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Introduction

With over 110 faculty members and 300 graduate students and postdoctoral fellows from 14 different faculties, the Russell Berrie Nanotechnology Institute (RBNI) is involved with all aspects of Technion life from graduate education to new faculty recruitment, establishment of new infrastructure centers, ties with industry and other academic institutions, commercialization of intellectual property, and initiation of new research directions.

Technion research at the Nano scale encompasses most facets of nanoscience and nanotechnology including nanoelectronics, nanooptics, nanomaterials, nanomechanics, and their interface with biotechnology and medicine.

RBNI's main channel for the promotion of innovative research is the "Nevet" (sprout in Hebrew) program aimed at the encouragement of new multidisciplinary collaborative research within and outside the campus. Grant applications submitted by two researchers are reviewed by a panel of leading scientists from all Israeli universities. Winning proposals are awarded a one-year seed grant which funds the research project and a student salary. The results obtained during that year and the proven collaboration record improve the prospects of the researchers in their subsequent application to external funding agencies.

In total, RBNI awarded 58 Nevet grants over the past four years (2006-2009). Twenty-five of these grants were awarded to Technion research groups from different disciplines, 11 were awarded to new collaborative research efforts between Technion and other Israeli universities, and the remaining 22 grants were awarded to new collaborative projects between Technion and foreign institutions.

This brochure showcases the initial results of the Nevet projects, and furthermore a glimpse into the cutting edge research underway in nanoscience and nanotechnology at Technion. We hope you enjoy it.

Sincerely,

Prof. Uri Sivan



Director of the Russell Berrie Nanotechnology Institute
Technion – Israel Institute of Technology

Insights into Molecular Imprinting of Proteins

Principal Investigators: Prof. Havazelet Bianco-Peled - Chemical Engineering, Technion
Prof. Simcha Srebnik - Chemical Engineering, Technion

Start Year ▶ 2006

The scientific goal of this research was to investigate the various factors that lead to poor selectivity and specificity of protein-imprinted polymer gels.

Molecularly imprinted polymers (MIPs) showing molecule-specific recognition of small molecules have been established in recent years. However, imprinting of large biomolecules, such as peptides and proteins has been confronted with difficulties. Achieving specific recognition of proteins will allow for important advances in nanotechnologies including catalysis, sensors, and detection of toxic or biowarfare agents. Several factors may contribute to poor imprinting of large molecules, including limited synthesis conditions, inherent flexibility of the macromolecules, and low degrees of cross-linking of the polymer matrix necessary to allow diffusion of the macromolecule. Using systematic experimental procedures and computer simulations, we aimed to investigate these and other factors that contribute to poor imprinting of proteins.

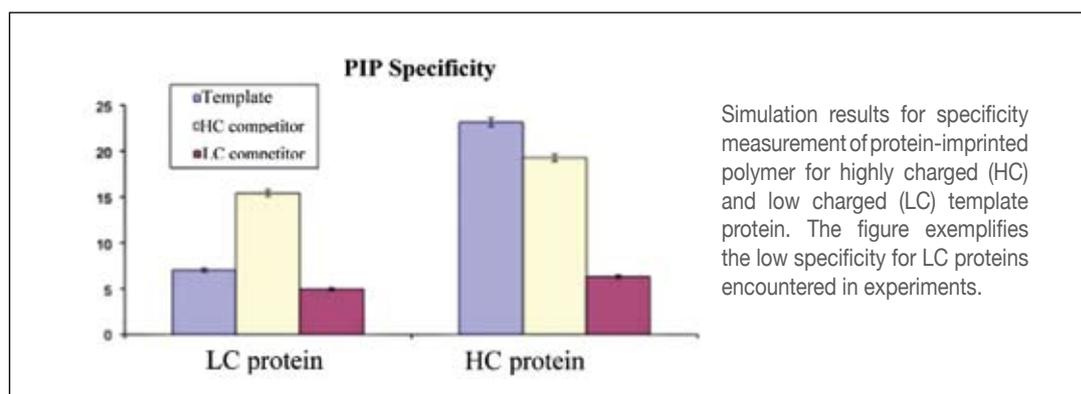
We developed a simple hybrid Monte Carlo – Kinetic Gelation simulation for molecular imprinting of proteins. We focused on the structure and functionality of the imprinted pore immediately following complexation and polymerization, focusing on the concentration ranges used in the experimental studies. The interaction of the protein with the imprinted pore is shown to be influenced by polymer density, with minimum recognition achieved at the protein-sized pore percolation limit of the gel. Additionally, we found that binding energy linearly decreases when increasing charge densities in the solution and on the protein. We define an equilibrium factor α , which measures the extent of recognition in imprinted gels compared to a model non-equilibrated system. Solution charge concentration has a significant influence on α , achieving a maximum value at a relatively low charge density. This result indicates that highly charged solutions will result in increased non-specific interactions, and reveals the advantage of low charged gels over highly charged ones for imprinting of proteins, as has been experimentally observed.

The interactions between lysozyme-imprinted hydrogel and their template protein were studied using adsorption measurements, competitive adsorption experiments and Isothermal Titration Calorimetry (ITC). The results were compared to the interactions between the imprinted polymer and a reference protein, cytochrome C. Experimental adsorption isotherms and competitive adsorption studies detected better affinity and higher capacity of the imprinted polymer toward the template protein. Moreover, analysis of ITC data identified major differences in the binding enthalpy of lysozyme when the imprinted and the non-imprinted polymers were compared. On the other hand, cytochrome C did not exhibit any major changes in the adsorption enthalpy when comparing the imprinted and the non-imprinted polymers. This is the first thermodynamic evidence for the creation of new binding sites in the process of protein imprinting.

This research lead to the following publications:

O. Kimhi and H. Bianco-Peled, *Langmuir* 23, 6335, 2007.

L. Levi and S. Srebnik, *Macromolecular Symposia* (In Press).



Understanding surface recognition and binding of electronic materials by biomolecules

Start Year ▶ 2006

Principal Investigators: Prof. Asher Schmidt - Schulich Faculty of Chemistry, Technion
 Prof. Uri Sivan - Physics, Technion
 Prof. Yoram Reiter - Biology, Technion

The interfaces between bioorganic molecules and inorganic surfaces play a key role in diverse scientific and technological research areas ranging from nanoelectronics and biomimetics, through biomineralization, to medical applications as drug delivery and implant biocompatibility. However, the chemical and physical basis of surface recognition by biomolecules still remains unclear. Elucidation of the interfacial interactions and of the structural and dynamical state of the surface bound molecules is of prime fundamental scientific importance. Likewise, these details are essential when the design of new functional interfaces is sought.

Our research aims to establish solid state NMR means for the atomic level characterization of the interfacial interactions of bioorganic molecules with inorganic surfaces. In particular we seek to identify the functional groups of the surface and of the biomolecules that facilitate binding, the binding geometry, and the dynamic state of the surface bound biomolecules as function of hydration level and temperature.

Results obtained so far:

The model system chosen for our study is alanine (specifically ^{15}N and ^{13}C labeled) loaded onto SBA-15 mesoporous silica with high surface area (840 m²/g). Inter- and intra-molecular dipolar recoupling NMR techniques (REDOR, SLF) were employed. $^{29}\text{Si}\{^{15}\text{N}\}$ and $^{15}\text{N}\{^{29}\text{Si}\}$ REDOR NMR revealed intermolecular interactions between the alanine N-amine to silica surface species, and served to infer the interaction stoichiometry and geometry [Scheme 1]. Alanine's interacting moiety was identified as the protonated, charged amine group, $-\text{NH}_3^+$, by $^{15}\text{N}\{^1\text{H}\}$ SLF with PMLG5 [Figure 1]; surface binding stoichiometry of the type $\text{N}\cdots\text{Si}_n$ with $n = 3$ or 4 was revealed by $^{15}\text{N}\{^{29}\text{Si}\}$ REDOR NMR, and the interacting Si moiety is identified, predominantly, the Q3 silanol species via $^{29}\text{Si}\{^{15}\text{N}\}$ REDOR NMR. Intermolecular, intranuclear $\text{N}\cdots\text{Si}$ distance of 4.2-4.5 Å was determined using $^{15}\text{N}\{^{29}\text{Si}\}$ REDOR NMR. Distinct dynamic states of the alanine molecules were identified by $^{15}\text{N}\{^{13}\text{C}\}$ REDOR NMR, showing fast averaging of the intramolecular $^{13}\text{C}\cdots^{15}\text{N}$ dipolar interaction. At the lowest hydration state ('dry', $< 2 \text{ H}_2\text{O}/\text{nm}^2$) we identify a single population of surface bound alanine molecules that undergo small amplitude, rapid, anisotropic reorientation while anchored via their ammonium moiety [Figure 2, left]. This motion is temperature independent between -20 to $+20$ C. At increased hydration level ('hydrated', $\sim 4 \text{ H}_2\text{O}/\text{nm}^2$) two additional populations are quantified [Figure 2, right]: i) surface bound alanine, ammonium anchored, with larger amplitude anisotropic motion, and ii) isotropic reorienting, water solvated alanine molecules [Scheme 2]. Elevating the temperature leads to re-distribution of the populations, with the more mobile ones becoming more pronounced. The different populations are attributed to alanine molecules embedded within different sizes of water clusters.

Our measurements provide for the first time direct observation of the atomic details of the interactions responsible for the binding of alanine to mesoporous silica surfaces. Interacting species both of the amino acid and the silica surface are identified, while exposing also the slow dynamic behavior and the role of water molecules. Fine surface details are elucidated, and also the high site-specificity of alanine binding.

Establishing the methodology for the above model system, our focus is currently extended to study the binding of more complex biomolecules and different classes of inorganic surfaces; in particular, heptapeptides that were identified to possess high surface affinity and selectivity will be targeted.

Does the research continue? In what way?

Additional model amino acids will be studied and compared with theoretical predictions. These studies are extended to the characterization of heptapeptides that bind to silica surfaces with high selectivity and affinity. Additional surface types will be examined.

This research comprises the Ph.D. research plan of one Ph.D. student.

Facilities used during the research

The study was conducted in the PI's Solid State NMR Research Laboratory. This Laboratory is currently expanded and upgraded via a matching RBNI fund, the Schulich Faculty of Chemistry, and individual researchers' funds.

Took part in this research:

Ira Ben Shir, Ph.D. student

Dr. Shifi Kababya, The Schulich NMR Facility

Scheme 1: Geometry and stoichiometry of surface bound alanine from solid state NMR.

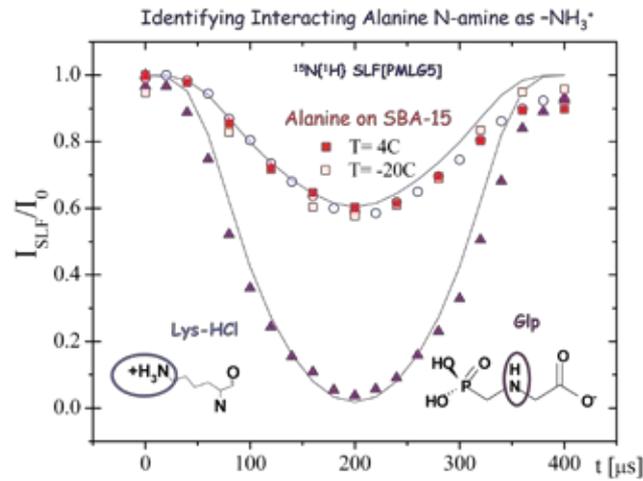
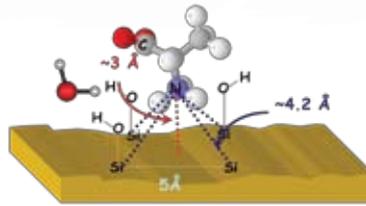


Figure 1 - Experimental $^{15}\text{N}\{^1\text{H}\}$ SLF[PMLG5] dipolar evolution of the $[1\text{-}^{13}\text{C},^{15}\text{N}]$ alanine loaded on SBA-15, 'dry' state, at -20 and 4 C and of two reference compounds: Lys-2HCl with -NH_3^+ (o) and the $>\text{NH}$ of ^{15}N -(phosphonomethyl)glycine (\blacktriangle). Overlap of Ala-SBA-15 data (\blacksquare) with that of Lys-2HCl identify the interacting N-amino as -NH_3^+ . Simulations of the SLF evolution further substantiate the identification.

Identifying the Dynamic State of Surface Bound Alanine

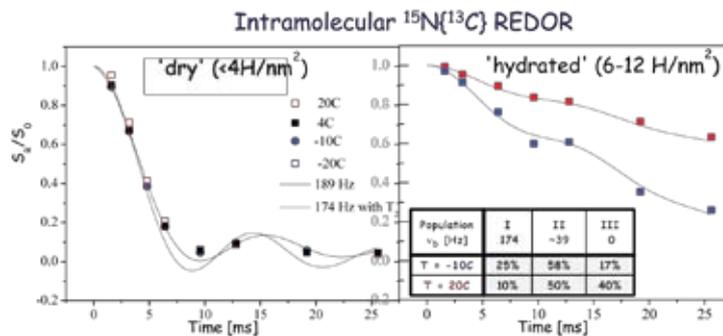
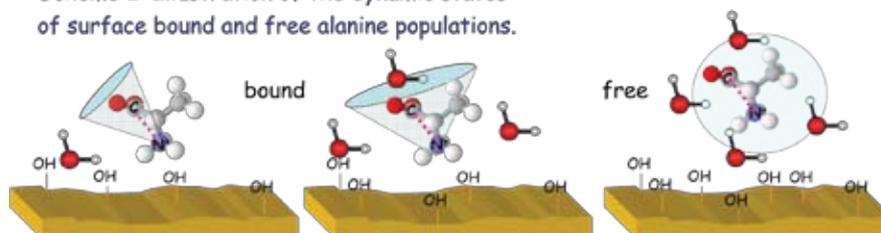


Figure 2 - Experimental $^{15}\text{N}\{^{13}\text{C}\}$ REDOR measurements of $[1\text{-}^{13}\text{C},^{15}\text{N}]$ alanine loaded on SBA-15, 'dry' and 'hydrated' states, vs. temperature. 'dry' state: REDOR simulation (black line, best fit) indicates the presence of a single alanine population with reduced $\text{N}\cdots\text{C}1$ dipolar coupling (86%) due to small amplitude, rapid reorientation of ($\text{N}\cdots\text{C}1$); 'hydrated' state - best fits obtained by summing three REDOR contributions with weights representing three distinct alanine populations: two bound with small and large amplitude reorientation, and a third of 'freely' reorienting, solvated molecules.

Scheme 2: Illustration of the dynamic states of surface bound and free alanine populations.



Nano particles to combat Osteoarthritis in human joints

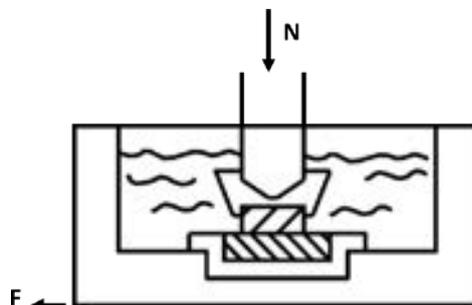
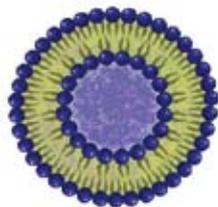
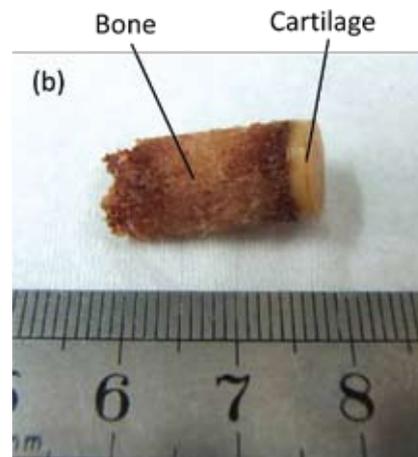
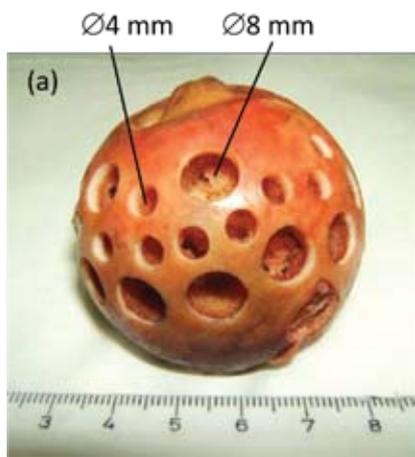
Start Year ▶ 2006

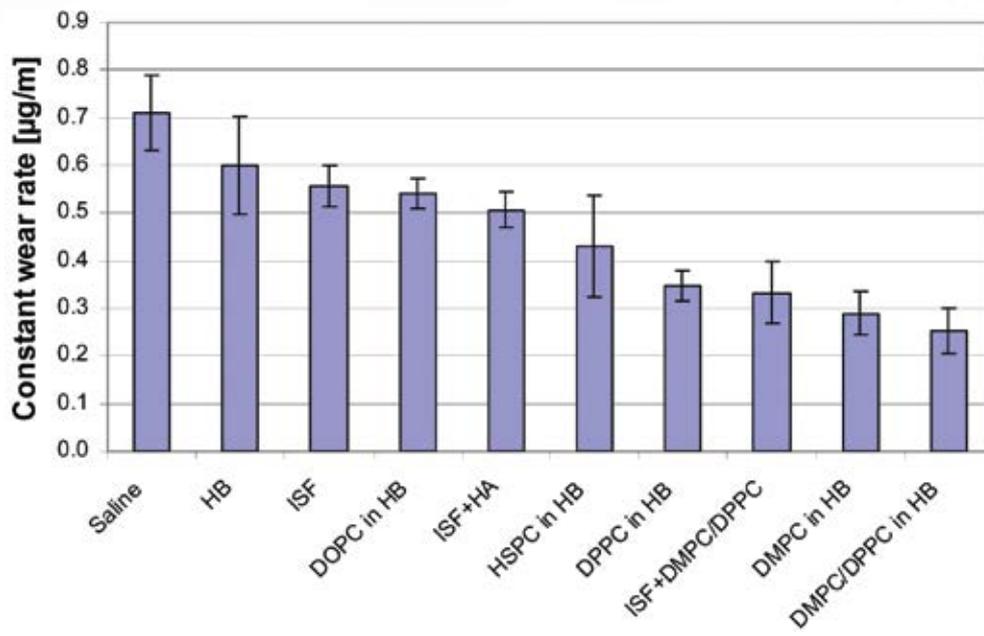
Principal Investigators: Prof. Izhak Etsion - Mechanical Engineering, Technion
 Prof. Alice Marudes - Bio-Medical Engineering, Technion

Efficient lubrication is essential for synovial joint mobility in both health and disease. It is well known that extremely low friction is required for proper functioning of synovial joints. In several medical treatments, bio-lubricants are injected into human joints to maintain their proper functioning. In the course of developing and screening such bio-lubricants, it is important to measure their effect under conditions similar to the ones in vivo. To this end, a first attempt was made to test the friction of two slices of human articular cartilage sliding over each other under various working conditions in the presence of different lubricating fluids. The results can be used for future research in the field of joint lubrication.

Results obtained so far:

A novel technique was developed to measure friction and wear of human cartilage on cartilage specimens. The research continued beyond the NEVET support period that ended in 2007 and is on going presently. Both friction and wear of human cartilage were reduced in the presence of Liposome nano-particles.





Nanoelectronic Device Based on Carbon Nanotubes and Semiconductor Nanocrystals

Start Year ▶ 2006

Principal Investigators: Prof. Efrat Lifshitz - Chemistry, Technion
Dr. Yuval Yaish - Electrical Engineering, Technion

The ultimate goal of the project focuses on the development of single electron transistor (SET), comprised of carbon nanotubes and a semiconductor nanocrystal.

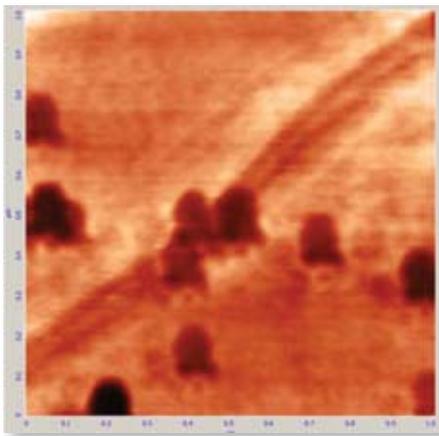
The carbon nanotubes will function as interconnect leads to the source, drain and gate electrodes of a transistor. These tubes will exhibit chemical stability, appropriate cross section matching and high capacitive coupling with the nanocrystal element. The semiconductor nanocrystal will be a key element, exhibiting a quantization of charge and facilitating an electrical transport only at specific degenerate points to be tuned by the external gate. These nanocrystals will be synthesized by a colloidal procedure to form spherical, rod and wire shapes, each of which will be anchored to the carbon nanotube by a covalent bonding. It is anticipated that the proposed SET would have a low operational voltages, low noise level, and room temperature operational capabilities.

Results obtained so far:

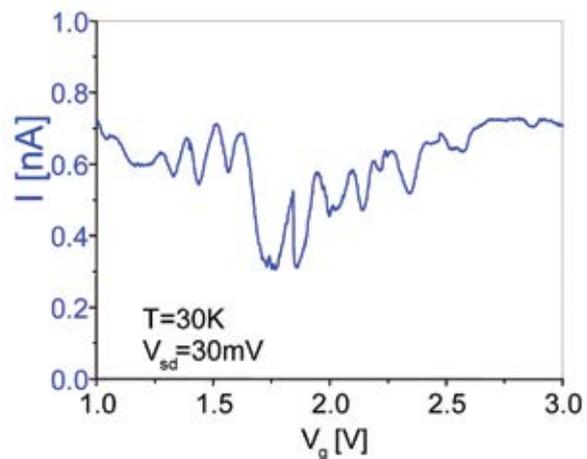
Various kinds of semiconductor nanocrystals and iron nanoparticles were synthesized. Their physical structures, as well as their optical properties were studied.

In addition, Carbon nanotube (NT) field effect transistors (FETs) were fabricated. We study their physical morphology and electrical properties. We have been able to functionalize the NT's surface with PbSe and iron nanoparticles. AFM, SEM, and TEM images were taken to verify these attachments. Particle attachments were utilized by two methods. The first one, which is more conventional, used peptide chemistry to covalently attach amine end group to carboxylic acids that exist on the NTs surface. The second method employed novel spray technique that was used on the NT FETs directly. Both methods were very successful and yield high percentage of nanoparticle attachments.

The nanometer size gap along the NT was fabricated using electromigration technique, in which a high current passes through the NT and causes its failure at some point. The gap size was rendered between few to tens of nanometer, and could be bridged by the nanoparticles. Electrical measurements were performed and coulomb blockade phenomenon was observed in some devices. However, other devices exhibit noisy I-V characteristics. In order to overcome this obstacle we design novel structure in which the short segment of the tube serves as island for single electron operation. The nanocrystals create charge perturbation on top of the NT island. Currently we pursue this direction.



Carbon nanotube bridged by Iron nanoparticle



Low temperature measurement of Single Electron Transistor based on carbon nanotube and Iron nanoparticle. Coulomb blockade phenomena can be observed

In Vitro Evaluation of a Composite Scaffold Made from Electrospun Nanofibers and a Hydrogel for Vascular Tissue Engineering

Principal Investigators: Prof. Dror Seliktar - Biomedical Engineering, Technion
Prof. Eyal Zussman - Mechanical Engineering, Technion

Start Year ▶ 2006

The design of a composite biodegradable scaffold for vascular tissue engineering was the main focus of this research. A composite material was made from a highly porous mesh of poly(epsilon-caprolactone) (PCL) nanofibers, fabricated by electrospinning and permeated with a hydrogel biomaterial made from PEGylated fibrinogen. The PCL nanofiber mesh provided the structural reinforcement whereas the PEGylated fibrinogen hydrogel provided a precisely tunable matrix for an improved biocompatible interfacing between cells and the PCL nanofibers. The architectural and mechanical properties of the PCL nanofiber mesh were examined using scanning electron microscopy (SEM) and uniaxial tensile testing. Aortic smooth muscle cells (SMCs) were encapsulated in the hydrogel phase and cultured in the composite scaffold for up to one week in vitro.

The ability of the composite structure to support cell attachment, proliferation and migration, was examined by microscopy with whole constructs and histological sections. The results indicated that the SMCs become highly spindled and proliferate in the composite material (see Figure 1). Time-lapse microscopy showed that the SMCs preferentially migrated towards the stiffer PCL nanofibers of the scaffold and populated the mesh at a higher cell density. In the PCL mesh region, the SMCs expressed a more contractile phenotype as indicated by smooth muscle alpha-actin staining. In contrast, the more compliant hydrogel region contained few smooth muscle alpha-actin positive SMCs. The electrospun PCL nanofibers exhibited significantly higher elastic modulus in comparison to the PEGylated fibrinogen hydrogel, suggesting that mechanics may play a role in the preferential migration and phenotype expression of the SMCs in the nanofiber region of the composite scaffold.

In conclusion, we verified that the composite material exhibited suitable biocompatibility for SMC culture and adequate mechanical properties for use as a scaffold material in vascular tissue engineering.

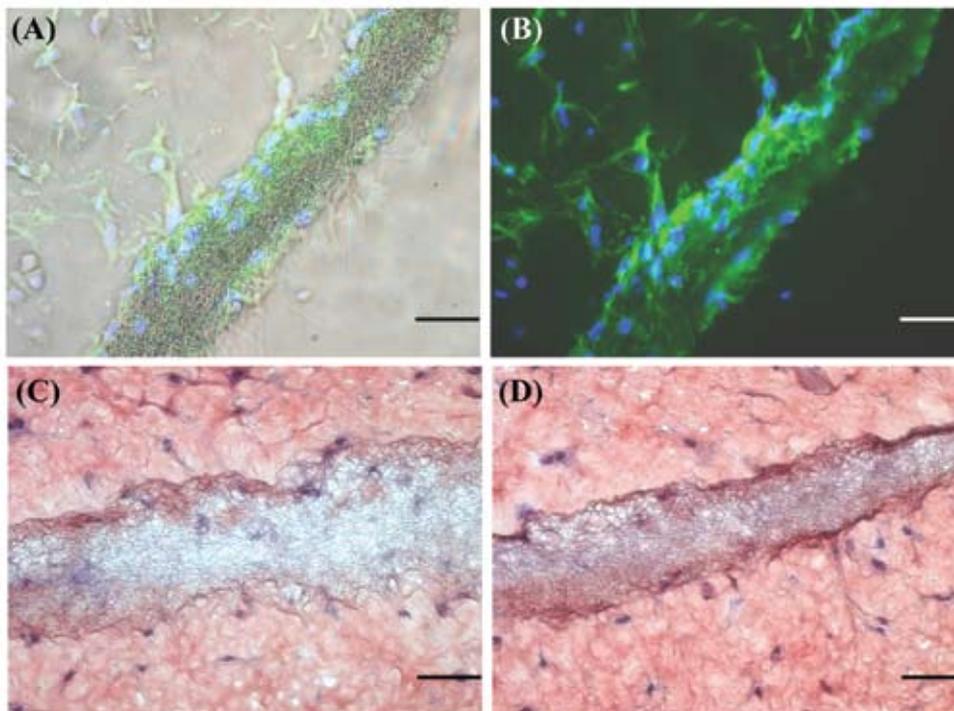


Figure 1: Smooth muscle cells (SMCs) spread and interact with both the hydrogel phase and PCL nanofibers of the composite scaffold. (A-B) Phase contrast and fluorescence micrographs of a cell-seeded construct made PCL nanofibers, showing SMCs spreading within the PEGylated fibrinogen hydrogel and the monolayer PCL nanofiber mesh (f-actin in green; nuclei in blue). The SMCs accumulate near the PCL nanofibers, as seen in thin sections of constructs stained with fluorescence and visualized by phase contrast alone (A) or superimposed with fluorescence (f-actin in green; nuclei in blue) (B). The PCL nanofiber mesh is visible in both the phase contrast images as well in the H&E stained sections of the specimen (C-D). Scale bar is equal to 50 μ m, unless specified otherwise.

Organized organic thin films as “smart” nano-interconnects

Start Year ▶ 2006

Principal Investigators: Prof. Rina Tannenbaum - Chemical Engineering, Technion
 Dr. Hossam Haick - Chemical Engineering, Technion
 Prof. Allen Tannenbaum - Electrical Engineering, Technion

The goal of this research was to develop a “smart molecular solder” (SMS) that can essentially operate at the molecular and the nanoscale level, and can selectively form precision molecular bridges between nano-pads and nanocomponents in printed circuit boards.

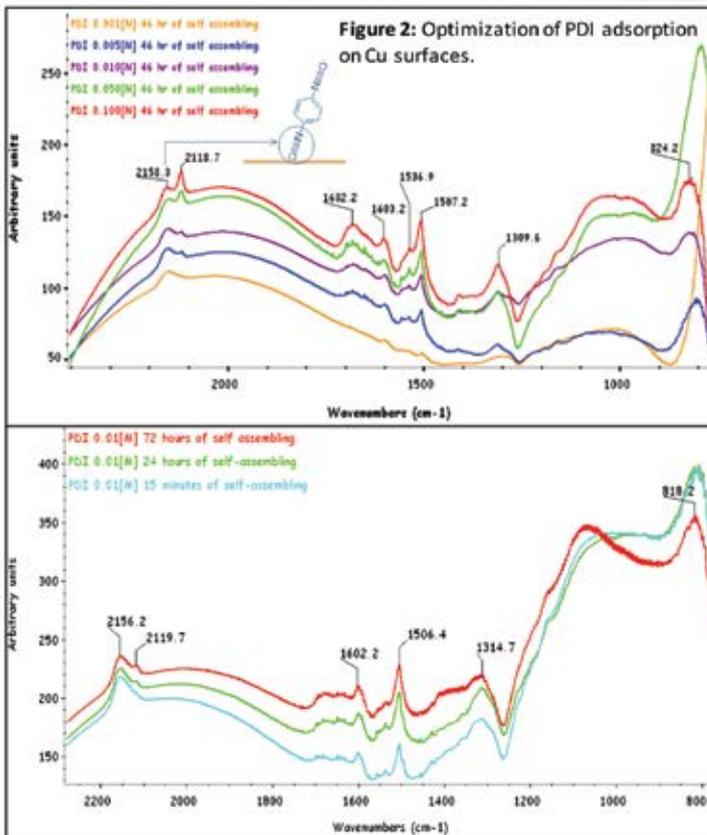
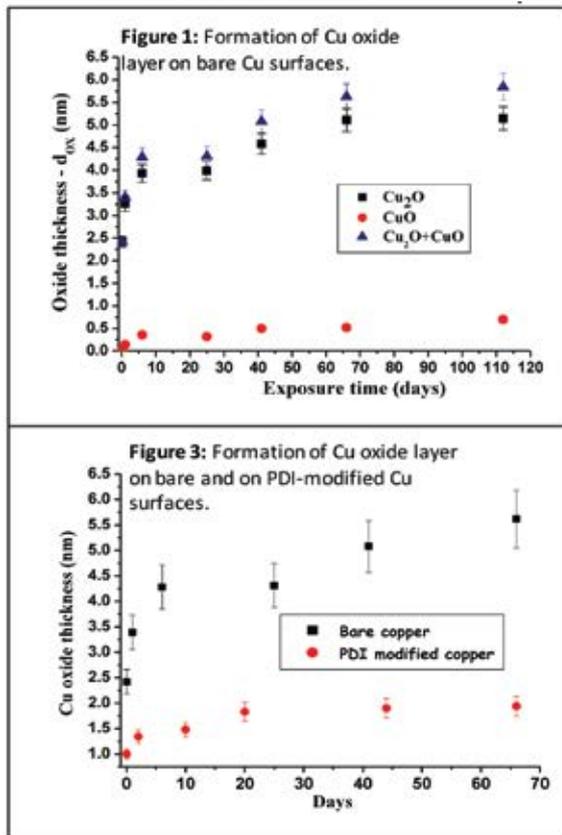
One of the main obstacles to achieving ever-higher component density of integrated circuits is the limit of accuracy of component placement available with current surface-mount technology. State of the art technology involves the use of the stencil printing process, in which a thin layer of solder-paste is deposited onto the metallic pads of a circuit board substrate, followed by the automatic positioning of components onto their designated places. The accuracy of component placement is limited by variations in the volume, area, and position of the solder-paste material deposited onto the pads, and by the lateral mobility of the components during the placement process, and hence, imposes limits on the yield and reliability of high-density circuits. To eliminate this bottleneck, a new surface-mount placement technology, operative in the nanometer regime is sought.

This proposal focuses on the construction of functional surfaces on the metallic nano-pads that will subsequently bind irreversibly and uniquely to the deposited nanocomponents, with very low error and very few processing steps. The “smart” adhesive will comprise of molecules that will bind selectively to metallic surfaces, i.e. nanopads, on one side and nanocomponents on the other, forming an interactive, bridging, conductive layer. The desired precision of the processes involved will also call for new ideas in feedback control. Measurements and evaluations of events at the molecular and nanoscale level will need to be translated into observable macroscopic quantities. Hence, mathematical models and resulting computer simulations of the type for which control/systems engineers have a particular expertise may be very helpful in driving some of the specific experiments. In particular, concepts from particle systems and discrete Markov chains to model the processes involved may be useful. Therefore, the synergistic collaboration of a material scientist and a control theorist will constitute a great opportunity for a comprehensive nano-interconnect system development.

Results obtained:

The first stage of the research concentrated on the study of the oxidation behavior of thermally prepared polycrystalline Cu thin films upon their exposure to ambient air for long time periods. We used the information obtained from line fitting of high resolution XPS spectra of Auger Cu LMM, Cu2p3/2 and O1s in order to investigate the Cu oxidation behavior and to determine individual overlayer thickness and the overall composite thickness dependence of the oxide layers on the exposure time. The results showed that the thickness of the native oxide layer ranged from 2.5 to 5.2 nm during the 112 days of exposure, while the overall oxide composite thickness ranged from 2.5 to 6.0 nm (Figure 1). Based on XPS, SE, and TEM analysis we proposed an overall oxidation mechanism consisting of three stages: (a) Formation of a p-type semiconductor Cu₂O layer due to the outward transport of copper ions towards the oxide-oxygen interface; (b) Formation of a Cu(OH)₂ metastable overlayer due to the interactions of Cu ions with hydroxyl groups that were present on the surface as a wetting layer formed due to the relative high humidity at room conditions; and (c) Very fast transformation of the Cu(OH)₂ metastable phase to the more stable CuO layer.

These three stages occurred concurrently and were dependent on each other [1,2]. The second stage of our research concentrated on the initial optimization of the self-assembly (SA) process of phenyl diisocyanide (PDI) molecules on thermally prepared Cu thin films. This was achieved via variations of PDI concentrations and the length of substrate immersion times (Figure 2) monitored by reflection-absorption infrared spectroscopy (PM-IRRAS). This was done in order to obtain an indication as to the minimum immersion time and PDI concentration required for an optimal self-assembled process in THF solution. The main conclusion from this work was that the self-assembly of PDI molecules on a Cu surface is a very fast process (in scale of minutes), leading to the formation of a “standing up” configuration of these molecules. However, a number of defects, consisting of polymerization of the PDI molecules and their agglomeration in solution prior to adsorption, may have also occurred during the self-assembly process [3]. Finally, we examined the effect of the formation of a self-assembled PDI thin film layer on the oxidation process of high purity polycrystalline Cu surfaces. Cu films prepared under the same conditions, but covered with a monolayer of PDI molecules adsorbed from solution, showed a 3-4 folds lower thickness of the copper oxide layer on the Cu surface, as compared to bare Cu surfaces (Figure 3). Hence, our initial findings imply that chemisorbed PDI molecules can serve as protective coatings for Cu oxidation.



Research publications:

1. Oxidation of polycrystalline copper thin films at ambient conditions, I. Platzman, R. Brener, H. Haick, and R. Tannenbaum, J. Phys. Chem. C 2008, 112(4), 1101-1108.
2. Formation and Characterization of Ultra-Smooth and Highly Stable Copper Surfaces, I. Platzman, C. Saguy, R. Brener, R. Tannenbaum and H. Haick, submitted.
3. Self-assembly of a conductive organic monolayer of diisocyanobenzene molecules adsorbed on Cu, I. Platzman, H. Haick and R. Tannenbaum, submitted.

Novel High Temperature Superconducting Ceramic Nanofibers from Electrospun Polymer-Based Precursors

Start Year ▶ 2006

Principal Investigators: Prof. Michael S. Silverstein - Materials Engineering, Technion
Prof. Eyal Zussman - Mechanical Engineering, Technion

The goal of the research was to produce high temperature superconducting ceramic nanofibers from electrospun polymer-based precursors.

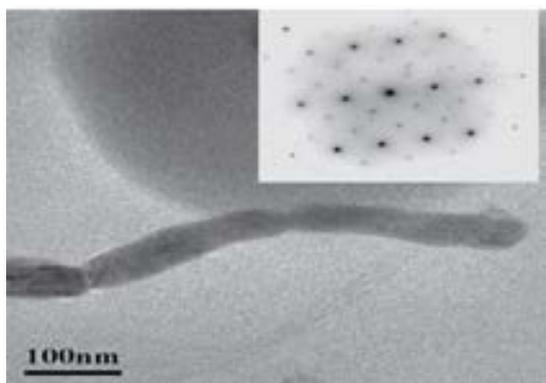
A versatile approach to the synthesis of YBCO nanofibers via electrospinning a polymer precursor solution was developed. The aqueous polymer precursor solution consisted of poly(acrylic acid) (PAAc) and a mixture of yttrium nitrate, barium nitrate and copper nitrate, henceforth termed (Y,Ba,Cu)-N, in which the atomic ratio Y/Ba/Cu is 1/2/3. The conductivity of the polymer precursor solution at 27 °C was 14.70 mS/cm, its zero shear viscosity was 52.00 cP, and its pH was 1.88. Adding the metal nitrates to the PAAc solution increased the ion concentration and, hence, its conductivity. The ions also shield the electrostatic repulsion between the partially charged PAAc molecules, making the PAAc molecules more compact, and, possibly increasing molecular entanglement.

The as-spun precursor nanofibers have a relatively uniform diameter, although there is some beading, resulting from a Rayleigh instability. The YBCO nanofibers were synthesized by pyrolysing the precursor nanofibers. Typical YBCO nanofibers were 50-100 nm in diameter and around of 10 μ m length. The nanofibers also contain relatively small amounts of yttrium oxide and copper yttrium oxide. Thus, this research has definitively established that electrospinning offers a simple method for synthesizing high aspect ratio nanofibers of ceramics with complex microstructures.

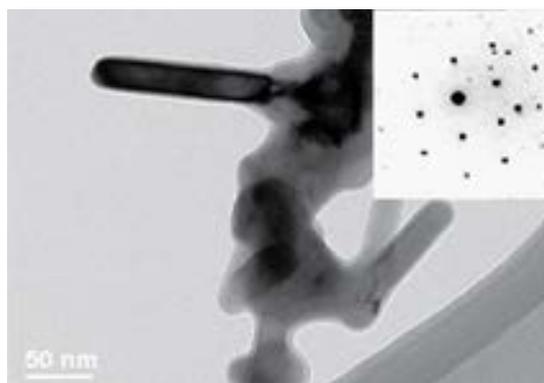
One student took part in this research.

Results Obtained:

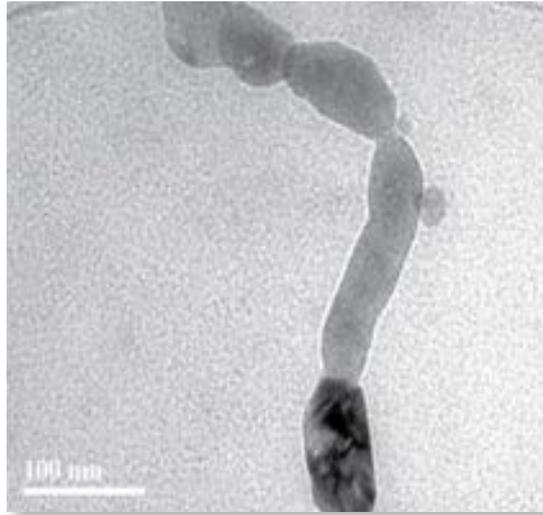
- Optimizing the conditions for electrospinning nanofibers based on PAAc solutions containing metal salts.
- Finding the pyrolysis conditions that could be used for producing YBCO from the nanofibers.
- Characterizing the resulting YBCO.
- A manuscript based on these results has been published in the Journal of Materials Science (Journal of Materials Science 2008, 42, 1664).



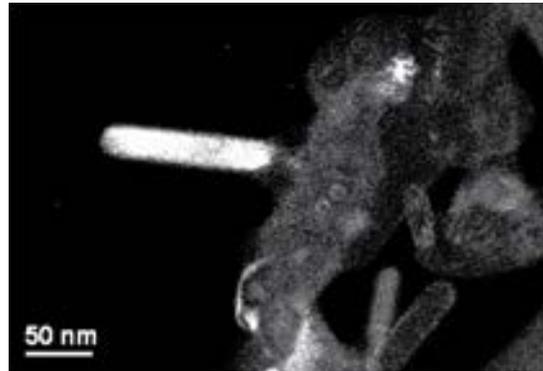
Transmission electron microscopy (TEM) bright field (BF) micrograph of a pyrolyzed nanofiber. Inset: selected area electron diffraction pattern (SAEDP).



TEM BF micrograph of a pyrolyzed nanofiber. Inset: SAEDP of a single nanofiber consistent with the [4,5,-2] zone axis for orthorhombic YBCO.



(3) TEM BF micrograph of a pyrolyzed nanofiber.



(4) TEM dark field micrograph of the pyrolyzed nanofiber in (2) taken from a single diffraction spot. The bright rod-like structure is a single crystal.

Quantum computing with Endohedral fullerenes on surfaces

Start Year ▶ 2006

Principal Investigators: Prof. Eli Kolodney - Schulich faculty of Chemistry, Technion
Dr. Aharon Blank - Schulich faculty of Chemistry, Technion

The goal of the research was to look into the possibility of employing high sensitivity electron spin resonance (ESR) "induction" detection and imaging methods, combined with (ion bombardment based) atomic implantation inside C_{60} molecule, in favor of spin-based quantum computing. One aspect of the work was to examine methods for generating isolated unpaired electron spins on surface, in the form of $N@C_{60}$ (Nitrogen atom inside a C_{60} molecule). A complementary effort in the research was to develop the new tool of ESR microscopy in order to enable the detection and manipulation of those spins. In that respect the original goal was to achieve a detection capability of ~100-1000 spins with spatial resolution that is better than 100 nm.

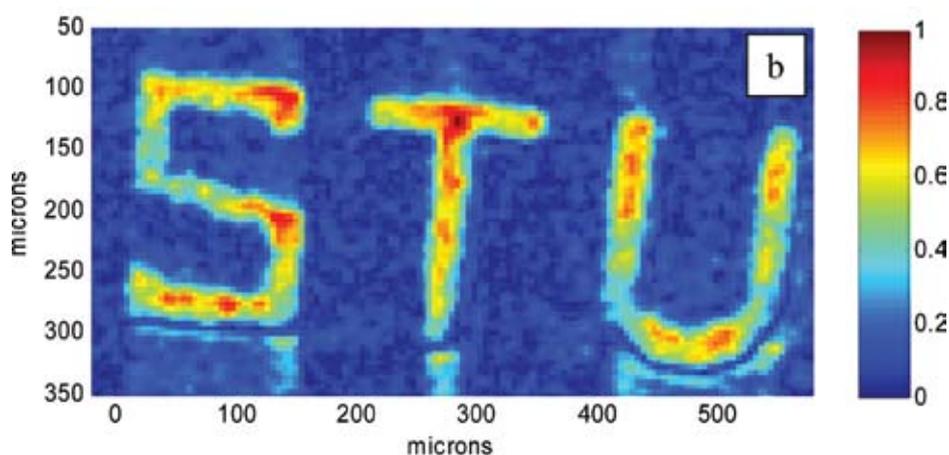
During the research we produced a variety of $N@C_{60}$ samples on a surface using ion implantation method. In a parallel effort an enriched sample of $N@C_{60}$ was imaged at high resolution by our ESR microscope, at a resolution of a few microns (see image below).

We used a variety of facilities in the micro/nano electronic center such as photolithography, plasma etching and SEM microscope.

Part of the research was described in a publication: Suhovoy E., and Blank A. "High Resolution ESR Imaging of $N@C_{60}$ Radicals on Surface", Israel Journal of Chemistry, 48 (2008) 45-51.

The funding of this research was used to provide fellowship to a student at the Blank group.

The lab of A. Blank continues the pursuit of high resolution ESR of solid samples at low temperature, aiming at achieving much better spin sensitivity and image resolution.



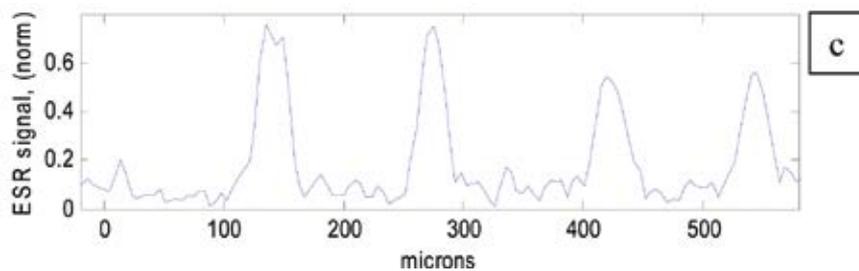


Figure caption:

Optical and ESR images of $N@C_{60}:C_{60}$ powder inserted into photolithography-prepared letters. (a) Optical image showing the powder inside the patterns (the lithography thickness is $120\ \mu\text{m}$). (b) ESR 2D image of the pattern. Here the gradient X-axis of the imaging probe is along the image y-axis (the sample was inserted to the probe with the words written along the Y gradient axis). (c) 1D cut of the ESR image along in the image x-axis (at $y = 225$ microns), showing the level of sharpness of the patterns imaged.

Magnetic quantum tunneling in Fe_8 with excited nuclei

Start Year ▶ 2006

Principal Investigators: Prof. Amit Keren - Physics, Technion
Prof. Menahem Kafory - Chemistry, Technion

The importance of nuclei to the quantum tunneling of magnetization (QTM) and to the relaxation of the magnetization in the molecular magnet Fe_8 was demonstrated experimentally by many authors. They compared the tunnel splitting Δ and relaxation rate of the standard Fe_8 sample with a deuterated sample. The enrichment with deuterium causes a decrease in Δ and in the relaxation time, in agreement with the decrease in the hyperfine field. However, when isotopes are exchanged not only does the hyperfine field that the molecule experiences vary but also the nuclear spin-spin relaxation rate T_2 changes. Both quantities might be important for the nuclear-assisted tunneling process, but isotope substitution cannot distinguish which quantity is more relevant. Therefore, it has not yet been established experimentally how exactly nuclei impact the tunneling process.

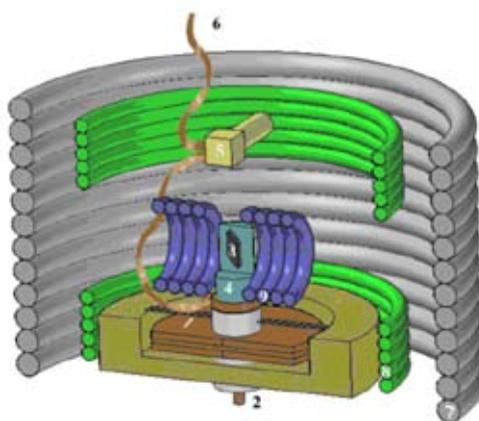


Figure 1: Cross sectional view of the Faraday balance with: (1) movable plate of the capacitor, (2) screw for capacitor's fixed plate height adjustment, (3) sample, (4) PCTFE, (5) gold plated casing of the thermometer, (6) thermal link to the DR mixing chamber, (7) main coil, (8) gradient coils, (9) RF coil.

The experiment reported here aims at distinguishing between the contribution of the hyperfine field and that of T_2 . We present magnetization measurements of Fe_8 during a field sweep while transmitting a radio frequency (RF) on a proton resonance. This transmission raises the proton temperature without changing the electron temperature due to the enormous proton T_1 . Consequently the proton's T_2 varies with no modification to the hyperfine field.

For this experiment, a Faraday force magnetometer shown in Fig. 1 was constructed inside the inner vacuum chamber (IVC) of a dilution refrigerator (DR), following the design of Sakakibara et al. with the addition of an RF coil.¹ This magnetometer is suitable for measurements in high fields and at sub-Kelvin temperatures with no metallic parts near the sample. This is important because we want to minimize the warming of metallic parts with the RF. The DR is equipped with a main superconducting magnet that produces the field H , and two oppositely wound superconducting magnets that produce a field gradient.

The sample is mounted on a small load-sensing device made of two parallel plates, which form a variable capacitor. The movable plate is suspended by two pairs of orthogonal crossed 0.2 mm diameter phosphor bronze wires attached to it with epoxy. The static lower plate is mounted on an epoxy screw for adjusting the initial capacity C_0 . When the sample is subjected to a spatially varying magnetic field B , it will experience a force. This force is balanced by the wires. The displacement of the plate is proportional to F and can be detected as a capacitance C change. The total capacitance response is then given by where A is a constant that depends on the elastic properties of the wires.

The results of measurements with and without the RF are summarized in Figure 2. We concentrate on the first magnetization jump which is closest to the time of irradiation. The solid lines denote sweeps with RF and the dotted lines denote sweeps without RF. We

repeated these runs several times and found that within our experimental resolution between individual sweeps, no effect of the RF can be detected.
Oren Shafir, PhD student, took part in this research

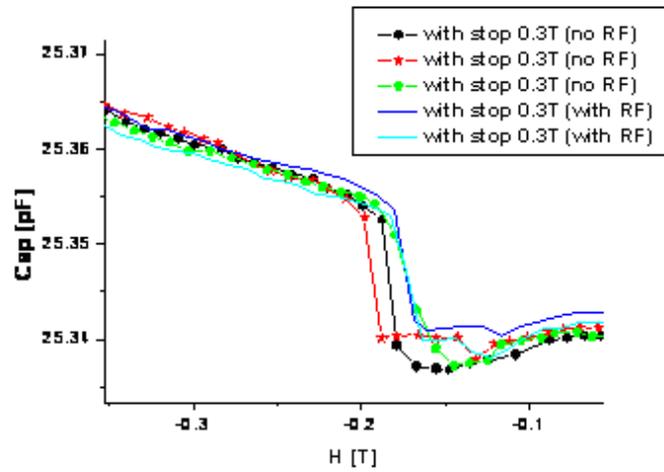


Figure 2: Capacitance (=Magnetization) measurement with and without RF. We saturate the nuclei and see no effect.

¹ Sakakibara, T., Mitamura, H., Tayama, T., Amatusuka, H. Jpn. J. Appl. Phys. 33, 5067 (1994).

Setting a Corner Stone for Nano-Swarms

Start Year ▶ 2006

Principal Investigators: Prof. Alfred M. Bruckstein - Computer Science, Technion
Prof. Elon Rimon - Mechanical Engineering, Technion

The ultimate goal is to give the nano-swarms the basic capabilities which we have given to ant-robots, such as motion-planning, covering, cleaning, gathering, and self-assembly. Armed with these capabilities, nano-swarms will be able to perform many useful and exciting tasks. For example, nano-swarms will patrol a human's blood vessels and maintain and repair arteries, just like ants maintain their tunnels; parts of a swarm will self-assemble into artificial blood-clots and tissues; nano-swarms will patrol the human-body and selectively target and attack spreading tumors, perhaps like our fire-fighting robots; Using chemotaxis and sensing, selective drug delivery will be possible, with local control of concentration and release by the individual nano-robots. There is a lot of preliminary work to be done in order to enable proper algorithm research and development for nano-swarms. We hope that our preliminary research will indeed form the basis for a longer-term research program, and eventually make a key contribution to nano-robotic research in general.

Most current effort in nano-robotics research and development is on the technological aspects of designing and making the actual robots. We feel that the algorithmic and control aspects of nano-robotics deserve more attention and a more consistent research framework. Furthermore, from our experience with so called macro-scale distributed ant-robotic systems, consisting of many simple and weak individual mobile robotic agents, we believe that the ant-robotic paradigm is the most appropriate for nano-robotics, due to the large conceptual similarity between the fields. Little has been done so far to research nano-robotic algorithms in general, and apply ant-robotic ideas and results to nano-swarms in particular. These are the main goals of this research: Build plausible models of future swarms of nano-robots, study their capabilities, and apply results from our expertise in motion-planning algorithms and ant-robotic systems to these models. Ultimately, when nano-robot manufacturing will mature, these algorithmic results will have a key role in determining the actual practical capabilities of nano-robots, and the applications they can serve.

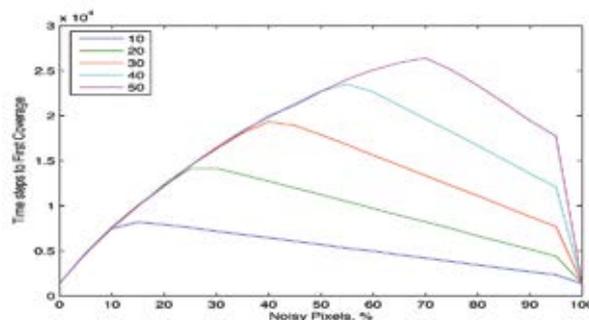
Results obtained so far:

The main results so far are the formulation of a challenging nano-robotics problem, concerned with modeling and development of novel energy efficient locomotion techniques in liquid environments. We believe that the feasibility research supported by RBNI has been extremely helpful in allowing us to make a thorough investigation into the missing pieces that would enable development of truly functional nano-robot devices.

3 graduate students took part in the research.

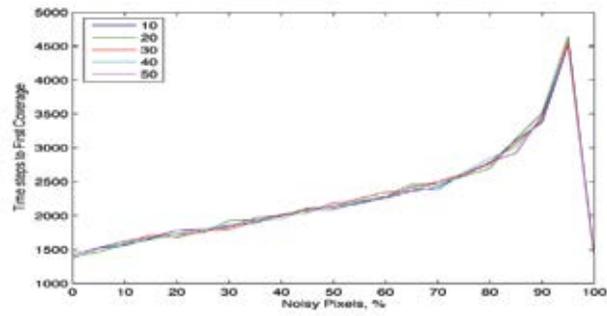
Research publications:

Oshrovich E., Yanovski V., Wagner I.A., Bruckstein A.M., "ROBUST AND EFFICIENT COVERING OF UNKNOWN CONTINUOUS DOMAINS WITH SIMPLE, ANT-LIKE A(GE)NTS", The International Journal of Robotics Research, Vol. 27(7), 815--832, 2008.

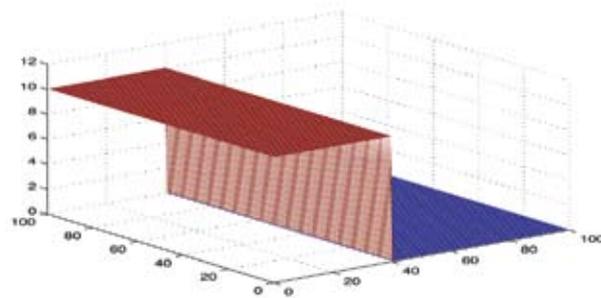


(b) Cover time in presence of initial pheromone profile 3

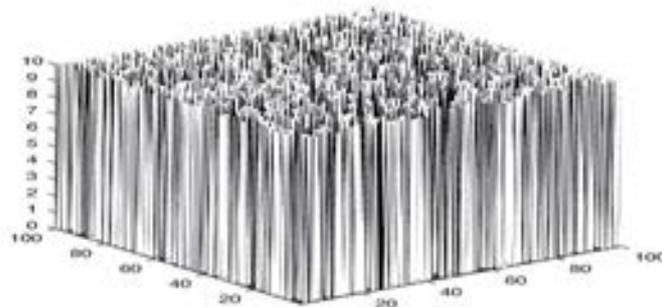
MAW time in presence of initial pheromone 3



(b) Cover time in presence of initial pheromone profile 2
MAW time in presence of initial pheromone profile 2



(a) Example of initial pheromone profile 3



(a) Example of initial pheromone profile 2

Preparation and Characterization of Smart Core-shell Nanoparticles

Start Year ▶ 2006

Principal Investigators: Prof. Dganit Danino - Biotechnology and Food Engineering, Technion
 Prof. Dr. Walter Richtering - Physical Chemistry, RWTH, Aachen
 Dr. Thomas Eckert - Physical Chemistry, RWTH, Aachen

Smart microgels attract much attention because of their versatility to many fields as, e.g., drug delivery applications, catalysts, and chemical separation processes. Very promising systems are based on cross linked PNIPAM- PNIPMAM. Core-shell (CS) microgels composed of these two temperature-sensitive polymers exhibit two volume phase transitions at temperatures assigned to the LCSTs of core and shell, respectively. With increasing temperature from below the core's LCST to a temperature in between the LCSTs of the two polymers, the solvent property of water changes from good to poor for the core, while it is still good for the shell. The polymer-polymer interaction becomes more important for the chains in the core and it collapses. When the temperature is further increased above the shell's LCST, the shell collapses in a second step.

CS microgels of different compositions were synthesized and characterized by scattering techniques at the RWTH, and a new general form factor model was employed for describing their morphology. At the Technion, we studied these systems by direct-imaging cryo-transmission electron microscopy (cryo-TEM). This method is very powerful, and provides direct, high-resolution details on the morphology and structure of the nanoparticles, that relate to their state in the bulk. Because of the very similar composition of core and shell, and therefore the relatively low contrast between them, it was under some conditions difficult to resolve these two domains. Thus, in order to determine the dimensions of the core and shell regions we additionally examined the core itself. To investigate the effect of temperature, core and CS samples were studied at the fully swollen (at 25°C), fully collapsed (at 50°C), and partially swollen (at 39°C) conditions. Samples were held in the controlled-environment vitrification system at the required temperature, vitrified in liquid ethane, kept in liquid nitrogen, and then examined in a Tecnai 12 G² TEM at cryogenic temperatures using low dose imaging.

Indeed, the temperature dependent size and density of the core microgel in the collapsed and swollen states were directly resolved by this technique. In the swollen state the size obtained from the regions with high contrast is smaller as compared to the scattering. However, the distance between the centers of neighboring particles fits to the total particle size obtained by scattering. That could indicate that the fuzzy corona of the particles which controls the distance between particles, is difficult to detect. Cryo-TEM micrographs from the core-shell microgel in the fully collapsed and fully swollen states agrees well to the scattering. At 25°C the particles seem to have a sharper surface as compared to the pure core. The increased contrast and apparently sharper surface of the core-shell microgels at 25°C as compared to the naked core at 25°C is due to the higher segment density. The size of the core-shell microgel is not much bigger than the size of the original core; however, the total mass is much higher (the mass of the shell is 2.5 times the mass of the core). As the shell restricts the core swelling, the density in the outer regions is higher as compared to the core. This correlates nicely with the SANS results.

In summary, we successfully prepared and investigated multisensitive, "smart" core-shell microgels and demonstrated for the first time that the shell restricted swelling of core-shell microgels can be visualized by direct imaging cryo-TEM. The direct high-resolution data we obtained from these multisensitive nanoparticles can directly be compared with density profiles obtained from scattering. This work can be extended to microgels with more complex structure. At the RWTH we are preparing new systems that are sensitive to temperature and pH and the properties of which can be tailored via the adsorption of polyelectrolyte multilayers. These nanostructures will be studied at the Technion by cryo-TEM, and cryo-SEM. In addition we plan to evaluate the use of microgels as remote controllable nanocarriers for controlled release. Based on the experimental results obtained in this cooperation, we are currently preparing a joint publication and discussing various options to obtain funding for a collaborative project.

Table 1: Summary of the parameters describing the structure of the core and the core-shell microgel particles as obtained from SANS.

sample	T °C	Φ_{core} %	W_{core} nm	σ_{in} nm	Φ_{shell} %	W_{shell} nm	σ_{out} nm	σ_{poly} %	R_{SANS} nm	R_h nm
Core	39								48	51
	25		43						120	127
CS-5/2.50	50	51.3	43.7	2.1	53.4	20.3	2.0	8.0	72	73
	39	31.8	54.1	5.8	9.7	15.8	8.9	6.9	99	110
	25	9.6	64.2	10.2	7.4	3.1	24.5	11.0	137	145

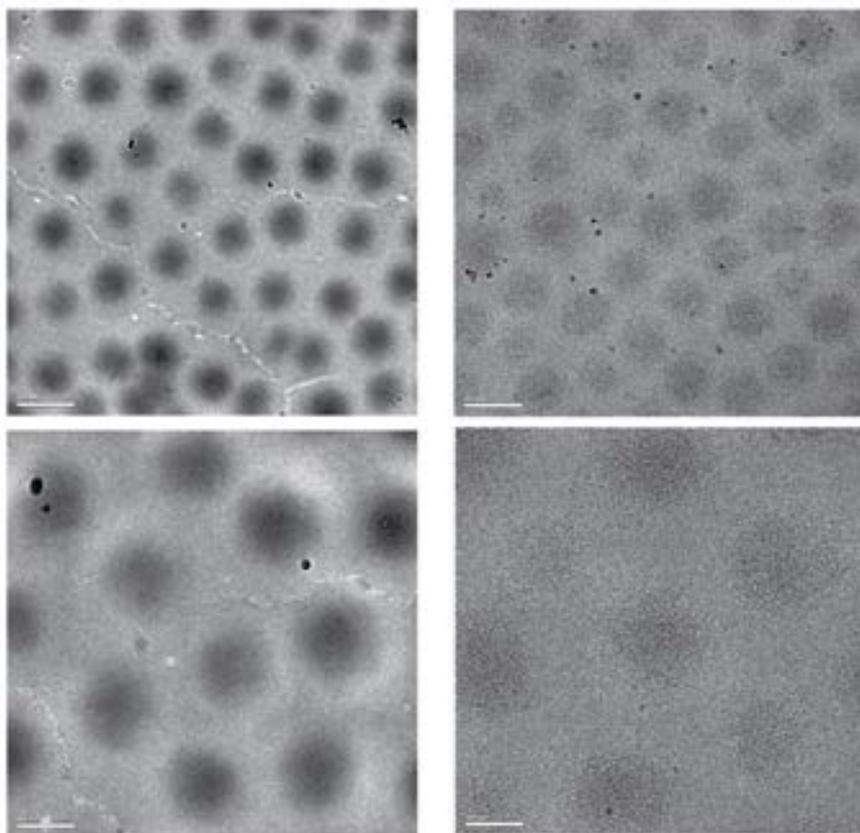


Figure 1: Cryo-TEM micrographs of the core microgel at 50 (left) and 25°C (right). Scale bars represent 200 nm in the upper pictures and 100nm in the lower pictures.

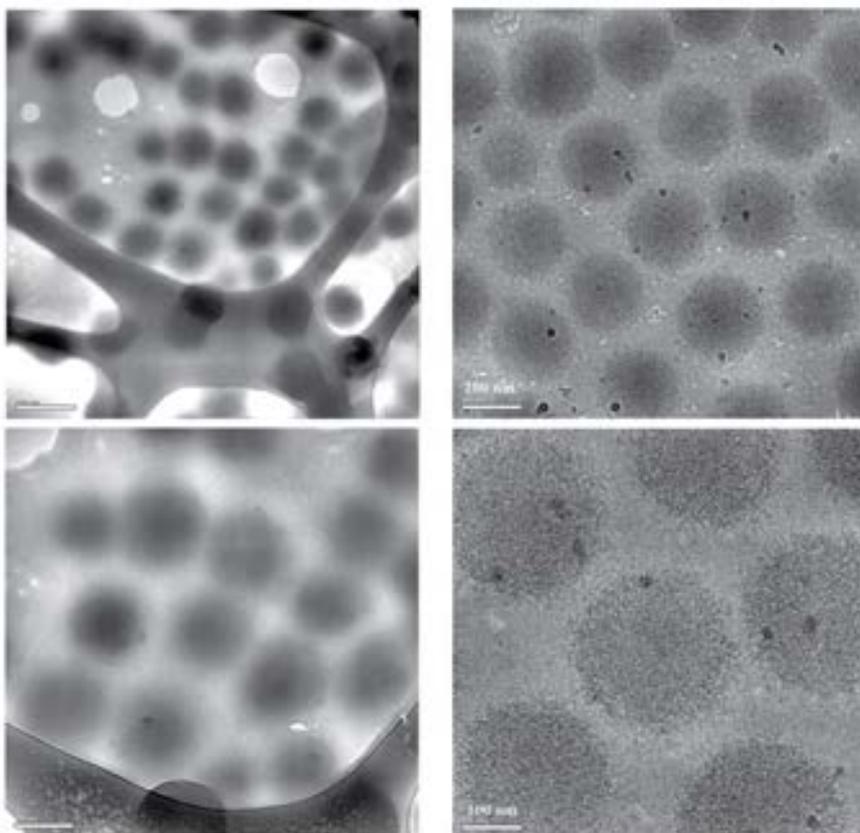


Figure 2: Cryo-TEM micrographs of the core-shell microgel at 50 (left) and 25°C (right). Scale bars represent 200nm in the upper pictures and 100nm in the lower pictures.

Novel mixed ionic electronic conductors based on nanostructured metal oxide superlattices

Start Year ▶ 2006

Principal Investigators: Dr. Avner Rothschild - Materials Engineering, Technion
Dr. Roger A. De Souza - Institute of Physical Chemistry, RWTH Aachen

This research aims at exploring an innovative approach to control the ionic transport properties of multilayer structures of SrTiO_3 and its derivatives. Towards this end we prepared ceramic pellets of Fe-doped SrTiO_3 and used them as targets for pulsed laser deposition (PLD) of thin films (Figure 1).

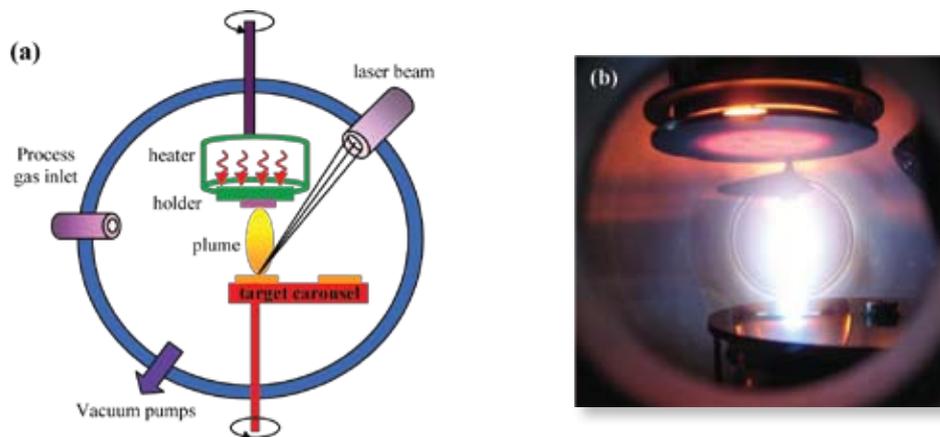


Figure 1. Schematic diagram of the PLD chamber (a) and a picture of the plume (b).

To achieve epitaxial growth the films were deposited on single crystal (001) SrTiO_3 substrates. As-received polished substrates displayed mixed surface termination comprising SrO and TiO_2 layers (Figure 2a). Immersion in buffered HF (BHF) solution selectively etched the SrO top monolayer, resulting in TiO_2 terminated terraces (Figure 2b). High temperature annealing (950°C , 2 h) resulted in ~ 200 nm wide smooth terraces with TiO_2 surface termination (Figure 2c), providing optimal conditions for epitaxial growth.

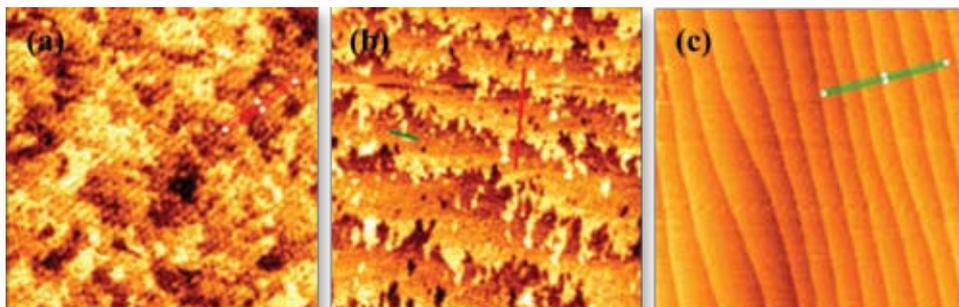


Figure 2. AFM images of SrTiO_3 (100) single crystal substrates in the as-received (polished) state (a), after BHF treatment (b), and after annealing (c). Scan area = $1 \mu\text{m} \times 1 \mu\text{m}$.

The film growth mechanism is sensitive to deposition conditions such as laser energy fluency, substrate temperature, oxygen pressure, and target to substrate distance. Figure 3 shows AFM images of the surface morphology of SrTiO_3 films grown under different conditions. The surface morphology in Figure (f) resembles very much that of the substrates (cf. Figure 2 c), indicating high quality epitaxial growth. Therefore, the respective deposition conditions were found to be the right conditions for our system. The film growth rate obtained under these conditions is about 1 nm for 20 laser pulses, as determined by film thickness measurements using an alpha-step.

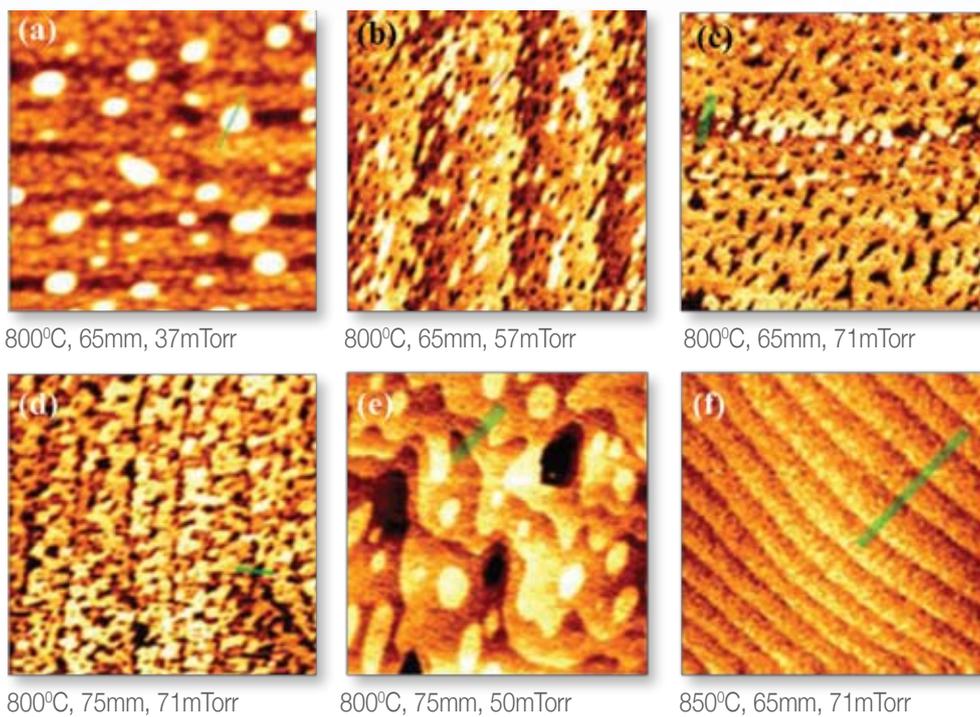


Figure 3. AFM images of SrTiO₃ films deposited on SrTiO₃ (001) substrates under different conditions as indicated below the AFM images. The laser energy fluency was 1 J/cm². Scan area = 1 μm × 1 μm.

The microstructure of our best quality films (as determined by preliminary screening using AFM) was examined using high-resolution TEM. An exemplary lattice image of a 5 nm SrFeO₃ film grown on SrTiO₃ (001) substrate is shown in Figure 4. The image clearly shows perfect epitaxial growth with atomically sharp interface between film and substrate. This demonstrates that we can grow high quality epitaxial films which is critical for achieving our research goals. Our next step is to extend this ability to multilayer structures.

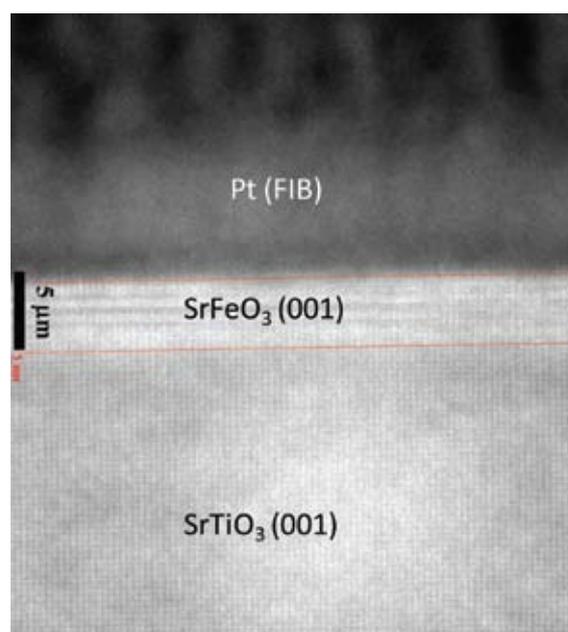


Figure 4. High resolution TEM lattice image of a 5 nm thick SrFeO₃ film grown epitaxial on a SrTiO₃ (001) substrate.

The free volume of grain boundaries and its effect on microstructural stability of nanocrystals

Start Year ▶ 2006

Principal Investigators: Prof. E. Rabkin - Materials Engineering, Technion
 Prof. Dr. G. Gottstein - Director, Institut für Metallkunde und Metallphysik, RWTH Aachen

The main goal of this project was developing a universal model for the grain growth in nanocrystals that can predict their stability limit and describe the kinetics of grain growth.

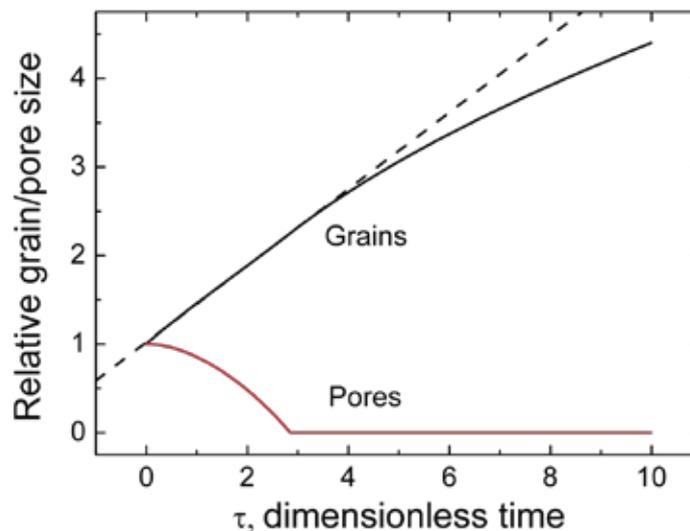
We considered a grain growth in two-dimensional nanocrystalline material with mobile pores at the grain boundary triple junctions. The source of this porosity may be either an incomplete sintering (residual porosity), or the free volume released by the grain boundaries during initial stages of grain growth. The kinetics of grain and pore growth were determined under the assumption that pore sintering and pore mobility are controlled by grain boundary and surface diffusion, respectively. It was shown that a nanocrystal can achieve full density in the course of grain growth only when the initial pore size is below a certain critical value which depends on kinetic parameters, interfacial energies, and initial grain size. Larger pores grow without limits with the growing grains, and the corresponding grain growth exponent depends on kinetic parameters and lies between 2 and 4. It is shown that for a nanocrystal with subcritical pores the average grain size increases linearly with time during the initial stages of growth, in agreement with recent experimental data on grain growth in thin Cu films and in bulk nanocrystalline Fe.

Publications:

L. Klinger, E. Rabkin, L.S. Shvindlerman, G. Gottstein

Grain growth in porous two-dimensional nanocrystalline materials

J. Mater. Sci. 43 (2008) 5068-5075



Typical dependence of the average grain and pore sizes of the nanocrystalline material on annealing time. Initial linear grain growth is followed by a parabolic one after the pores disappear.

Nanodomains as catalytic substrates for non-enzymatic synthesis of RNA from pre-biotic reactants

Principal Investigators: Prof. Yaron Paz - Chemical Engineering, Technion
Prof. Sima Yaron - Biotechnology and Food Engineering, Technion

Start Year ▶ 2007

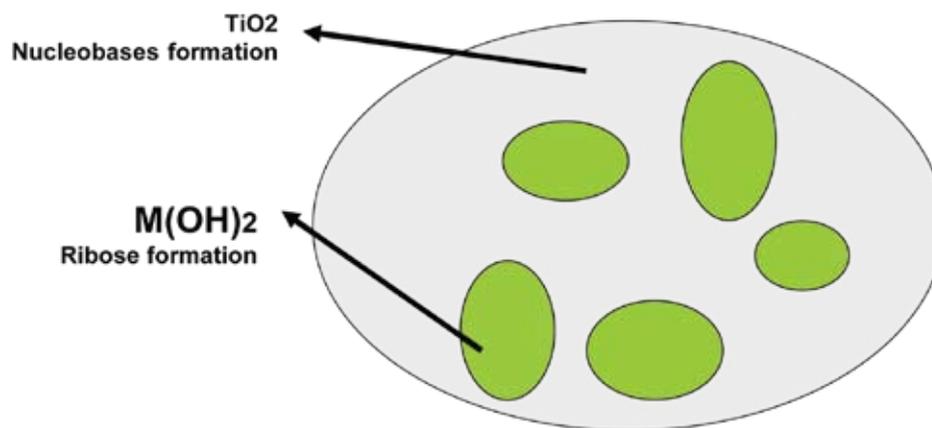
The objective of this proposal is to study a possible non-enzymatic route towards RNA formation from pre-biotic substances, based on surface-catalyzed nucleotide synthesis.

Within the framework of the RNA world hypothesis, a possible non-enzymatic catalytic route towards RNA formation is under study. The basic concept is to use composite particles containing nano-domains of TiO_2 and divalent metal hydroxides. The titanium dioxide will be responsible for the photo assisted synthesis of the nucleobases whereas the hydroxide domains will catalyze the ribose synthesis. It is expected that the short distance between the nucleobases pool and ribose synthesis location (together with adsorbed phosphate) will facilitate the formation of nucleotides, or even oligonucleotides.

This is a revolutionary, yet very difficult program to carry out, a sort of high risk- high gain project. Within this project, methods for quantification of the various building blocks of nucleotides were optimized, and the adsorption of these building blocks onto the photocatalyst was studied, thus paving the way for the formation of the composite particles by a high pressure reaction.

The length of the contact lines between the two components of the hybrid particles is expected to be crucial. Unfortunately, there is no easy way to measure the length of contact lines in an ensemble of composite particles. It is for this reason that we had to work on developing means for approximating it. The work on both the main project and its spin-off method for contact line estimation are still underway.

The work was done mainly by senior undergraduate students. We are in search for graduate students, capable of performing this complex project.



A scheme of a "nucleotide nanofactory" made of divalent metal hydroxide islands on a titanium dioxide particle.

A hydrogel-based nerve regeneration conduit with nano-scale feature control

Start Year ▶ 2007

Principal Investigators: Dr. Shy Shoham - Biomedical Engineering, Technion
Prof. Dror Seliktar - Biomedical Engineering, Technion

The purpose of this study was to explore a novel two-photon lithography technique for creating nerve guidance channels in PEGylated protein hydrogels for functional nerve regeneration in peripheral nervous system injuries. We developed the two-photon lithography system and validated the protocol for directing point-specific photoprinting of geometric landscapes at sub-micro spatial resolution. The photoprinting is accomplished in a light sensitive biocompatible polymeric precursor solution which upon light activation initiates a polymerization reaction to form a hydrogel matrix. The hydrogels are prepared from a biosynthetic biomaterial composition which is ideally suitable for nerve regeneration. The precursor of the hydrogel contains a biological backbone that is coupled to a synthetic polymer cross-linker called poly(ethylene glycol) (PEG).

A non-toxic photo-sensitive reaction is used to polymerize the precursor into the hydrogel matrix in the presence of cells and tissues. We show how PEGylated protein hydrogels made from fibrinogen and collagen are able to encourage outgrowth of neuronal and non-neuronal cells from explants of dorsal root ganglion (DRG) into the hydrogel matrix. The DRG experiments are a model system for testing unidirectional axonal guidance through channels inscribed into the hydrogel by the two-photon lithography system. In preliminary data, DRG cells are seen migrating out from the DRG and into channels inscribed into the hydrogel matrix. The proposed work was built on the preliminary results to demonstrate the importance of 3-D spatial geometric resolution of the lithographic system in guiding nerve cells towards functional regeneration. A further aim of the project was to characterize the functional regeneration of axonal outgrowth in the nerve guidance channels of the hydrogel using a unique imaging system developed in our laboratories.

Results obtained so far:

We have designed and assembled a custom two-photon photolithography system for this project (using an inverted design suitable for biological samples). We then developed custom software which breaks 3-D SolidWorks™ computer model into layer by layer landscape images and then into microscopic photo-excitation patterns. We were able to demonstrate submicron scale accuracy in excitation geography in albumin hydrogels.

Publications:

Sarig-Nadir O, Livnat N, Zajdman R, Shoham S and Seliktar D, Laser photoablation of guidance microchannels into hydrogels directs cell growth in 3-D, *Biophysical Journal* 96, 4743-4752 (2009).

Published conference proceedings:

Livnat N, Sarig-Nadir O, Seliktar D & Shoham S, Three-dimensional guidance of DRG neurite outgrowth using multi-photon photoablation, Proc. IEEE 4th International Neural Engineering Conference, Antalya, Turkey (2009).

Livnat N, Sarig-Nadir O, Zajdman R, Seliktar D & Shoham S, A Hydrogel-Based Nerve Regeneration Conduit with Sub-Micrometer Feature Control, IEEE 3rd International Neural Engineering Conference, Kohala Coast, Hawaii (2007).

Students who took part in the research:

Offra Sarig-Nadir
Noga Livnat
Ruthy Zajdman

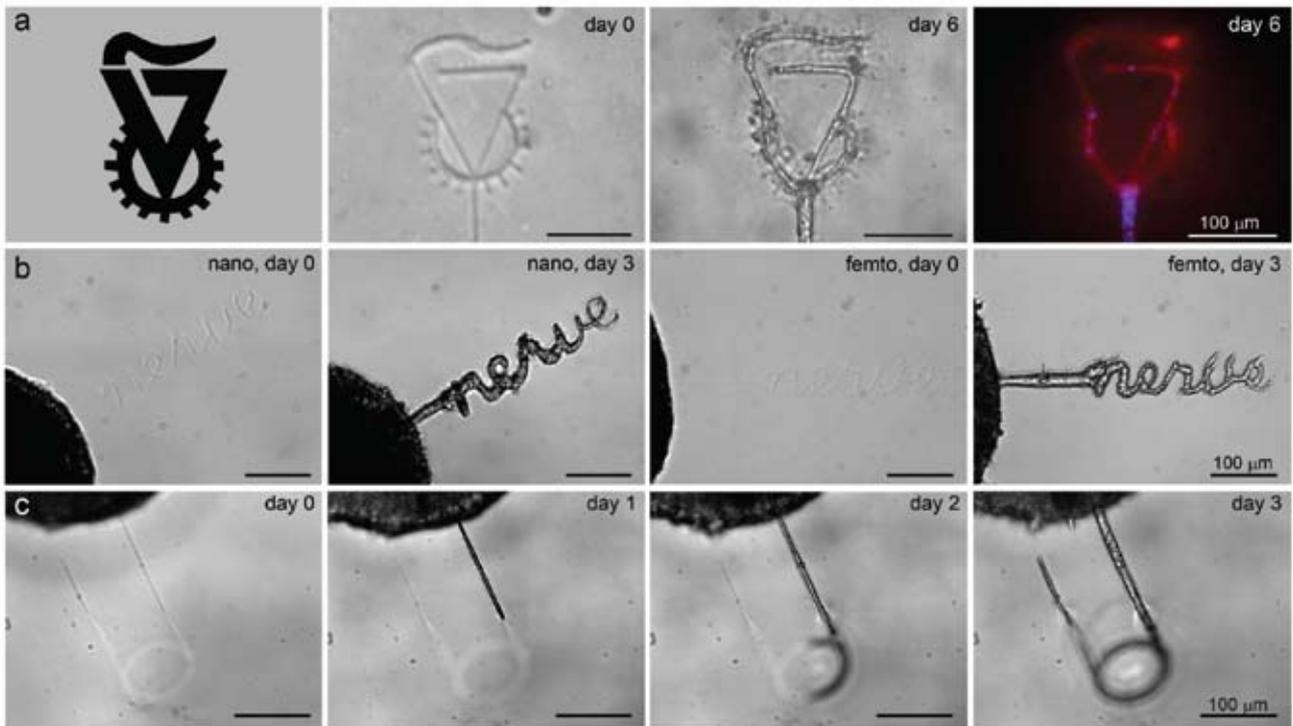


Figure: Directed DRG cell outgrowth in complex patterns of microchannels inscribed within hydrogels. a, Inscription of the shape of the Technion University symbol is shown in a Hydrogel-B construct before and after six days of DRG cells invasion into the microchannels; immunolabeling of the DRG cells with BIII-tubulin (neural marker, red) and DAPI (nuclei, blue) is shown (scale bar=100 μm). b, An inscription of the word "nerve" is shown in a Hydrogel-C construct using the nanosecond (left) and femtosecond (right) laser systems, with the DRG cells invading on day 3 (scale bar=100 μm). c, A 3-D pattern of a microchannel is shown in a Hydrogel-C construct (nanosecond laser system). DRG cell invasion into the microchannel is shown on day 1, day 2 and day 3, where cells traverse the focal plane as a function of the Z axis position of the microchannel inside the hydrogel (scale bar=100 μm).

Molecular-motor mediated bio-microrheology

Start Year ▶ 2007

Principal Investigators: Dr. Daphne Weihs - Biomedical Engineering, Technion
Dr. Alex Leshansky - Chemical Engineering, Technion

The main aim of this project is to develop a tool for active and passive microrheological studies in living cells, without applying external forces. Correlating the propulsion force exerted by the molecular motors on their cargo to the resulting displacement speed can provide information on the material response of the system. The living cell is a complex system, hence, first steps toward developing the probing tool should be simplified and tested in vitro to determine critical parameters that will be needed in the future. Here, the in vitro phase is divided to two parts: the first one is the assembly of fluorescently labeled microtubules on a charged surface and the second is the motility assays, done by using the kinesin motor proteins bound to labeled nano-particles. The in vitro phase will allow us to determine the parameters controlling transport of cargo within the intracellular environment.

Molecular motor proteins mediate intracellular transport of organelles and vesicles, which is a vital process for cell function and viability. The molecular mechanism of motor protein mediated transport has been studied extensively; specifically, the biochemical interactions, directionality, and speed. However, little is known about the interactions of the cargo with its environment which influence the mechanics of cellular compartments. Those mechanics may be evaluated by the medium rheological properties as measured by tracer motion. In addition, molecular motors apply directed forces on cargo as part of the normal function of the cell. Hence, molecular motor transport can be exploited as a very precise and controlled mechanism of directed displacement in the cell; that can provide details on the local rheology and molecular motor activity and motion characteristics. To determine the effects of environment rheology on molecular-motor mediated transport of cargo, we have used an in vitro system of reconstituted microtubules and molecular motor extracts. We have changed the surrounding fluid rheology and have begun to evaluate the effects on particle transport.

Results obtained so far:

Microtubule polymerization: The optimal conditions for microtubule polymerization were obtained by series of tests of different dilutions, component concentrations, and polymerization time to determine the optimal density of microtubule polymers, average length of 1-2 μm . We obtained excellent results, separate and nearly straight microtubules attached to the glass substrate (see image) and ready to be used for the motor protein motility assays. The system was stable for at least 4 hours at room temperature.

Cell protein-extract motility assay: A general motility assay was performed as control by replacing the pure kinesin motor- protein by protein extract from 293T cells line incubated with florescent particles. We employed this approach to test the following points:

- System stability and behavior in the presence of the whole extract components
- The ability of the fluorescent particles to adsorb the relevant proteins
- Microtubule ability to bind the motor proteins adsorbed to the particles
- Optimize tracking of particles adsorbed on the motor proteins, on the microtubules

After confirming the presence of polymerized microtubules the microscope sulfate-modified particles were observed in a different wavelength of light. Random Brownian movement of the unattached particles, suspended in the liquid buffer was observed, while particles that were attached to microtubules exhibited directed motion combined with restricted-diffusion. The motion along microtubules was intermittent and varying in directionality. That was expected due to the statistical adsorption of the all the soluble extract to the particle including all native motor-proteins that are directionally specific either to the plus or the minus end of the microtubule. Thus, particles were intermittently transported to the plus or minus ends of the microtubule. We were as of yet unsuccessful in our attempts to purify only kinesin motor proteins; hence we have purchased the motor unit from a vendor, which is currently used in our experiments.

The work is being continued in the lab to obtain extra data and allow an external grant to be written. We are currently employing a bought motor protein to run the tracking experiments.

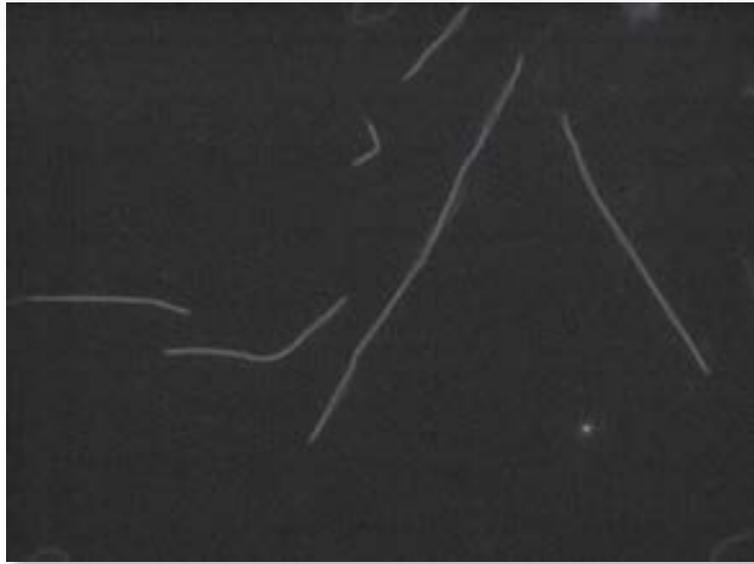


Figure: Single microtubules grown linearly on a glass coverslide. Those microtubules can serve as tracks for molecular motor transport studies.

Nonlinear dynamics, internal resonances and complexity in arrays of nanomechanical oscillators

Start Year ▶ 2007

Principal Investigators: Prof. Oded Gottlieb - Mechanical Engineering, Technion
Prof. Eyal Buks - Electrical Engineering, Technion

The scientific goal of this research is to investigate the complex nonlinear dynamics of nano-resonator arrays and to provide a quantitative comparison between a deduced continuum theory and a controlled set of experiments. The specific objectives defined include: i) array manufacture, ii) derivation of an array dynamical system based on nonlinear continuum mechanics theory, iii) calibration experiments to yield the mechanical properties required for the theoretical model, iv) validation of system response via asymptotic and numerical methods, and v) derivation of the system bifurcation structure to examine thresholds of complex response theoretically and experimentally.

Arrays of nanomechanical resonators are employed as smart actuators and sensors and may allow a major enhancement of imaging speed in atomic force microscopy. To allow such advancement it is crucial to understand the dynamics of such arrays in both the linear and nonlinear regimes of operation. Our mechanical resonators, which are fabricated using e-beam lithography, have typical dimensions in the nm scale. In many cases the smallest feature size is comparable or smaller than microscopic length scales of the bulk material such as grain size or average distance between defects. Modeling the dynamics of such arrays is highly challenging due to the strong coupling between the resonators and the relatively low damping in a vacuum and even ultra-high vacuum environment. In this research program, we study the nonlinear dynamics of such arrays both experimentally and theoretically in order to achieve a better qualitative and quantitative description of their dynamics.

Results to date:

1. Design and manufacturing of a 3 element array (Figure 1-top) and a 40 element array (Figure 1-bottom) where each element consists of a mixture of Palladium-Gold (170 nm) and Chrome (10 nm layer).
2. Derivation of a nonlinear continuum mechanics initial-boundary-value problem (IBVP) for the parametrically excited array which includes visco-elastic elements incorporating a pre-tensioned Voigt-Kelvin constitutive law. The IBVP includes coupled fields defined by partial differential equations and boundary conditions for each element in the array. Thus, each element in the array includes stiffness terms due to pretension and bending, and visco-elastic damping. The coupling between the elements is due to an electrodynamic nearest neighbor parametric excitation and the nonlinear terms are governed by time dependent coefficients that are obtained after integration of the longitudinal equation of motion employing fixed boundary conditions. We note that for negligible inertia, the IBVP does not exhibit any linear visco-elastic damping content.
3. Reduction of the spatio-temporal IBVP to a multi-degree-of-freedom modal dynamical system was enabled by employing an assumed mode Galerkin assumption near the principle parametric resonance. The equations of motion of the dynamical system are governed by linear and cubic stiffness that are a function of pretension and bending, linear and cubic visco-elastic damping, and a linear nearest neighbor form of parametric excitation. We note that both nonlinear stiffness and damping in the modal system are dependent only on the geometry and elastic properties of the IBVP. A simple test of model validity is to estimate the unknown residual stress in the system from the measured natural frequencies, and to determine whether its value is less than the documented yield stress for the array material.
4. Calibration and nonlinear parameter estimation of a single element (in the 3 element array) subject to both external (Figure 2) and parametric excitation. The measured primary resonance frequency (103.85 kHz) enables estimation of an initial tension (26) based on a computed (law of mixtures) for the element density (17g/cc) and elastic modulus (96GPa). Thus, the nondimensional linear damping, nonlinear stiffness and damping parameters in the modal dynamical system can be shown to be within the domain of validity for a theoretical asymptotic multiple-scale analysis.
5. Asymptotic analysis of the theoretical three element system reveals co-existence of coupled periodic out-of-phase and in-phase solutions (Figure 4). However, while the experimental analysis of the corresponding array yields a similar response structure, the resulting frequency response (Figure 3) depicts a non-smooth response which is not explained by the theoretical model. Investigation of the experimental array response, reveal several additional phenomena that may be responsible for spurious self-excitation of the individual elements by the optical measurement system (Figure 5). These issues are currently under investigation in both 3 and 40 element arrays.

List of Postdocs and Graduate Students who took part in the research:

Ashok Pandey – postdoctoral research associate (PHD-Indian Institute of Science).

Tova Mintz – graduate student in final stages of MSc.

List of Publications:

- i) Mintz, T., Nonlinear dynamics and instabilities of a three element microbeam array subject to electrodynamic parametric excitation, MSc Thesis, in preparation, 2009.
- ii) Gottlieb O, Buks, E., Pandey, A. Mintz, T., Zaitsev, S., Hornstein, S, and Blutnik, G., Model based estimation of nonlinear viscoelastic damping of doubly clamped microbeams subject to parametric excitation, in preparation, 2009.
- iii) Pandey, A., Gottlieb, O., Mintz, T. and Buks, E., Nonlinear dynamics and internal resonances of a parametrically excited microbeam array, in preparation, 2009.

Facilities used during the research:

E-beam lithography was employed for fabrication of samples.
 Optical displacement sensor was employed for the measurements.

Appendix: Figures

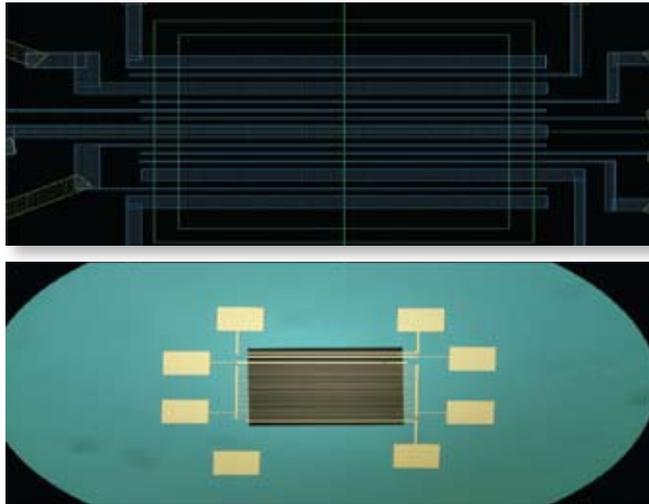


Figure 1: Layout: (top) of a double 3 element array with a single calibration element, and (bottom) a 40 element array with a single calibration element.

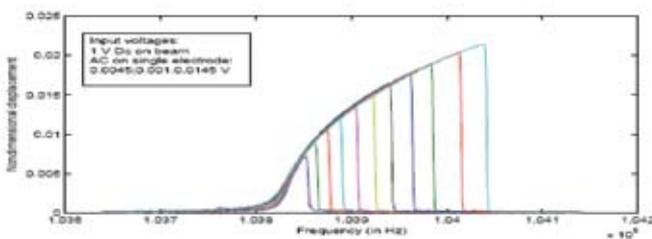


Figure 2: Experimental frequency response of a single element that is subject to combined parametric and external excitation.

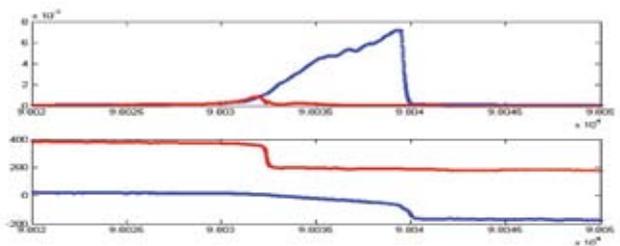


Figure 3: Experimental frequency response of the 3 element array: amplitude (top) and phase (bottom) with a forward (blue) and backward (red) sweep.

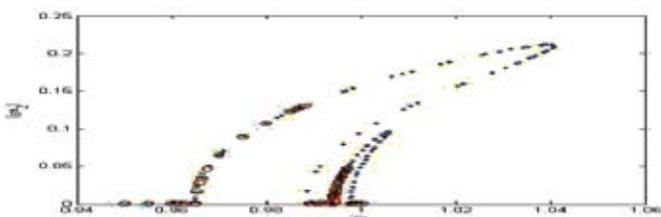


Figure 4: Theoretical frequency response of 3 element array (amplitude of the central element) where co-existing out-of-phase (large amplitude) and in-phase (small amplitude) determine a complex bifurcation structure.

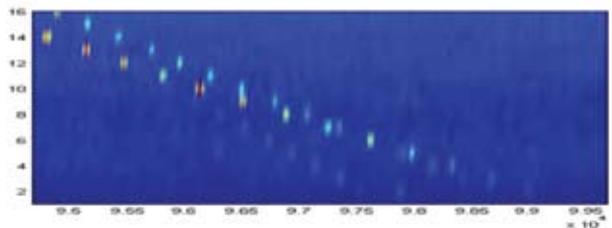


Figure 5: Non-negligible response (power vs. frequency) of the 3 element array due to the optical measurement system without electrodynamic excitation.

Nano-Electrical-Mechanical Systems based on Carbon Nanotubes

Start Year ▶ 2007

Principal Investigators: Dr. Joan Adler - Physics, Technion
Dr. Yuval Yaish - Electrical Engineering, Technion

The Scientific goal of this research is to study nano-mechanical resonators based on nanotubes with experiment and simulation.

The many potential applications of carbon nanotubes include ultra high mass, force and pressure sensors. These are based on monitoring the vibrational frequency shift as a result of attached mass or applied force. We made a molecular dynamics study of vibrations of several suspended nanotubes, recording the locations of the atoms once steady state was achieved. The fundamental frequency of the thermal vibrations as well as their higher modes was analyzed by decomposing the overall vibration of the nanotube into different modes by the application of Fast Fourier Transforms. We then excited specific modes by applying periodic forces on the nanotube in the resonant frequency.

We initially studied thermal vibrations for a 93.38 Angstrom (7,7) SWCNT. At a point slightly displaced from a node we found that the amplitudes of the first and second modes were higher than those of the third and fourth modes. We then applied a periodic force with the frequency of the 3rd mode, and found that the amplitude of this mode was substantially increased, confirming the validity of our calculations. Extensive measurements as functions of length and radius were made hinting at a non-linearity which we are now exploring further.

The bulk of this project is being carried out by RBNI student Ms. Polina Pine, and is ongoing with some major breakthroughs obtained quite recently. Support for the management of the data generated by the programs was provided by then undergraduate Physics student, Mr. Avi Abramov who has now become an RBNI graduate student.

There is one publication to date and one in preparation:

1. "Visualization techniques for modeling carbon allotropes", J. Adler and P. Pine, Computer Physics Communications, 180, pp. 580-582, 2009.
2. P. Pine, Y. Yaish and J. Adler, in preparation.

Several posters and invited conference talks have been given about these results, including one that won Ms Pine a prize at the EU women-in-nano meeting in February 2008 in Slovenia.

The main facility used is the NANCO cluster computer.

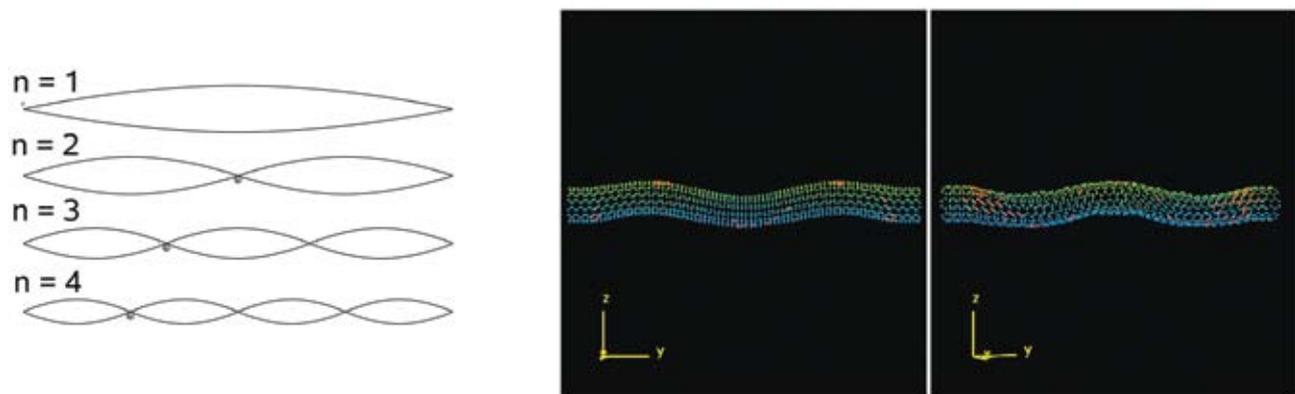
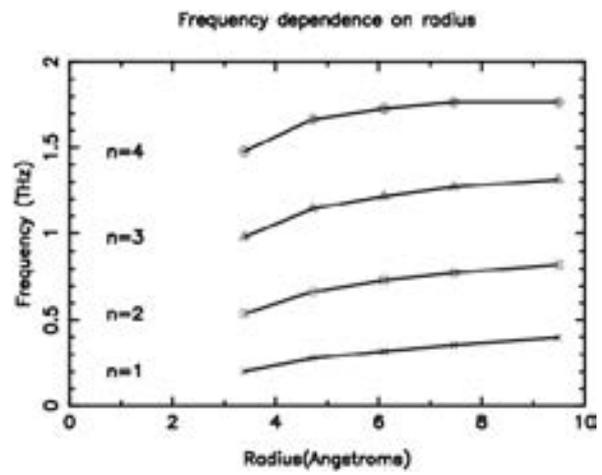
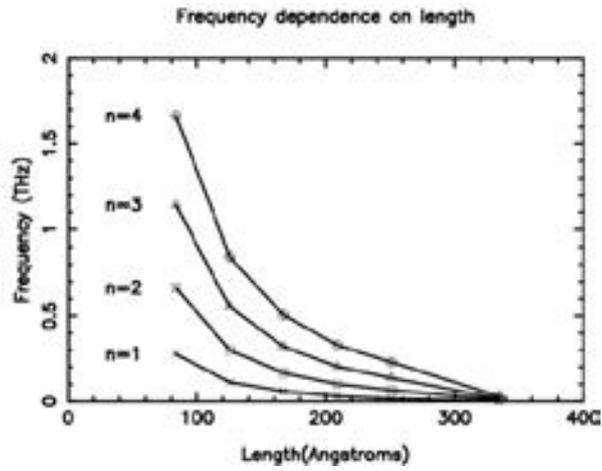


Image at left shows the first 4 modes of vibration of a string. Both nanotubes have frozen ends. The images show stages in the vibrations when an ac force of a frequency identical to that of the third mode of vibration is applied. The tube is color coded for height and stretched bonds between 1.6 and 1.7 angstroms are drawn in red to show where the tubes stretch most. Data - Polina Pine, Animation - Joan Adler



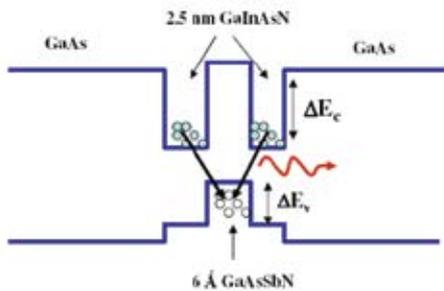
Graphs of the frequencies of the first 4 modes as functions of nanotube length and radius from both the simulations and an analytic continuum model.

MOCVD grown dilute nitride heterostructures for optoelectronic applications

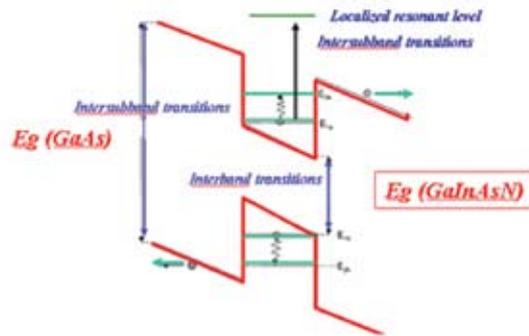
Start Year ▶ 2007

Principal Investigators: Prof. Dan Fekete - Physics and Solid State Institute, Technion
 Prof. Gad Bahir - Electrical Engineering and Microelectronics Research Center, Technion

Schematic band diagram of W type II QW structure used for the laser active region



Schematic bandstructure of nitride based QWIP



The InGaAsN Alloy has attracted considerable attention in recent years owing to the unique nitrogen (N)-driving physical properties and possible applications for optoelectronic devices. With the InGaAsN alloys, lasers emitting at the 1.3 and to some extent also at 1.5 μm ranges have been demonstrated, which expected to make optical communication accessible to GaAs-based devices. The dilute N materials can also be used for intersubband transition (ISBT) near IR based optoelectronics; quantum well infrared photo detectors (QWIPs) and quantum cascade lasers (QCLs) due to their larger conduction band offset discontinuity.

However, the growth of optoelectronic devices based on GaInAsN material (in particular by MOCVD) has been a new challenge for the epitaxy research field due to divergent properties of arsenides and nitrides. One of the main challenges in growing GaInAsN QW lasers by MOCVD is the difficulty of incorporating N into GaInAs QW while maintaining high In content.

In this work we developed a unique new approach to the growth of dilute nitride by MOCVD. First we studied the dynamic of nitrogen incorporation during the growth of GaAs/GaInAsN QW. We developed a graded nitrogen flow process which compensates the decreasing in nitrogen incorporation during QW growth. Using this growth process we grew high quality QWs with emission wavelength in the range of 1.3 micron at room temperature.

In addition, we developed a novel atomic layer epitaxy (ALE) growth process where we exposed the substrate surface to group III (In) precursors in absence of group V (N) precursors followed by exposing the surface group V (N) precursors in absence of III (In) precursors. Using ALE we prevent the interaction between In and N and thus achieving high nitrogen content. Applying ALE we grew GaAs/InAsN QWs with In content of 50% and 2% N confirming our unique approach. Following the success of our new growth process we based our devices on QWs and not on QDs as proposed originally.

Based on our understanding of dilute nitride growth by MOCVD we focused our preliminary device implementation demonstration on two different devices;

- We developed Dilute nitride based W shape type II quantum well laser that works in the optical communication wavelength region (with potential for $\lambda > 1.5\mu\text{m}$). The laser structure was grown and processed and the characterization is currently done these days.
- We developed a new polarization-independent intersubband based quantum well infrared photodetector that works at room temperature at 1.4 microns. The results of this study were accepted for publication in the Applied Physics Letters (publication list) based on this publication we submitted an Invention Disclosure document.

Asaf Albo, Ph.D. student, took part in this research.

Publications:

A. Albo, D. Fekete, and G. bahir, "Unpolarized intersubband photocurrent in Te doped GaInAsN/GaAlAs quantum well IR photodetector", Phys. Stat. Sol. (c) 5, 2323-2325 (2008).

Asaf Albo, Alon Vardi, Dan Fekete and Gad Bahir, "Polarization independent intersubband based GaInAsN quantum well photodetector with dominant detection at 1.42 μm ", Appl. Phys. Lett. 94, 093503 (2009).

A. Albo, D. Fekete, and G. bahir, "Strain induced nitrogen incorporation in atomic layer epitaxy growth of InAsN by MOCVD", Applied Physics Letters, 95, 051102 (2009).

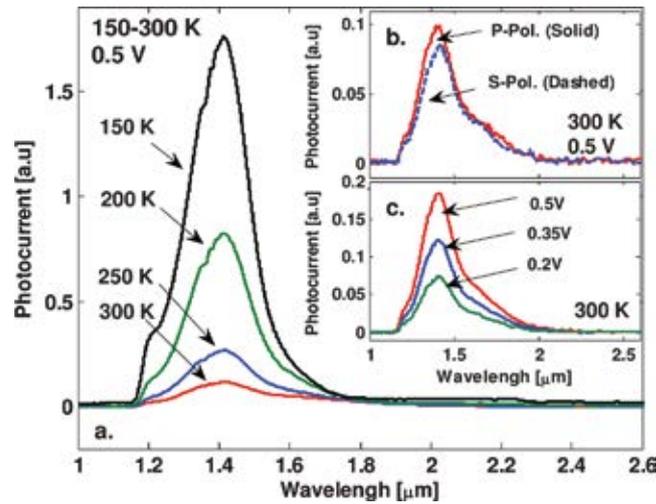


FIG. 1. Room temperature PC spectral response of the QWIP in wedge illumination geometry at various temperatures (150–300 K) under bias of 0.5 V (a). Polarization sensitive spectra; S (dashed) and P (solid) polarizations under bias of 0.5 V (b). Spectral response under various bias voltages (0.2–0.5 V) (c).

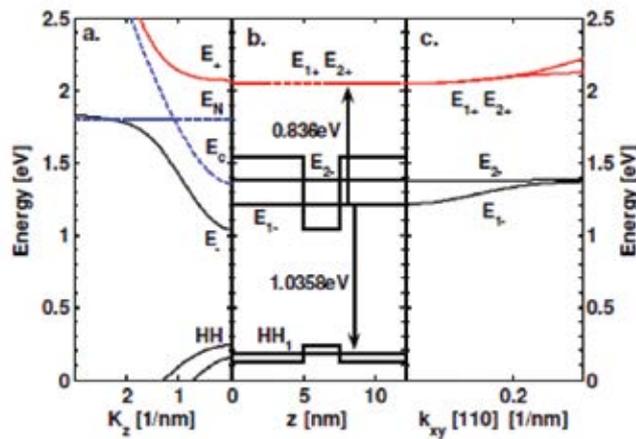


FIG. 2. Ten band $k \cdot p$ calculations of the energy band dispersion curves of GaIn_{0.25}AsN_{0.02}/GaAs coherently grown bulk layer (a). E_N and E_C (blue lines) are the energies of the original states. Energy subband levels in a 25 Å GaIn_{0.25}AsN_{0.02}/GaAs QW (b) and QW energy subband dispersion at (110) direction in the QW plane (c). In our model the valence band edge of GaAs before spin-orbit split-off was chosen as an energy reference point.

Control of Drug Release Using Core-shell Fibres

Start Year ▶ 2007

Principal Investigators: Prof. Eyal Zussman - Mechanical Engineering, Technion
Prof. Subbu S. Venkatraman - School of Materials Science and Engineering, NTU, Singapore

This research goal is to study the incorporation of bioactives into core-shell nanofibers and subsequent dispersion of such nanofibers into polymeric films that will eventually be implanted.

Localized drug delivery from medical devices is now acknowledged to be the optimum route of delivery of potent bioactive molecules, in order to eliminate wastage and unwanted side effects. This is particularly true of chronic diseases such as cancer, where sustained delivery over many days and months is of immense benefit to the patient. Another example is of drug-eluting stents, where the problem of restenosis is addressed by localized delivery of anti-proliferatives.

This work suggests a strategy for controlled drug release using electrospun core-shell fiber structures. The proposed approach presents a method to encapsulate therapeutic molecules and releasing them in controlled fashion. The fibers consist of two layers, with the outer polymer sleeve serving containing the inner core, in which the drug is encapsulated (see Figure 1). By varying the physical and chemical properties of the core and shell solutions, we have shown that the release rate of a hydrophilic drug is controllable. Experimental results show a clear difference in the release pattern between fibers made of PCL, PLLA, and PEO and core-shell fibers, where each of the compartments is composed of a different polymer.

2 students took part in this research:

Sandeeo Kumar Tiwari, from NTU.

Roey Tzezana, from the Technion.

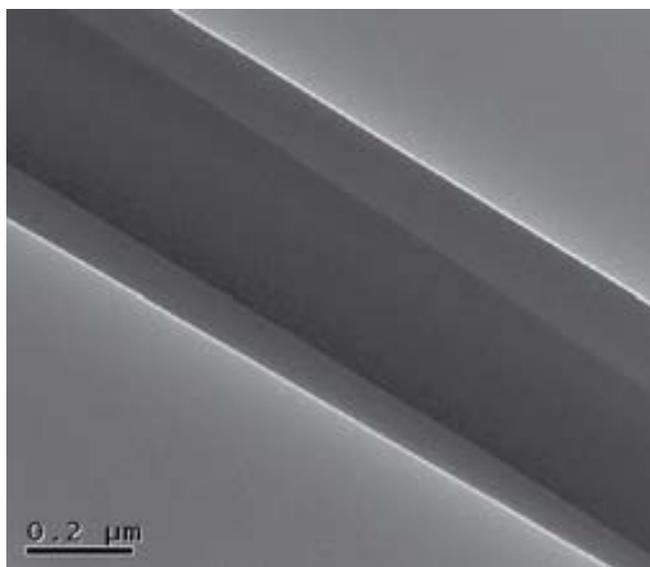


Figure 1: TEM Image of electrospun core shell fibers: PCL-PCL. Drugs are embedded in the core fiber and will be released through the shell.

Hemocompatible Surfaces for Implants

Principal Investigators: Prof. Dror Seliktar - Biomedical Engineering, Technion
Prof. Freddy Yin Chiang Boey - Materials Science & Engineering, NTU, Singapore

Start Year ▶ 2007

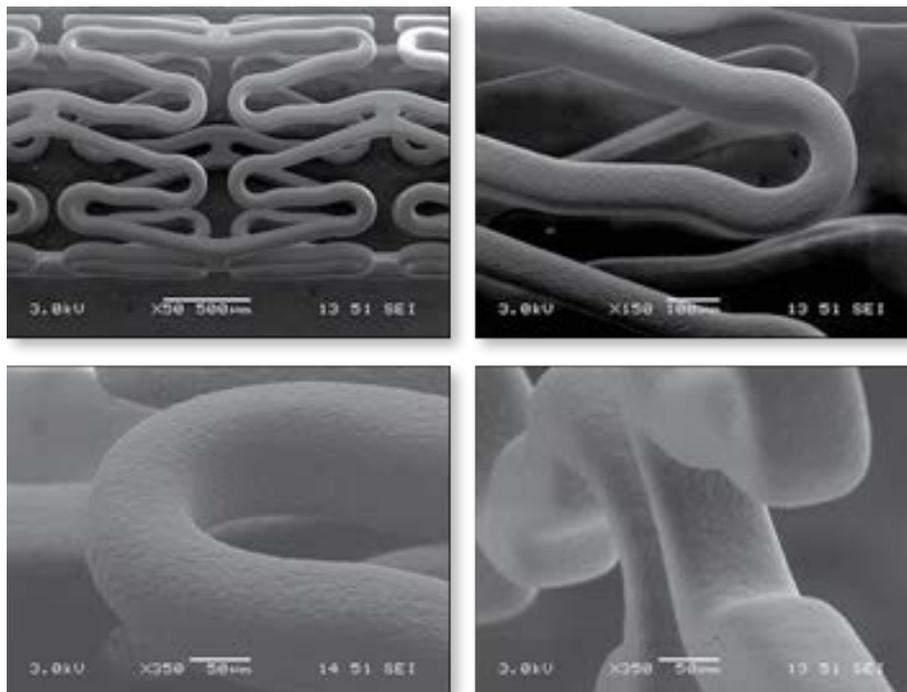
An important unresolved problem in implanted biomaterials is that of thrombogenicity. No implanted biomaterial to date has been approved for blood contact for longer than a few hours, in spite of several years of research. We propose the study of selected coatings on biomaterial substrates, that have the potential to be an attractant surface for certain types of blood cells that will contribute to enhancing blood compatibility. Earlier research at NTU has concentrated on physico-chemical modification of polymer surfaces to enhance endothelialization in vitro, with some degree of success at identifying the correct type of modification. Work at Technion in its turn has led to the development of novel polymerizable "biocompatible gels" that may be applied as a coating on selected substrates.

Techniques for measuring blood compatibility in vitro have been developed at NTU, in addition to methods for quantifying endothelial cell attachment. The current proposal has now combined the research strengths of the two universities to generate methods of attaching stable coatings of fibrin-based hydrogels onto implantable polymers; to evaluate the cellular interactions of such surfaces; and to understanding the mechanisms of the observed interactions. In this work, we have selected substrate polymers with some history of acceptance in implant applications. To these polymers, surface modifications were done to enable the attachment of stable coatings. We further studied the coatings to the substrates, including stability of the adhesion of the coating. We evaluated the cellular interactions, including endothelial cells in vitro, to achieve the desired confluence. Supporting studies of serum protein attachment were performed to understand the mechanisms of cell adhesion. The techniques developed at NTU were used for this preliminary work, and further novel techniques were developed at the Technion. The final outcome of this work includes the identification of a coated substrate in film form that is stable, and has enhanced endothelial cell growth on its surface.

Students who took part in the research:

Dennis WANG (visiting Ph.D. student from Singapore)

Dr. Iris Mironi-Harpaz (post-doc)



SEM image of polymer-coated stent w/drug

Self-assembly induced nanostructures for surface modification

Start Year ▶ 2007

Principal Investigators: Prof. Abraham Marmor - Chemical Engineering, Technion
 Prof. Yeng Ming Lam - Materials Engineering, NTU, Singapore
 Prof. Subodh Mhaisalkar - Materials Engineering, NTU, Singapore

Nanometer scale patterns formed by self-assembled copolymers have been considered as alternatives to replace or augment high resolution lithographic technologies such as X-ray, electron beam and interface lithography to enable a variety of nanotechnologies. In particular, block copolymers have recently received much attention not only because of the scale of the microdomains (tens of nanometers), their various chemical and physical properties (e.g. differential etching rates) but also due to the convenient size and shape tenability of microdomains afforded by simply changing their molecular weights, compositions and the interactions between the different components in a system.

Modified block copolymers have proved to be a more promising way of preparing ordered bulk heterostructures. The goal of this work is to fabricate ordered template structures using microphase separation of copolymers (Fig.1). Using selective solvents, one part of the microphase is "etched" resulting in regular size nanopores or in some cases. The size and morphology of these templated nanostructures may confer interesting surface properties on the substrate.

One such property that is of much practical interest is super-hydrophobicity. As a first stage of the project, we produced regular patterns (Fig. 2), in order to test the basic theory underlying the explanation of super-hydrophobicity. To this end, various shapes of pillars and holes were prepared in PDMS, so that the effects of shape and solid surface to air area ratios can be studied (Fig.2). Measurements of contact angles on many of these surfaces were made, but the results are yet inconclusive. It appears that many more measurements under better controlled conditions are necessary, including measurements of contact angle hysteresis in addition to the most stable contact angle. Such measurements are being performed at present. The collaboration between the two groups is excellent, with a long-term view. A joint research proposal is being prepared to ensure the continuation of this collaboration.

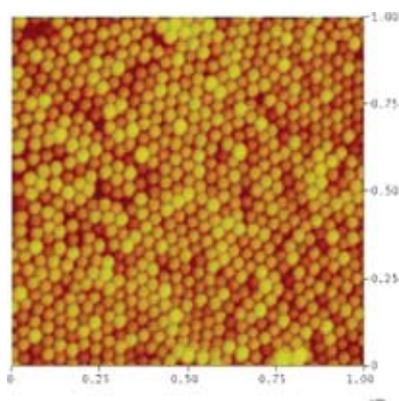


Fig. 1: Self-assembled morphology of PS-b-P4VP copolymer films spin-cast on silicon.

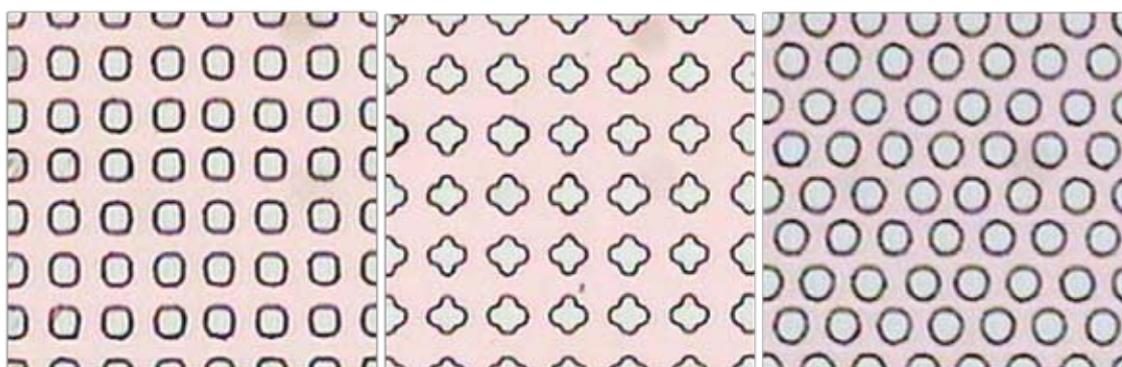


Fig. 2: Some examples of patterns formed in this project to study the effects of shape and solid-surface to air area ratio on super-hydrophobicity.

Polymer field-effect transistors based on lamellar materials

Principal Investigators: Prof. Gitti L. Frey - Materials Engineering, Technion
Prof. Subodh G. Mhaisalkar - School of Materials Science and Engineering, NTU, Singapore

Start Year ▶ 2007

Research goal was to integrate lamellar composites of conjugated polymers and inorganic layers into field-effect transistors. Two types of layered materials were investigated: self-organized lamellar conjugated polymer/sol gel silica films, and exfoliated tin dioxide ultra thin films.

Results: The Technion group has developed a non-aqueous sol-gel process that permits the co-assembly of conjugated polymers and silica precursor into mesostructured hybrid thin films. By controlling the synthesis conditions, it was possible to prepare lamellar mesophase silica with the layers oriented parallel to the substrate surface and the conjugated polymer guest species incorporated in the hydrophobic layers. Evidence for the lamellar mesostructure and a schematic illustration of the nm-thick alternating sol-gel silica/conjugated polymer composite are shown in Figure 1.

In this project we attempted to integrate the lamellar conjugated polymer/sol gel silica films into field-effect transistors with the prospect that the incorporated conjugated polymer serve as the semiconductor, while the silica sol-gel layers in the lamellar structures serve as interfacial layers. Unfortunately, all devices showed extremely low currents and no field effect behavior.

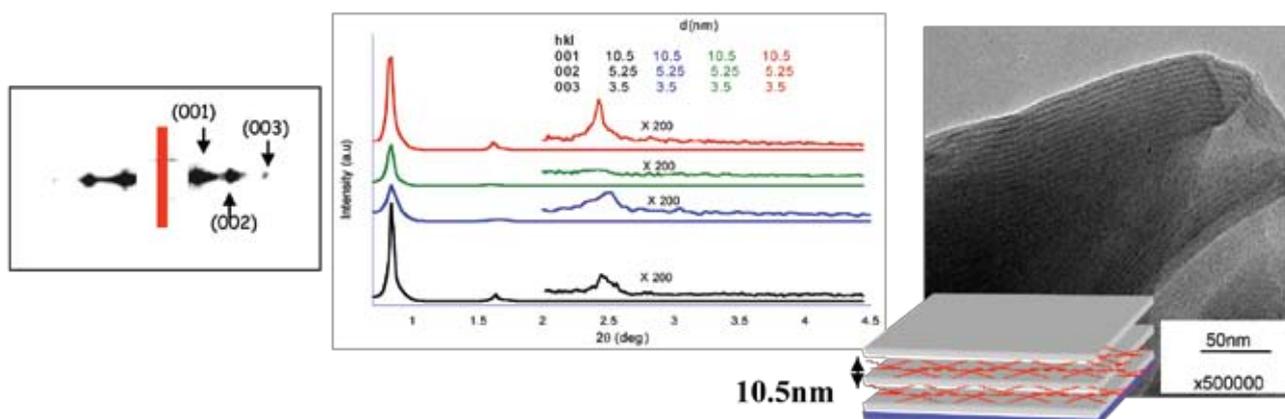


Figure 1: small angle x-ray scattering, 1D X-ray patterns, transmission electron micrograph and schematic illustration of the conjugated polymer-incorporated lamellar sol-gel silica mesostructure.

The layered compound SnS_2 displays a wide range of the electronic properties suitable for a variety of electronic devices. The layered structure of these materials enables it to be chemically processed into ultrathin films via the intercalation and exfoliation method. Ultra-Thin films of the SnS_2 have been prepared through Li intercalation and exfoliation in water. The molecularly-scale thickness of the films was confirmed using HRTEM, as shown in Figure 2. Attempts to integrate these films as active materials in FETs were not successful either.

Dr. Shashank Shekhar, post-doc fellow, took part in this research.

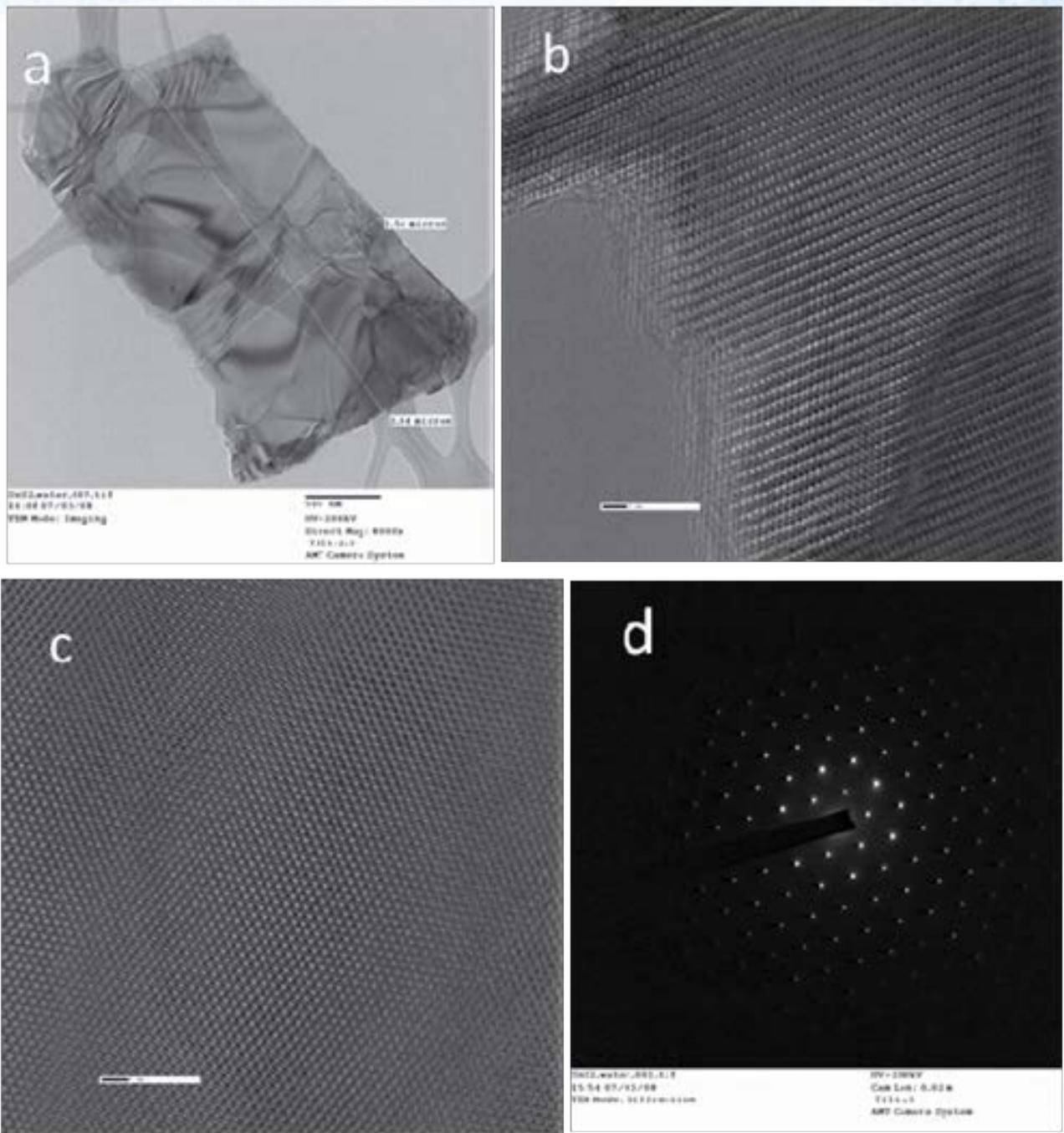


Figure 2: HRTEM micrographs (a-c) and FFT pattern (d) of an exfoliated molecularly-thin SnS₂ layer. The black space bar in the figures is: (a) 500 nm, (b) 1 nm, (c) 1 nm revealing the hexagonal arrangement of the atoms in the SnS₂ layer.

From self assembled monolayers to fully operational devices - pattern and print of field effect transistors

Principal Investigators: Prof. Nir Tessler - Electrical Engineering, Technion
 Prof. Wu Jishan - Chemistry, NUS
 Prof. Peter Ho - Physics, NUS

Start Year ▶ 2007

Organic electronics in general and organic field effect transistors (OFETs) in particular have a potential to impact a wide range of technologies including flexible displays, low cost tags, and point-of-care diagnostics. However, the performance of OFETs has to further improve and it has become apparent that molecular scale control is essential. In particular, finding new approaches to the low-cost patterning and fabrication of organic circuits on a variety of substrates is crucial. This will also open the path to new device architectures and new physics.

The most promising processing platform for these materials is believed to be liquid solution-based techniques, including screen-printing and ink-jet printing. This project investigates and demonstrates the possibility of controlling the confinement and hence the patterning of liquid thin films using photo-switchable self-assembled monolayers. This will provide a key building block towards low-cost large-area fabrication of organic FET circuits, and at the same time open new opportunities for novel high-performance device architectures using printing methods. The proposal brings together the chemistry and device fabrication and analysis expertise of NUS Chemistry, Physics and the Technion.

Results obtained so far:

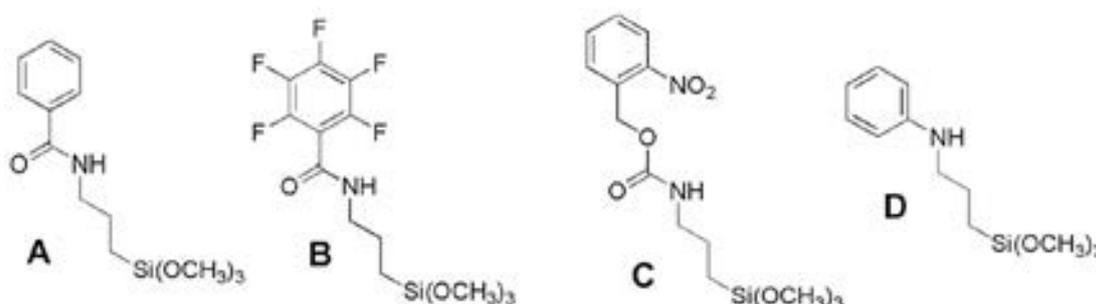


Figure 1: Molecular structure of the molecules designed to self assemble.

As a first step we designed small molecules that could attach to silicon oxide and have a good potential to form a monolayer. This led us to choose a binding group of the type $\text{Si}(\text{OCH}_3)_3$. The second criteria was to be able to induce varying wetting properties and hence several, and different, end groups were chosen (see Figure 1). Finally, the link between the binding group and the end group was designed to be light sensitive such that it would undergo chemical reaction which would alter the wettability properties at the exposed regions.

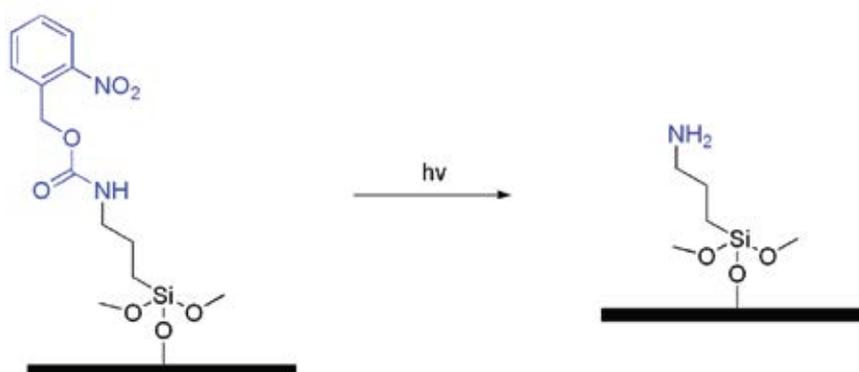


Figure 2: An example for a generic light induced reaction that changes the end group and hence changes the wetting properties of the substrate.

Initial testing of the applicability of optically induced change in the wetting properties and the formation of a predefined pattern were tested using water-based solution of a conductive polymer.

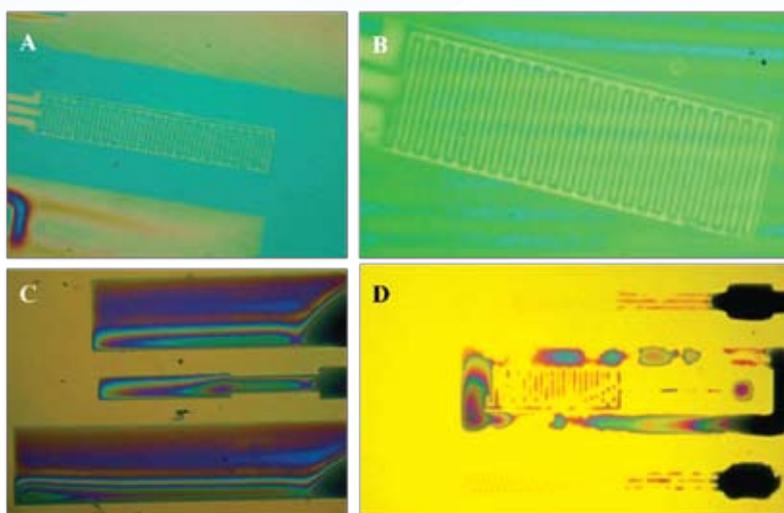


Figure 3: Initial testing of patterned self-assembled monolayer as templates for self-organized patterns. The different figures show different processing conditions some of which look successful. While the initial testing are promising, there is still work to be done in optimizing the template formation and adding the ink-jet printing method as a large scale fabrication method.

Gas sensors based on novel organic/inorganic hybrid structures

Principal Investigators: Dr. Avner Rothschild - Materials Engineering, Technion
 Prof. Eyal Zussman - Mechanical Engineering, Technion
 Prof. Seeram Ramakrishna - Faculty of Engineering, NUS

Start Year ▶ 2007

The aim of this project is to develop ultrasensitive gas sensors based on nanostructured TiO₂ layers produced by electrospinning and enhance their selectivity towards specific analytes by surface functionalization.

Electrospun TiO₂ gas sensors produced by electrospinning display exceptionally high sensitivity towards small gas molecules such as NO₂ and CO [1]. The processing conditions during the electrospinning and subsequent annealing steps have strong influence on porosity, particle size and shape and other microstructural features and consequently on the gas sensitivity. By optimizing these conditions we achieved significant improvement in performance and demonstrated ability to detect NO₂ and CO down to the single ppb levels [2]. The goal of this project is to explore new directions to tailor the selectivity of these remarkably sensitive materials towards specific chemical vapors by attaching organic molecules acting as selective receptors to the surface of the TiO₂ nanoparticles [3].

- [1] Kim et al., Nano Letters 6 (2006) 2009.
- [2] Landau et al., Chem. Mater. 21 (2009) 9.
- [3] Lala et al., Sensors 9 (2009) 86.

Results obtained so far:

Microstructure evolution as function of processing conditions in electrospun TiO₂ layers was investigated and optimal conditions for high gas sensitivity were discerned (Figs. 1 and 2).

Ultra-high sensitivity and ability to detect extremely low concentrations of gas such as NO₂ and CO down to single ppb levels were demonstrated (Fig. 3).

TiO₂ thin films and electrospun nanofibers were prepared and sent to NUS for surface functionalization.

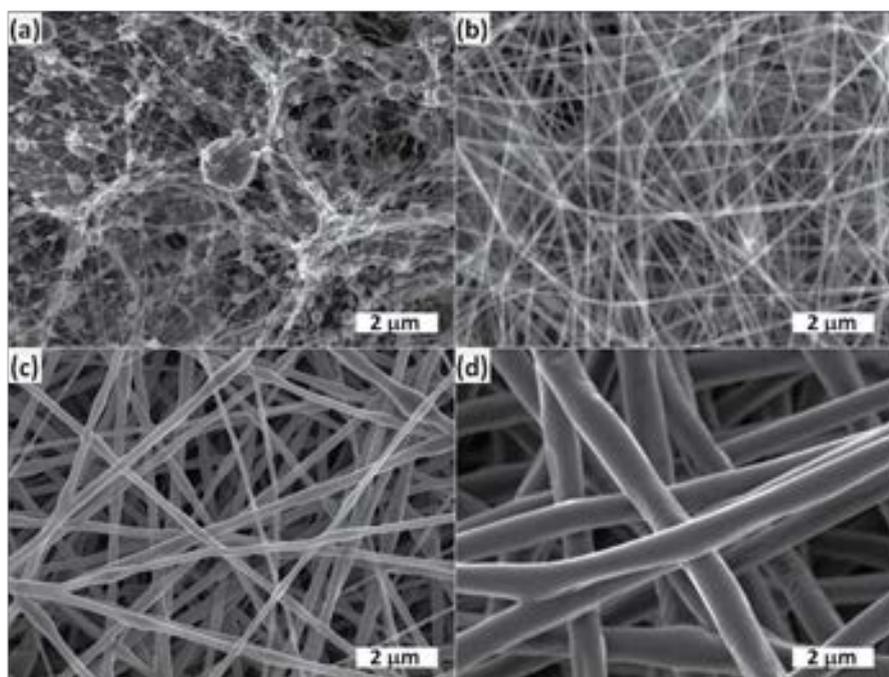


Fig. 1: SEM micrographs of electrospun layers with polymer concentrations of (a) 2, (b) 5, (c) 8, and (d) 12 wt % following electrospinning and vacuum drying and prior to thermal treatments.

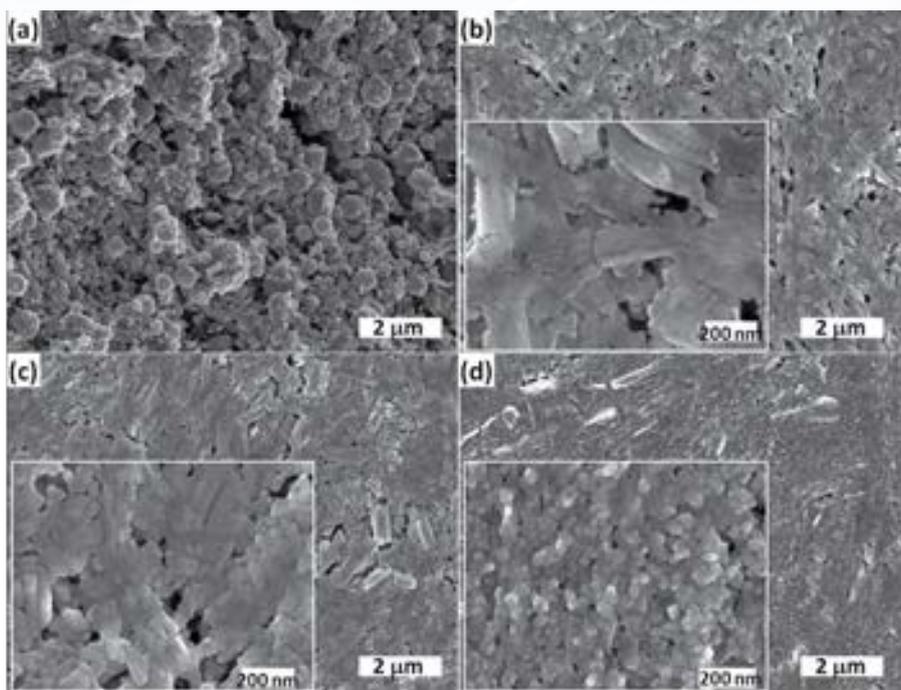


Fig. 2: SEM micrographs of electrospun layers with polymer concentrations of (a) 2, (b) 5, (c) 8, and (d) 12 wt % following hot pressing and calcination at 500°C.

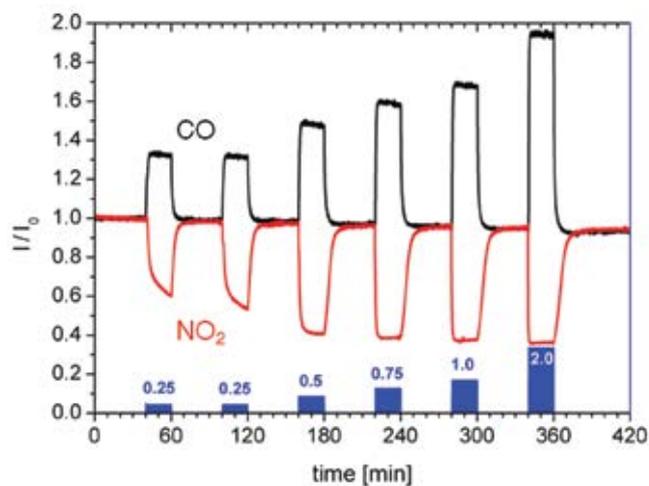


Fig. 3: Electrical response of electrospun TiO₂ sensor (12 wt %, calcined at 750 °C) upon cyclic exposure to CO or NO₂ pulses at 400°C. The gas exposure profile (concentration in parts per million) is indicated at the bottom.