obtaining a rigorous analytic description in the singular limit of thin Debye layer. This will shed light on the global effects of nano-scale phenomena.