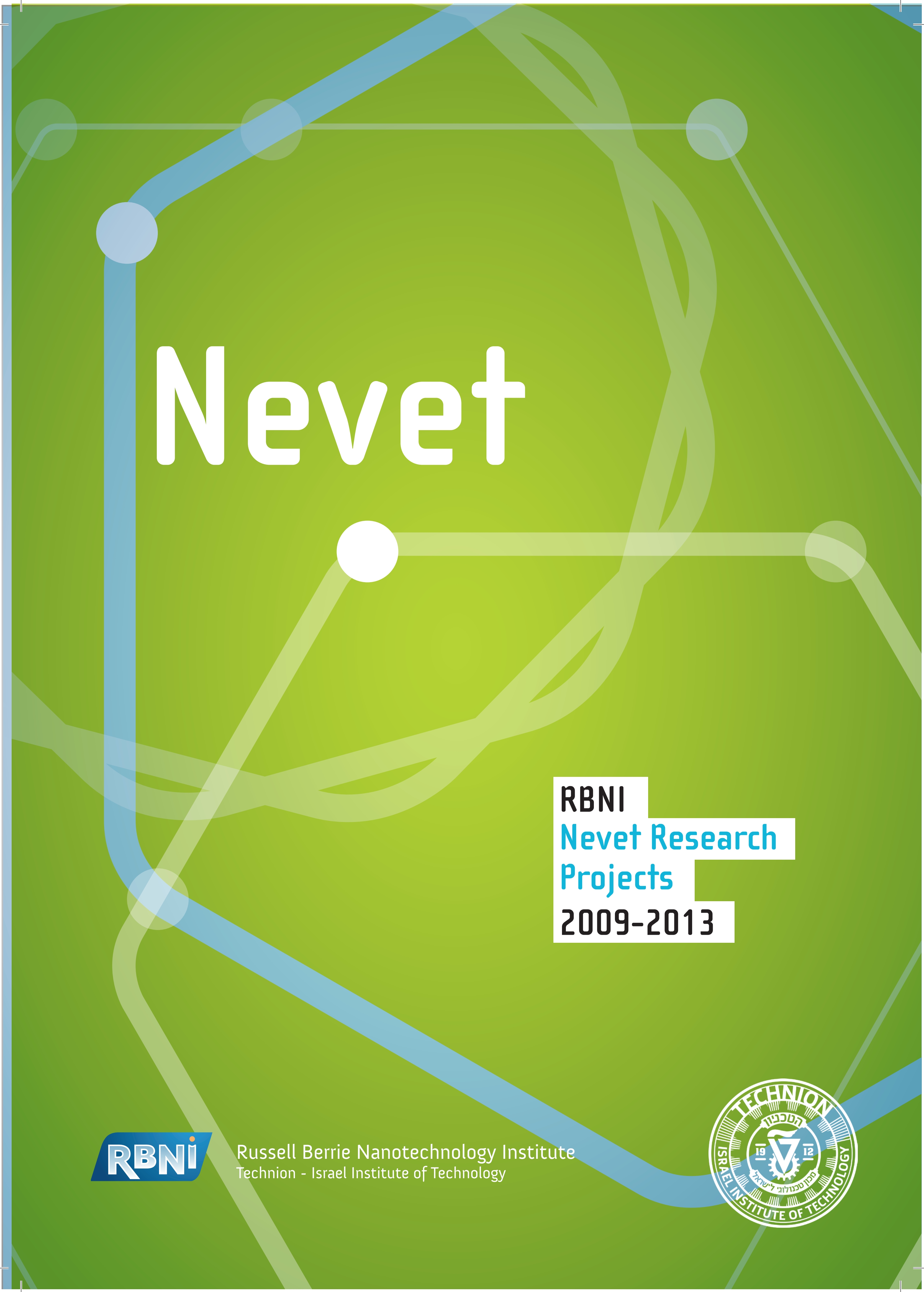

Nevet

RBNI
Nevet Research Projects
2009-2013

Russell Berrie Nanotechnology Institute
Technion - Israel Institute of Technology

nevet

CONTENTS
2009-2013

2009

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The Russell Berrie Nanotechnology Institute (RBNI) at Technion is the home for all nanoscience and nanotechnology activities on campus

With over 150 faculty members and 250 graduate students and postdoctoral fellows from 14 different faculties, RBNI affects all aspects of Technion life. Students education, new faculty recruitment, establishment and upgrade of infrastructure centers, upgrading of researchers labs, ties with industry and other academic institutions, intellectual property commercialization, and initiation of new research directions.

Technion research at the Nano scale spans the multiple facets of nanoscience and nanotechnology including nanoelectronics, nanophotonics, nanomaterials, nanomechanics, and the interface of all these fields with biotechnology and medicine.

RBNI's main vehicle for the promotion of innovative research is the "Nevet" (sprout in Hebrew), program aimed at the encouragement of new multidisciplinary collaborations within and outside the campus. Nevet proposals are submitted by two researchers and those chosen (selected by a committee of experts) are awarded a one year seed grant. The results obtained during this year and the proven collaboration record improve the prospects of the researchers in subsequent applications to external funding agencies.

Altogether, RBNI awarded 110 Nevet grants in the past 8 years (2006-2014); Fifty eight Nevet grants were awarded between 2006-2009 and a summary of their research results are presented on RBNI website: www.rbni.technion.ac.il (Research chapter).

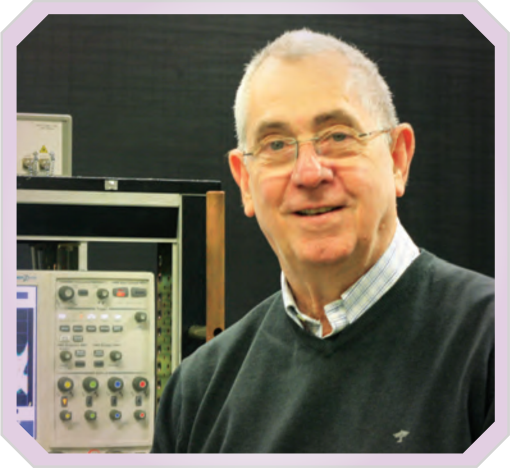
Fourty one grants were awarded between 2010-2013; 26 of these grants involved two Technion researchers from different disciplines, 11 were awarded to collaborations between Technion and other Israeli universities, and the remaining 4 grants were awarded to collaborations between Technion and foreign institutions. Eleven additional new grants were awarded in 2014.

Two major changes related to the Nevet program took place recently. First, a new Technion program (funded jointly by RBNI and the The Lorry I. Lokey Interdisciplinary Center for Life Sciences and Engineering) was initiated in 2013. It mandates a collaboration between one researcher from the life sciences faculties and another from an engineering department and it aims to strengthen the field of quantitative biology. In 2013, we funded four such research projects. Secondly, the international scope of the Nevet program was widened significantly to include several new universities in Europe, and North America.

This brochure offers a glimpse into the cutting edge research in nanoscience and nanotechnology at Technion. It summarizes results of the Nevet projects between 2010-2013, and additionally, an overview of the 2009 projects results that were presented only as abstracts in the previous brochure.

We hope you enjoy it.

Sincerely,
Prof. Gadi Eisenstein
Director of the Russell Berrie Nanotehcnology Institute
Technion – Israel Institute of Technology



nevet

multidisciplinary research collaboration between Ben-Gurion University-Technion

PROJECT

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

Launch year: 2009

Principal investigators:
Prof. Dror Seliktar - *Technion IIT, Department of Biomedical Engineering*
Prof. Raz Jelinek - *Ben-Gurion University of the Negev, Department of Chemistry and the Ilse Katz Institute for nanotechnology*

Participating students: 2

SCIENTIFIC GOAL

The use of polydiacetylene/sol-gex matrixes for studying cell proliferation and metabolism in three dimensions.

ABSTRACT

Cell mobility plays a crucial role in many of the most basic biological processes, including tissue development, tissue healing, and disease progression. Most eukaryotic cells are able to generate motile forces that allow them to migrate inside 3D tissues with ease and efficiency. In vitro, cells are readily able to migrate on various tissue substrates (in 2D) and within 3D matrices that can support their migratory requirements (i.e. proteolysis, cell adhesion, etc.). Despite the importance of cell migration, the in vitro and in vivo mechanisms of motility are still poorly understood. In vivo models of cell migration are complicated by a plethora of other cellular events occurring simultaneously, which limit efforts to expand on the mechanistic understandings of the migration processes. Much of what is known about cell motility is, in fact, derived from 2D in vitro models which generally represent suboptimal systems for studying cell migration. Until recently, there have been few 3D matrices available for studying cell migration; most 3D culture matrices that can support cell growth do not allow for the precise control of the material's physical properties for specifying the experimental environment. The Seliktar group has recently introduced a unique biomaterial hydrogel matrix that may be used for this purpose. The matrix is based on a protein-polymer conjugate that can be cross-linked into a hydrogel in the presence of cells and tissue (i.e. PEG-fibrinogen hydrogel). The research aimed to create a novel platform for in situ visualization and documentation of cell mobility through incorporation of chromatic polydiacetylene (PDA) nanoparticles (NPs) within these hydrogel matrices. The PDA NPs, developed and studied extensively in the Jelinek laboratory, undergo dramatic color and fluorescence transformation induced by external biological stimuli, including physical pressures exerted by cells, and molecules secreted through cell metabolism. Accordingly, when embedded in the novel cell-seeded hydrogels, the particles facilitated real-time in situ illumination of cellular trajectories and allow investigation of parameters affecting cell motility, including cell-mediated proteolysis of the 3D matrix, local cell-adhesion, and localized remodeling of the protein polymer backbone of the hydrogel.

RESULTS OBTAINED TO DATE

Specific Aim 1: Preparation of biocompatible hydrogels having different compositions, which will contain the PDA NPs. Experimental protocols have been developed based upon existing expertise in the two participating laboratories - construction of biocompatible hydrogels (Seliktar) and composite gels comprising PDA nanoparticles (Jelinek). We started to develop and optimize protocols to both preserve the biocompatibility of the hydrogel matrix, as well as retain the chromatic properties of the NPs. Issues that have been addressed include the degree of distribution and aggregation of the NPs within the hydrogel pores, maintaining the NPs fluorescence properties following UV cross-linking, preservation of the PEG-fibrinogen structural properties, and retaining control of the physicochemical properties of the hydrogels having the NPs encapsulated within.

Specific Aim 2: Incorporation of cells into the PDA/hydrogel constructs and evaluating their survival and motility. The experimental design in this aim focused on encapsulation of different types of endothelial cells within the composite gel constructs followed by microscopy-based documentation of cell motility and cell viability. We started to carry out cell tracking experiments using time-lapse phase contrast microcopy for monitoring cells in 3D hydrogels. Issues that were addressed include the maintaining the degree of viability above 80% with the PDA/hydrogel constructs by changing the composition and concentration of the NPs and hydrogel constituents, as well as identifying a range of PDA/hydrogel properties that will be amenable to short-term cellular remodeling.

FIGURES

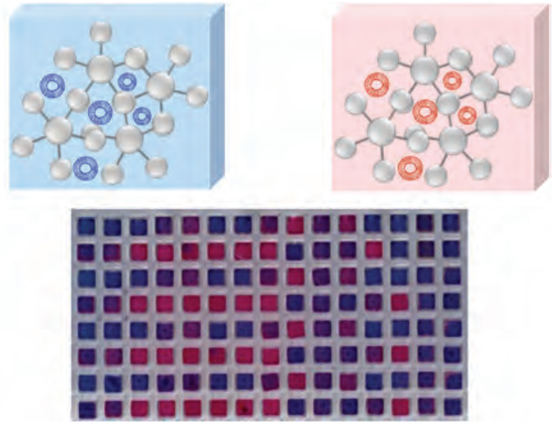


Figure 1. Structural organization of PDA/sol-gel system (top) and a scanned image of the PDA/sol-gel plate (bottom)

FACILITIES

Fluorescent Spectrometer

PROJECT

Self-organization in actin-based cell motility

Launch year:	2009
Principal investigators:	Prof. Kinneret, Keren - *Technion IIT, Physics Department* Prof. Anne Bernheim - *Ben Gurion University of the Negev, Department of Chemical Engineering*
Participating students:	3

SCIENTIFIC GOAL

Develop synthetic physical model systems to study actin polymerization and force generation on soft interfaces.

ABSTRACT

The cytoskeleton is comprised of an active network of filamentous proteins which gives the cell its mechanical resistance and plays important roles in many cellular processes. The ability of the cytoskeleton to execute a diversity of tasks depends on its ability to self-organize and to constantly remodel itself. Many vital cellular processes, such as cell motility and division, involve cytoskeletal dynamics close to soft surfaces, particularly, fluid membranes. The mechanisms governing cytoskeletal self-organization and dynamics near such surfaces are still largely unexplored. In this project we propose to develop synthetic physical model systems to study actin polymerization and force generation on such soft interfaces in a simplified and controlled environment, detached from the complexity of the living cell. Microfluidic devices will be developed to generate surfaces of well defined shapes. We plan to study the effect of curvature, surface tension, as well as the type and composition of the motility machinery on the forces generated and their subsequent effect on surface deformations.

RESULTS OBTAINED TO DATE

The aim of these projects was to study the self-organization of actin networks near soft interfaces. Both groups developed model systems to that end. The Technion team developed a system of water-in-oil emulsions in which the motility supporting machinery is encapsulated and functional within cell-sized droplets surrounded by oil. They developed a scheme to localize ActA, which is a factor that promotes actin branching, to the water-oil interface by chemically conjugating it to hydrophobic fluorescent groups. Using this amphiphilic actin nucleator that spontaneously localizes on the inner interface of water-in-oil emulsions they were able to realize artificial actin networks that resemble the actin cortices seen in live cells. The dynamics of these artificial cortices and the relation between the density of the actin nucleators and the size of the emulsion droplets were examined in detail.

In parallel, the BGU team developed systems that consist of lipid membranes to which branched actin nucleators localizes. Conjugation of the nucleators was done via specific lipids (e.g., PIP2 Phosphoinositide) and proteins that localize to the membrane. A system consisting of purified proteins was used to initiate the polymerization of the networks on the membrane surface. In the work we tested the role of the membrane topology and membrane composition on the dynamics of reorganization of actin on that surface. The initial work that was supported by the NEVET program was then the subject of a full proposal presented to the DFG. The project was granted.

FIGURES

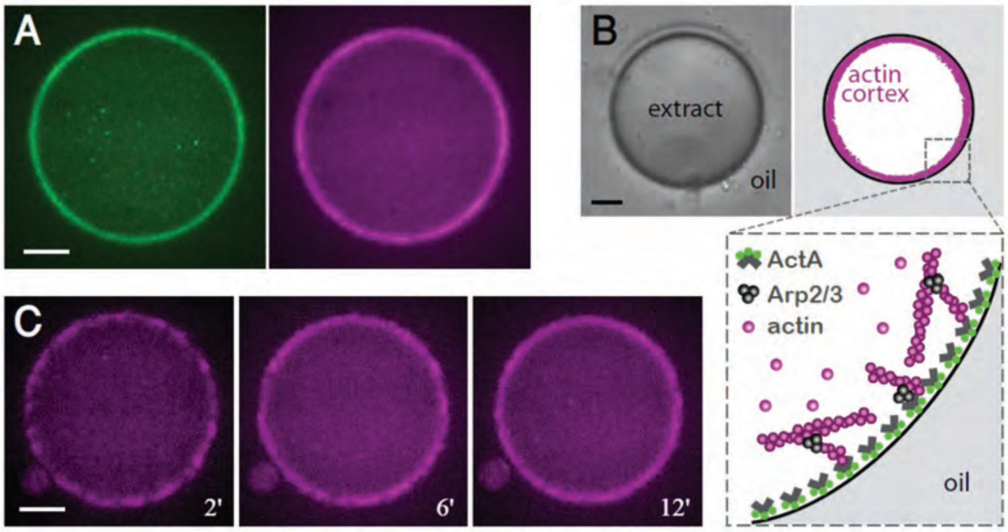


Figure 1. Reconstitution of actin cortices. (A) Spinning disk confocal images of bodipy-conjugated ActA (left) and rhodamine-labeled actin (right) in a water-in-oil emulsion. (B) A bright-field image (top left) and a scheme (top right) of an actin cortex formed at the inner interface of an aqueous droplet surrounded by oil. The zoomed scheme (bottom) illustrates the localization of the amphiphilic ActA to the water-oil interface, which leads to local activation of Arp2/3 and nucleation of a cortical actin network. (C) Spinning disk confocal images from a time-lapse movie show the formation of a homogenous actin cortex. The time after droplet formation is indicated. Scale bars: 10μm.

FACILITIES

Clean rooms, TEM

nevet

multidisciplinary
research
collaboration
between Ben-Gurion
University-Technion

PROJECT

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

Launch year:	2009
Principal investigators:	Prof. Daniel Rich - *Ben Gurion University, Department of Physics* Prof. Dan Ritter - *Technion IIT, Department of Electrical Engineering*
Participating students:	2

SCIENTIFIC GOAL

The goal of this project was to enable Profs. Rich and Ritter to establish a collaborative effort to realize single-photon (λ~1.5 μm) emitters using single InGaAs quantum dots (QDs). Such a single-photon source has the potential for enabling many new applications in the field of long range quantum information technology. The QDs were to be fabricated by growing InP/InGaAs/InP layers selectively on nanometer scale openings in thin dielectric layers deposited on InP substrates, using metal-organic molecular beam epitaxy. This approach for the fabrication of the QDs is radically different from the widely explored self-assembly method. It aims at producing fully controlled QD structures, without the statistical size distribution characteristic of the self-assembly approach. Previous experiments at Technion revealed that the growth of nm-scale structures is feasible, but their characterization by optical methods, is very complex. In this proposal, we suggested to simultaneously probe the optical and structural properties of the nanostructures by spatially and temporally resolved cathodoluminescence (CL). The information obtained from the CL experiments will make it possible to better understand how to control the position and composition of single nanostructures.

ABSTRACT

The project emphasis was modified as a result of a malfunction in some very expensive instrumentation. Our infrared (IR) photon counting system malfunctioned and prevented the CL measurements of InGaAs/InP quantum dots (QDs), as originally planned. Insufficient funds prevented the repair of this detector. Therefore, we focused our efforts in one of our current topics which is the CL studies of GaN/AlN quantum dots grown on Si(111). We were able to perform these measurements using one of our current detectors that operate in the visible wavelength range. As will be described in the budget summary below, most of the funds for this project were used to service our scanning electron microscope (SEM), which is the primary instrument used for our measurements and other projects. We studied the excitation- and polarization-dependent optical properties of GaN/AlN self-

assembled quantum dots (QDs) grown on Si(111) substrates. Ensembles of QDs were subject to various external stress configurations that resulted from the thermal expansion coefficient mismatch between the GaN/AlN layers and the Si(111) substrate and ranged from in-plane uniaxial stress, primarily along the <11-20> directions, to in-plane biaxial stress, having magnitudes ranging from 20-30 kbar. Limited regions of uniaxial stress were obtained by exploiting naturally occurring microcracks that form during the post-growth cooling. These microcracks act as stressors in order to create the highly localized regions of uniaxial stress. The local strain tensors for such QDs, which are subject to an interfacial stress perturbation, have been determined by modeling the dependence of the QD excitonic transition energy on the interfacial stress. Cathodoluminescence (CL) measurements of the excitonic transitions exhibit an in-plane linear polarization anisotropy in close proximity to microcracks. The polarization anisotropy is strongly dependent on the sample temperature and the electron beam excitation conditions used to excite the QD ensemble. Localized CL spectroscopy of the QDs exhibits emissions from both the ground and excited states, whose relative contributions depend on the level of excitation and temperature. Experimental results indicate that the polarization anisotropy vanishes at high temperatures (~300 K) with an increasing excitation of the QDs, while the anisotropy decreases more slowly with excitation at low temperatures (~60 K). A theoretical modeling of the effect of carrier filling on the polarization anisotropy and the excitonic transition energy was performed, as based on three-dimensional self-consistent solutions of the Schrödinger and Poisson equations using the 6x6 k·p and effective mass methods for calculations of the e-h wavefunctions and electron and hole quasi-Fermi levels for varying levels of state filling. We attribute carrier filling and a thermal excitation of holes into higher energy QD hole states during excitation to account for the observed gradual decrease in the polarization anisotropy with an increasing electron-hole pair excitation density at T = 300 K.

We continued with studies of GaN/AlN QDs that were grown by the Stranski-Krastanov method on Si(111) using molecular beam epitaxy. During the subsequent cooling from growth temperatures, the thermal expansion coefficient mismatch between the Si substrate and GaN/AlN film containing vertically stacked QDs leads to an additional biaxial tensile stress of 20 – 30 kbar in the III-nitride film. We have selectively modified this thermal induced stress in the QD layers by etching a cross-hatched pattern into the as-grown sample using inductively coupled Cl_2/Ar plasma reactive ion etching. The Nano-Fabrication facilities of the Ilse Katz Institute were used to pattern the samples for this study. The results show that a suitable choice of stripe width from ~2 to 10 μm and orientation can create regions of in-plane uniaxial stress that enable a selective and local control of the polarized luminescence from ensembles of QDs which were probed with spectrally, spatially, and temporally resolved cathodoluminescence.

RESULTS OBTAINED TO DATE

O. Moshe, D. H. Rich, S. Birner, M. Povolotskyi, B. Damilano, and J. Massies, *Electronic and optical properties of GaN/AlN quantum dots on Si(111) subject to in-plane uniaxial stresses and variable excitation,* J. Appl. Phys. 108, 083510 (2010).

O. Moshe, D. H. Rich, B. Damilano and J. Massies, *Polarized emission from GaN/AlN quantum dots subject to uniaxial thermal interfacial stresses,* J. Vac. Sci. Technol. B 28 (4), C5E25 (2010).

O. Moshe, D. H. Rich, B. Damilano and J. Massies, *Selective control of polarized emission from patterned GaN/AlN quantum dot ensembles on Si(111),* Appl. Phys. Lett. 98, 061903 (2011).

PROJECT

Synthesis and magnetic properties of Au-Fe nano-onions and core-shell nanoparticles

Launch year:	2009
Principal investigators:	Prof. Eugen Rabkin - *Technion IIT, Faculty of Materials Science and Engineering* Prof. Roni Shneck - *Ben-Gurion University of the Negev, Department of Materials Engineering*
Participating students:	2

SCIENTIFIC GOAL

Our aim in this project was to produce the core-shell Fe-Au nanoparticles employing solid state dewetting technique. We hypothesized that because the surface energy of Au is significantly lower than that of Fe, the homogeneous Au-Fe alloy particles produced at high temperatures will transform into the Fe core - Au shell composite particles upon annealing in the two-phase region of the phase diagram. The thermodynamics of these composite particles had to be analyzed with the aid of thermodynamic modeling.

ABSTRACT

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

RESULTS OBTAINED TO DATE

Electron-beam deposition was used to deposit Fe-Au bi-layers of various thicknesses on c-plane oriented sapphire ((0001) single crystal α-Al$_2$O$_3$) substrates. The samples were annealed in a quartz-tube furnace under forming gas flow (Ar-10%H$_2$, 99.999% pure) at various temperatures in the range of 950-600 °C. The microstructure, texture, and surface topography of as-deposited and annealed samples were analyzed with the aid of scanning and transmission electron microscopies (SEM and TEM), X-ray diffraction (XRD), and atomic force microscopy (AFM). It was uncovered that deposition of Fe and Au layers on sapphire employing electron beam deposition technique results in quasi single crystalline layers with exceptional thermal stability against agglomeration. The latter proceeds by nucleation and slow growth of hexagonally-shaped and highly faceted holes to the substrate. Two papers addressing these phenomena were published [1-2]. The two-phase Au-Fe particles were obtained employing a two-stage annealing, aiming at firstly producing the particles of homogeneous Fe-Au alloy, followed by a longer precipitation treatment at 600 °C. To our surprise, no core-shell morphology expected on the basis of surface energies of Fe and Au was observed in the two-phase particles. Instead, Fe particles always precipitated at the edges of the particles of the Au-Fe alloy, resulting in composite particle with Au-rich and Fe-rich particles coexisting side by side. The high-resolution electron microscopy observations revealed a thin (1-2 nm in thickness) layer of Au-rich phase on the surface of Fe particles, at the grain boundaries between the neighboring Fe precipitates, and at the Fe-sapphire interface [3]. This ultrathin Au-rich segregation layer lowers the surface energy of Fe particles and enables the composite particle morphologies observed in the experiment.

We developed a thermodynamic model based on the concept of weighted mean curvature, which describes the kinetics and morphology of precipitation occurring simultaneously with the dewetting process. With the surface energy of Fe and of the Fe-sapphire interface modified by the segregating layer of Au, this model successfully described the morphology of composite particles *(see Fig. 1)*.

Our results indicated that anisotropy of surface energy and diffusivity, as well as surface segregation of one of the components strongly affect phase transformations in particles of binary alloy, even for particles with lateral dimensions reaching one micrometer.

FIGURES

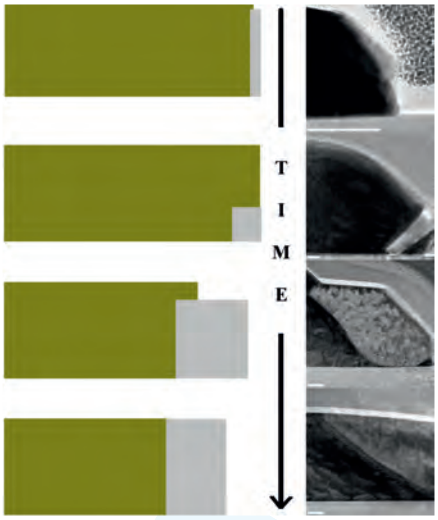


Figure 1. Qualitative comparison between kinetic model and experiment: the time-evolution of an Fe nucleus, which grows with time and undergoes a transition from inside to outside of the Au particle. The scale bars are 50 nm. The brighter phase in the TEM images represents Fe [3].

FACILITIES

Micro- nanofabrication unit at the Department of Electrical Engineering
Electron Microscopy Center at the Department of Materials Science and Engineering
Focused Ion Beam (FIB) system
X-ray diffractometer

nevet

multidisciplinary research collaboration between Bar Ilan University- Technion

PROJECT

Magnetic nanoparticles with designed surfaces for polymer film nanocomposites: Advanced materials through control of interfaces

Launch year:	2009
Principal investigators:	Prof. S. Margel - *Bar-Ilan University, Department of Chemistry* Prof. Wayne D. Kaplan - *Technion IIT, Faculty of Materials Science and Engineering* Prof. Michael S. Silverstein - *Technion IIT, Faculty of Materials Science and Engineering*
Participating students:	1

SCIENTIFIC GOAL

The objectives of this research were to develop innovative magnetic nanocomposites (nanoparticles with designed surfaces in polymer films); to characterize their structures and properties; and to understand how the structures and properties of these novel nanocomposites were influenced by the nature of the nanoparticles, the nature of the nanoparticle surfaces, the processing technique, and the interfaces within the nanocomposites.

ABSTRACT

Nanoparticles often have unique electrical, chemical, mechanical or magnetic properties. Magnetic nanoparticles are of interest for many advanced technology applications. A few percent nanoparticles added to a polymer matrix can have profound and synergistic effects on the properties, but it is essential to prevent agglomeration and to ensure adhesion to the polymer matrix. The objectives of this research were to develop and characterize innovative polymer composites containing magnetic nanoparticles.

RESULTS OBTAINED TO DATE

Magnetic nanoparticles composed of maghemite (γ-Fe_2O_3) with narrow size distributions (between 5 and 100 nm) were synthesized using two different routes as demonstrated through transmission electron microscopy (TEM) and light scattering. One route was used to generate hydrophilic Fe_2O_3 nanoparticles and the second route was used to generate hydrophobic Fe_2O_3 nanoparticles. Magnetic nanoparticles were generated *in-situ* within porous crosslinked poly (2-hydroxyethyl methacrylate) (PHEMA) to prevent agglomeration and to enhance adhesion. The porous PHEMA was immersed in an aqueous solution of iron chloride ($FeCl_3$). Interestingly, the amount of solution that the polymer would absorb was significantly smaller than the amount of pure water it would absorb. The polymer was dried after absorbing the $FeCl_3$ solution. The white porous polymer monolith became brown in the $FeCl_3$ solution and remained brown after drying, indicating that the $FeCl_3$ had been incorporated within the monolith.

The porous morphology was not affected by the process of absorbing the $FeCl_3$ solution and drying, as demonstrated through scanning electron microscopy (SEM). There were no large-scale $FeCl_3$ particles visible on the cross-section fracture surface of the monolith. The $FeCl_3$-containing porous polymer was then immersed in an aqueous solution of sodium hydroxide (NaOH) for oxidation of the $FeCl_3$ to Fe_3O_4. Immersion in the NaOH caused the polyHIPE to swell and enhanced the absorption. The porous polymers were then washed with water and dried. The porous polymers remained brown, indicating that the inorganic nanoparticles remained within the monolith.

FIGURES

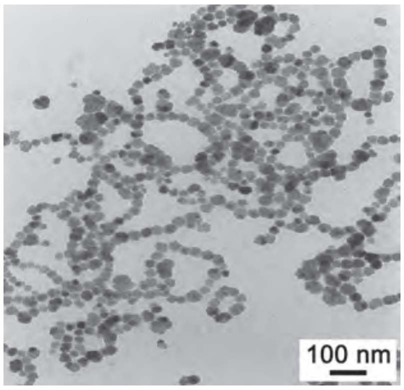


Figure 1. TEM micrograph of the hydrophilic magnetic maghemite nanoparticles.

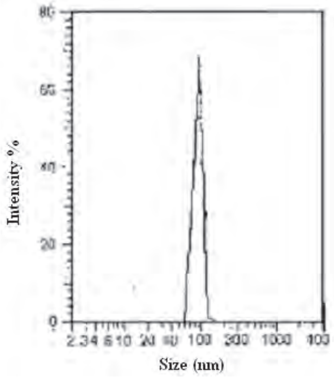


Figure 2. Particle size distribution of the hydrophilic magnetic maghemite nanoparticles as determined using light scattering from a nanoparticle dispersion in water.

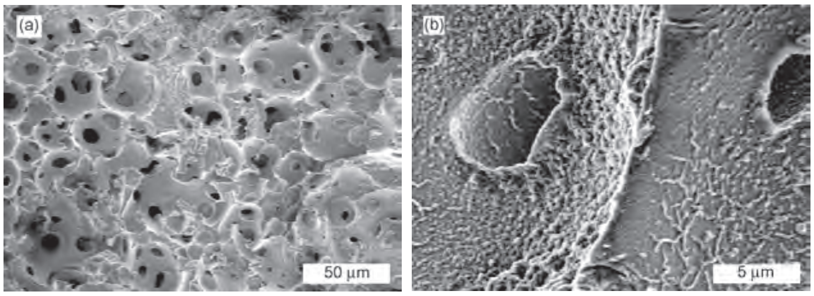


Figure 3. SEM micrographs of a porous crosslinked PHEMA cross-section fracture surface following immersion in an $FeCl_3$ solution and drying.

FACILITIES

SEM, TEM

PROJECT

Nano Scale Oxide Coatings for Membranes

Launch year:	2009
Principal investigators:	Prof. Chaim Sukenik - *Bar-Ilan University, Department of Chemistry* Prof. Carlos Dosoretz - *Technion IIT, Faculty of Civil and Environmental Eng.* Prof. Raphael Semiat - *Technion IIT, Faculty of Chemical Eng.*
Participating students:	Avner Ronen, Yaakov Carmiel

SCIENTIFIC GOAL

Nano Technology to minimize biofouling.

ABSTRACT

Antibacterial coating on the membranes surface:

One of the primary goals of the NEVET project was to coat polysulfone (PSU) membranes with an antibacterial coating. The selected coating was TiO_2, due to the experience of the BIU group with depositing thin films of this oxide, and the demonstrated success of such films in inhibiting bacterial biofilm formation.

From experimenting with PSU sheets, it was found that activation with air plasma gave the best results. Immersion in sulfuric acid (20%, 2 hours) also gave good results, but it took too much time. Exposure to fuming sulfuric acid damaged the sample.

Deposition of TiO_2 on air-plasma activated membranes using a liquid phase deposition (LPD) method gave excellent results in terms of film coverage and uniformity when compared to non-activated membranes *(Figure 1)*. EDAX analysis also showed higher titanium concentration in the activated samples. However, the coating seemed to be too thick for our application and examination of a cross-section made by focused ion beam (FIB) estimated the thickness of the titania layer as 80 nm. To lower the film thickness, a number of variations in LPD conditions were explored. The most successful approach was to use a solution that was aged for 18 hours and then filtered before film deposition *(Figure 2)*. In this way, 6 hours of deposition resulted in a dense film with small holes (most are <100 nm). In order to check the time factor, depositions of 3 and 4 hours were also done. 4 hours deposition gave a similar result to the 6 hours, and EDAX analysis showed about the same titanium concentration (within the error range of the measurement). The 3 hours deposition showed no coating and so did the EDAX analysis. The process appears to be non-linear and would require significant effort to be fully optimized.

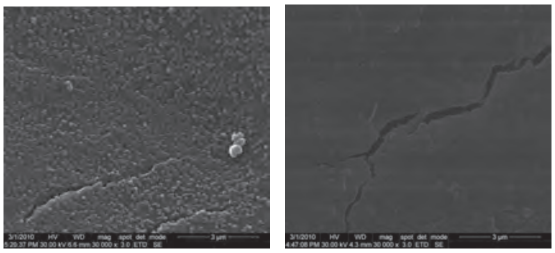


Figure 1. SEM images of PSU membranes after 4 hours in a fresh deposition solution. (a) no activation. (b) activation by plasma, 5 minutes.

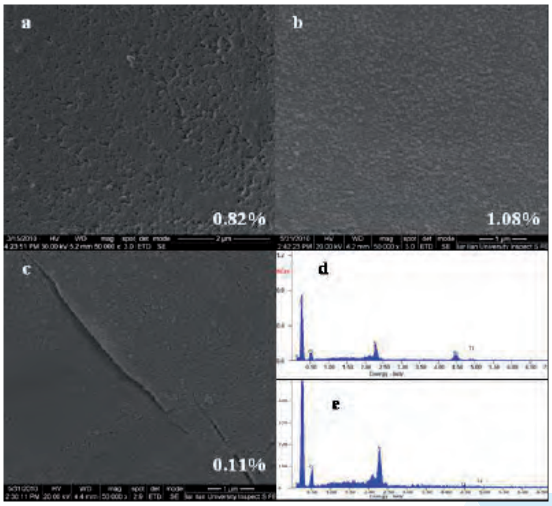


Figure 2. (a-c) SEM images of PSU membranes after 6, 4 and 3 hours (correspondingly) in filtered aged soultion. The numbers in the corners are the titanium atomic concentration as measured by EDAX. (d-e) EDAX spectra of (b) and (c).

Apart from the LPD method, atomic layer deposition (ALD) was also used to deposit thin (12 nm) TiO_2 layers on the membranes. XPS analysis of the coated membranes and their comparison to silicon wafer substrates showed similar amounts of TiO_2, indicating a good coverage of the surface.

Samples with both the LPD and the ALD titania coatings method were tested at the Technion in a flow chamber for bacterial growth. To our disappointment, neither sample showed significant inhibition of bacterial biofilm growth.

Antibacterial modification of the feed spacer:

The concept of suppressing biofouling formation using an antibacterial feed spacer was investigated in a small scale cross flow system mimicking a spiral wound membrane configuration. A novel antibacterial composite spacers containing zinc oxide nano particles was produced by modification of a commercial polypropylene feed spacer using sonochemical deposition.

Commercial polypropylene feed spacers were harvested from a commercial sea water type-spiral wound membrane module (Toray). The samples were submerged in ethanol solution (96%) and cleaned in an ultrasonic bath (three cycles of 30 minutes each at room temperature). Cleaned samples were immersed in 0.05 M zinc nitrate hexahydrate solution and ultrasonicated for 180 minutes (70% intensity) using an ultrasonic horn tip (Vibra Cell 40 W/cm^2, 20 KHz) at a controlled temperature of 15° C. The physical properties of the modified spacer were evaluated using high resolution/energy dispersive spectrometry-scanning electron microscopy and atomic force microscopy imaging (HRSEM, EDS, AFM).

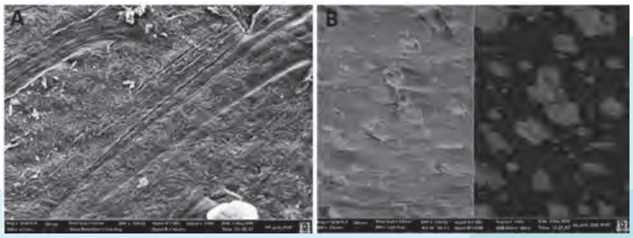


Figure 1. HRSEM morphology of the polypropylene feed spacers (magnification x30K). (A) Micrograph of the unmodified spacer. (B) Micrograph of the ZnO-modified spacer. Left hand-side: surface of the modified spacer (SE detector); Right hand-side: surface of the modified spacer (BSE detector), dark area represents polypropylene and bright area represents ZnO.

The influence of the sonochemical deposition can be seen in the white deposit on the surface of the spacer (*Fig. 1B*). This deposit is comprised of a material with releativly high density (as expected for metals or metal oxides compared to the polymer matrix). Secondary electron (SE) imaging of the surface showed a relatively smooth structure in general terms, suggesting the ZnO-Np to be in part embedded in the polymer matrix with only the upper layer exposed on its surface. Backscattered secondary electron (BSE) imaging indicated that the distribution of nanoparticles on the polypropylene surface were in a broad size range, from a few nanometers to a few micrometers (*Fig. 1B*, right hand side). ZnO coverage area was calculated by image processing to be 60-70%.

The ability of the modified spacers to repress biofilm development on membranes was evaluated in flow-through cells simulating the flow conditions in commercial spiral wound modules. The experiments were performed at laminar flow (Re=300) with a 200 kDa molecular weight cut off polysulfone ultrafiltration membrane using *Pseudomonas putida* S-12 as model biofilm bacteria. The modified spacers reduced permeate flux decrease at least by 50% compared to the unmodified spacers (control).

Biofilm development was evaluated using high resolution scanning electron microscopy and confocal laser scanning microscopy imaging (HRSEM and CLSM). HRSEM images depicted significantly less bacteria attached to the membranes exposed to the modified spacer, mainly scattered and in a sporadic monolayer structure *(Fig 2.)*.

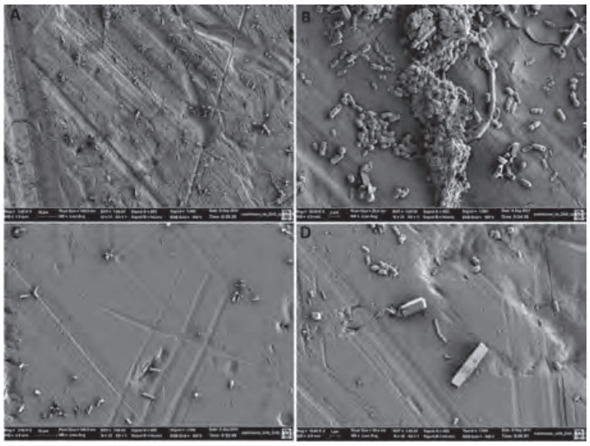


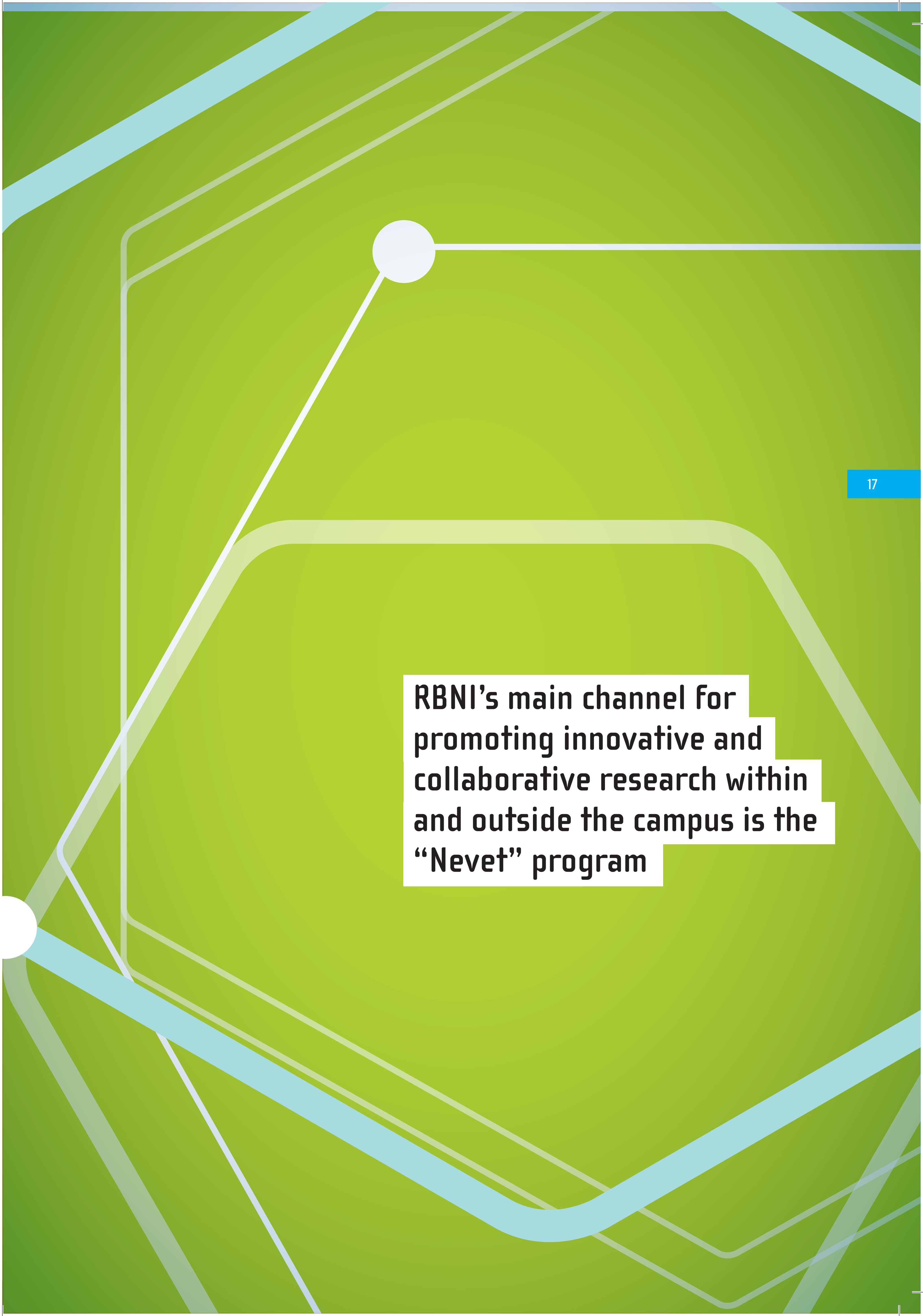
Figure 2. HRSEM micrographs of 200 kDa polysulfone ultrafiltration membrane adjacent to spacers after 50 hours of exposure to flow with 10^4 CFU.mL^{-1} *P. putida* S12. A,B: Membrane adjacent to an unmodified spacer (magnification x2K, x10K); C,D: Membrane adjacent to a modified spacer (magnification x2K,x10K).

RESULTS OBTAINED TO DATE

Biofilm on a membrane device operating in cross-flow mode could be controlled by means of an antibacterial spacer. The results are encouraging in terms of a potential generic technology for biofilm control in membrane systems. The use of “active” materials like ZnO seems to be a plus, while their placement within the filtration module (on the spacer or on the PSU membrane) needs to be investigated further.

FACILITIES

SEM/EDS, AFM, CLSM, EDAX



RBNI's main channel for promoting innovative and collaborative research within and outside the campus is the "Nevet" program

nevet

multidisciplinary
research
collaboration
within Technion

PROJECT

Nanostructuring of PEG-Fibrinogen Polymeric Scaffolds

Launch year:	2009
Principal investigators:	Prof. Dror Seliktar - *Technion IIT, Department of Biomedical Engineering* Prof. Havazelet Bianco-Peled - *Technion IIT, Faculty of Chemical Eng.*
Participating students:	3

SCIENTIFIC GOAL

Create nanostructures in poly (ethylene glycole)-Fibrinogen (PF) hydrogels for tissue engineering using self-assembled block copolymer micelles and understand the structure-property relationship associated with these nanostructures in cell culture applications.

ABSTRACT

Two methods for nanostructuring of PF hybrid scaffold were developed. One method is based on embedding Pluronic® F127 micelles in the hydrogels, while the other involves conjugating modified Pluronic® F127 molecules to fibrinogen to create a “smart” precursor molecule which can be further cross-linked. We studied the nanostructure, mechanical properties and interactions with cells of both systems. Our studies demonstrate that nanostructuring of PF scaffold provides an effective mean to control the properties of these hydrogels.

RESULTS OBTAINED TO DATE

This research focused on poly (ethylene glycole)-Fibrinogen (PF) hybrid scaffold for tissue engineering prepared by the cross-linking of PEGylated fibrinogen precursors molecules. We hypothesized that nanostructuring of PF scaffold would provide a mean to control both their physical properties and their interaction with cells. To examine this hypothesis we utilized the self-assembly tendency of the biocompatible amphiphilic block-copolymers poly(ethylene oxide)/poly(propylene oxide) (Pluronic®). The overall objective of this research was to study the structure-property relations in nanostructured PF hydrogels in order to gain an additional mean to control their properties.
Two methods of utilizing Pluronic® were explored: (1) embedding Pluronic® F127 micelles in the hydrogels (2) conjugating modified Pluronic® F127 molecules to fibrinogen to create a “smart” precursor molecule which can be further cross-linked.

In order to create PF hydrogels with embedded Pluronic® F127 micelles we developed methodologies for nanostructuring of PF hydrogels. The formation of partially ordered micellar structures, surrounded by PEG-fibrinopeptide network was verified and characterized using a combination small angle x-ray scattering *(Figure 1)* and transmission electron microscopy *(Figure 2)*. The mechanical properties were evaluated using rheology measurements and correlated to the nanostructure. The embedded block-co-polymer micelles increased the storage modulus of the as-prepared hydrogels, however their release, evaluated by swelling and Pluronic® release experiments, resulted in a dramatic decreased of the storage modulus over time. Cell behavior was investigated using cell seeding and outgrowth studies. Following preliminary results demonstrating that Pluronic® addition influences morphology, further studies used image analysis to quantify the interaction with cells. These experiments revealed that cell development depends in a non-linear fashion on the percentage of the added Pluronic® F127. In hydrogels with cross-linker addition, the cells spreading ability increased with increasing Pluronic® F127 concentrations.

Nanostructured scaffolds based on “smart” conjugated Pluronic® F127- fibrinopeptide (FF127) molecules were also developed. We investigated the mechanism for hydrogel formation via reversible (physical cross-linked) and irreversible (chemically cross-linked) routs. Small angle X-ray scattering and transmission electron microscopy were employed and model describing the network structure was suggested. It was found that the mesh size of the hydrogel was lower when the gel was crosslinked at low temperature, and as a result the hydrogel had high storage modulus at body temperature.

FIGURES

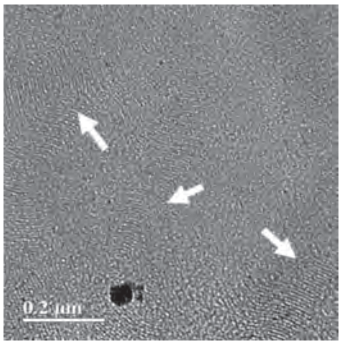


Figure 1. Cryo-TEM micrographs of PF hydrogel with 10% w/v Pluronic® F127. Arrow points to areas of ordered micells.

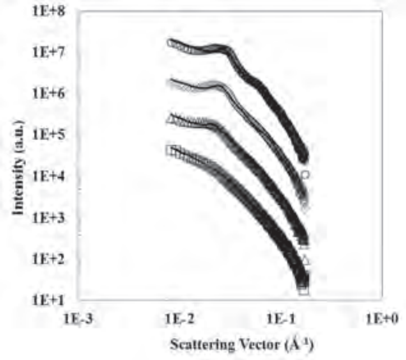


Figure 2. Normalized scattering intensity curves of PF hydrogels at 37°C with (□) 0% wt, (Δ) 3% w/v, (◊) 7% w/v and, (O) 10% w/v Pluronic® F127. The intensity curves were multiplied by factor for better visualization. Solid lines are fits to a theoretical model developed in this work.

FACILITIES

Small angle X-ray scattering, cryo-TEM, light scattering

nevet

multidisciplinary research collaboration within Technion

PROJECT

Nanoporous Responsive-Hydrogels Containing Magnetic Nanoparticles

Launch year:	2009
Principal investigators:	**Prof. Michael S. Silverstein** - *Technion IIT, Department of Materials Science and Engineering* **Prof. Ester Segal** - *Technion IIT, Department of Biotechnology and Food Eng.*
Participating students:	2

SCIENTIFIC GOAL

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

ABSTRACT

Hydrogels are three-dimensional cross-linked polymer networks capable of undergoing a reversible volume change in response to environmental stimuli. Such reversible volume changes make hydrogels excellent candidate materials for sensing, drug delivery, and microfluidics. The swelling rate is inversely proportional to the square of the characteristic dimension of the hydrogel. To reduce the response time to a usable level, it is therefore necessary to reduce the gel size dramatically. To answer this challenge, we suggest to synthesize highly porous hydrogel nanocomposites containing super paramagnetic nanoparticles. Iron oxide (Fe_3O_4) nanoparticles are incorporated in the synthesis scheme of N-isopropylacrylamide (NIPAM) through polymerization in the continuous phase of high internal phase emulsions (HIPE). Application of high frequency alternating magnetic fields (AMF) is used to generate heat in the magnetic particles and actuate the volume phase transition of the thermoresponsive poly (NIPAM) nanocomposite. The detailed effects of the synthesis conditions and AMF on the volumetric change during the phase transition of the nanocomposites are investigated.

RESULTS OBTAINED TO DATE

First, iron oxide nanoparticles (Fe_3O_4) are prepared by a chemical co-precipitation method. The Fe_3O_4 precipitate is re-dispersed in an aqueous medium using the surfactant sodium oleate. The morphology, size and size distribution of the nanoparticles are determined by transmission electron microscopy (TEM) and dynamic light scattering (DLS). The nanostructure of the resulting Fe_3O_4 is presented in Fig. 1a along with the corresponding electron diffraction pattern. The magnetic properties of nanoparticles are characterized using a superconducting quantum interference device (SQUID). Second, poly (NIPAM) hydrogels are synthesized using several polymerization approaches e.g., through polymerization in the continuous phase of high internal phase emulsions (HIPEs). The nanocomposites are prepared by adding the inorganic nanoparticles to the pre-gel solution at different stages and compositions. Fig. 1c depicts inner structure of poly (NIPAM)-containing iron oxide nanoparticles. The highly porous structure of the poly(NIPAM) is clearly observed, while the magnetic particle can detected by using backscattered electron images *(see Fi. 1d)* and cryo-TEM. The resulting nanocomposites show both thermosensitivity and magnetic properties. These nanocomposites are envisaged to be ideal for potential biomedical and micro/nanofluidics applications.

FIGURES

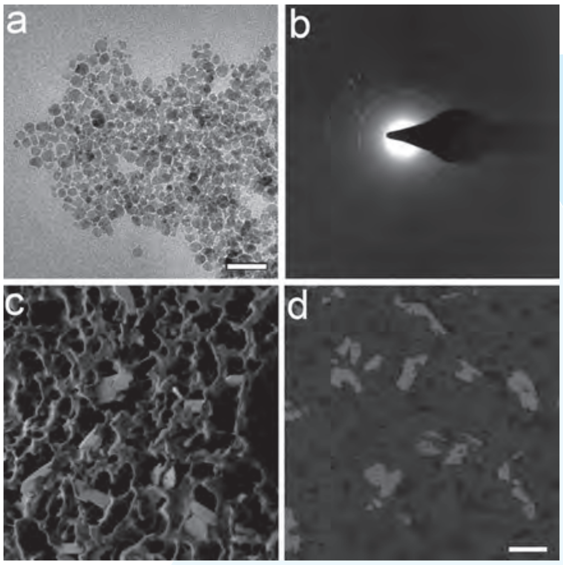


Figure 1. TEM micrograph, (a), and electron diffraction pattern (b) of as-synthesized iron oxide nanoparticles (bar is 50 nm). High-resolution SEM micrographs of nano-porous N-isopropylacrylamide hydrogel-containing iron oxide nanoparticles, (c) secondary electrons, (d) backscattered electrons (bar is 1 μm).

FACILITIES

Electron Microscopy Center of Soft Matter (Faculty of Chemical Engineering)

PROJECT

Self-excited Oscillations in NanoOptoMechanical Systems

Launch year: 2009

Principal investigators:
Prof. Eyal Buks - *Technion IIT, Department of Electrical Engineering*
Prof. Oded Gottlieb - *Technion IIT, Department of Mechanical Engineering*

Participating students: 1 postdoctoral scholar and 1 PhD student

SCIENTIFIC GOAL

Our main objective is to develop novel low power actuators, and mechanical sensors that exploit optomechanical instabilities for achieving ultra-high sensitivity.

ABSTRACT AND RESULTS OBTAINED TO DATE

We experimentally and theoretically study forced and self-excited oscillations of an optomechanical cavity, which is formed between a fiber Bragg grating (FBG) that serves as a static mirror and a freely suspended metallic mechanical resonator that serves as a moving mirror *(see Fig. 1)*. In the domain of small amplitude mechanical oscillations, we find that the optomechanical coupling is manifested as changes in the effective resonance frequency, damping rate *(see Fig. 2)*, and cubic nonlinearity of the mechanical resonator *(see Fig. 3)*. Moreover, self-excited oscillations of the micromechanical mirror are observed above a certain optical power threshold *(see Fig. 4)*. A comparison between the experimental results and a theoretical model that we have derived and analyzed yields a good agreement. The comparison also indicates that the dominant optomechanical coupling mechanism is the heating of the metallic mirror due to optical absorption.

FIGURES

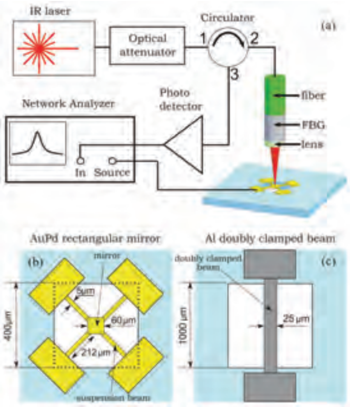


Figure 1. The experimental system. A graded index lens at the end of the optical fiber is used to focus the light on the mirror. A FBG located inside the fiber can serve as a second mirror to create a relatively high-finesse cavity at wavelengths that fall inside the Bragg region. Panels (b) and (c) exhibit the top views of the micromechanical mirrors employed in the experiments.

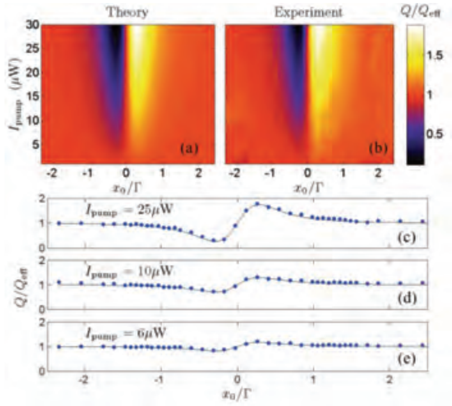


Figure 2. Changes in the effective quality factor as a function of the optical detuning and the optical power incident on the cavity.

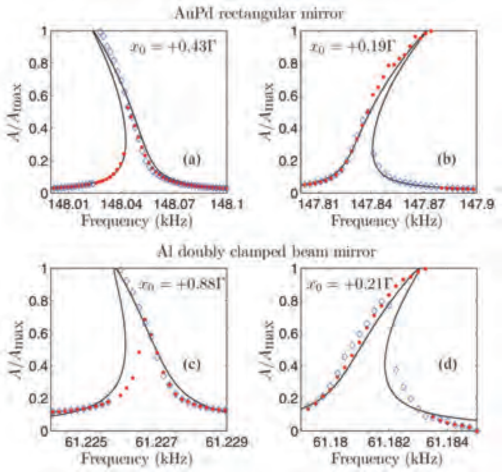


Figure 3. Changes in the small amplitude nonlinear behavior as a function of the optical detuning.

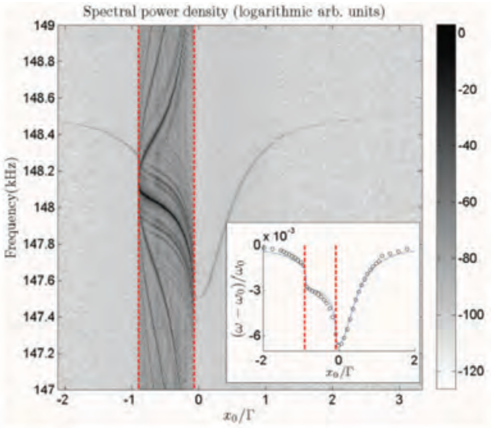


Figure 4. Spectral power density of the reflected optical power as a function of frequency and optical detuning. The region in which self-oscillations occur is denoted by dashed red lines. The thermal motion peak can be readily recognized outside this region.

FACILITIES

MNFU

PROJECT

Analysis of streaming potential phenomena

Launch year: 2009

Principal investigators:
Prof. Ehud Yariv - *Technion IIT, Faculty of Mathematics*
Prof. Itzchak Frankel - *Technion IIT, Faculty of Aerospace Engineering*

Participating students: Ory Schnitzer

SCIENTIFIC GOAL

Resolve the controversy surrounding streaming-potential phenomena in the thin-double-layer limit.

ABSTRACT

The proper modeling of the thin double-layer limit in these problems has been a matter of long-standing controversy, which was apparently resolved in the seminal paper of Cox (1997). In paper #1 we have shown a fundamental inconsistency in Cox's analysis, and provided the correct thin-double-layer model. Cox has apparently overlooked the intrinsic relation between the Hartmann and Peclet numbers in the limit of thin double layers. When using Cox's assumption of moderate Hartmann numbers, this linkage actually results in asymptotically large Peclet numbers. Owing to the dominant convection, the present analysis yields an asymptotic structure considerably simpler than that of Cox (1997): the electro-viscous effect now already appears at lower asymptotic order and is contributed by both Maxwell and viscous stresses. The present paradigm is illustrated for the prototypic problem of a sphere sedimenting in an unbounded fluid domain with the resulting drag correction differing from that calculated by Cox (1997). Independently of current matching, salt-flux matching between the Debye layer and the bulk domain needs also to be satisfied. This subtle point has apparently gone unnoticed in the literature, perhaps because it is trivially satisfied in field-driven problems. In the present limit this requirement seems incompatible with the uniform salt distribution in the convection-dominated bulk domain. This paradox is resolved by identifying the dual singularity associated with the thin-double-layer limit in motion-driven problems resulting in a diffusive layer thickness beyond the Debye layer.

The scaling relationship identified in paper #1 defines a one-family class of limit processes appropriate to the consistent analysis of this singular problem. In that paper the focus has been on the generic problems associated with moderate Hartmann number (and accordingly large Peclet number), where the streaming-potential magnitude is comparable to the thermal voltage. In paper #2 we considered the companion generic limit of moderate Peclet numbers and large Hartmann numbers, deriving the appropriate macroscale model wherein the Debye-layer physics is represented by effective boundary conditions. Since the induced electric field is asymptotically smaller, calculation of these conditions requires higher asymptotic orders in

analysing the Debye-scale transport. Nonetheless, the leading-order electro-viscous forces are of the same relative magnitude as those previously obtained in the large-Peclet-number limit. The structure of these forces is different, however, first because the small Maxwell stresses do not contribute at leading order, and second because salt polarization results in a dominant diffuso-osmotic slip. Since the salt distribution is governed by an advection–diffusion equation, this slip gives rise to electro-viscous forces that are nonlinear in the driving flow. The resulting scheme is illustrated by the calculation of the electro-viscous excess drag in the prototype problem of a translating sphere.

RESULTS OBTAINED TO DATE

1. *Streaming-potential phenomena in the thin-Debye-layer limit. Part 1. General theory*
   E. Yariv, O. Schnitzer and I. Frankel, Journal of Fluid Mechanics, 685 306-334, 2011
2. *Streaming-potential phenomena in the thin-Debye-layer limit. Part 2. Moderate Péclet number*s
   O. Schnitzer, I. Frankel and E. Yariv, Journal of Fluid Mechanics, 704 109-136, 2012

multidisciplinary research collaboration between Karlsruhe-Weizmann-Technion

PROJECT

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

Launch year: 2009

Principal investigators:

Prof. Ester Segal - *Technion IIT, Department of Biotechnology and Food Enginnering*
Dr. Ljiljana Fruk - *Universitaet Karlsruhe, Centre for Functional Nanostructures*
Dr. Michal Sharon - *Weizmann Institute of Science, Department of Biological Chemistry*

Participating students: 2

SCIENTIFIC GOAL

The long-term objective of this proposal is to develop a method for the characterization of the 20S-substrate proteome by using a multifunctional nanostructured SiO_2 scaffold. We propose to design and construct a biosensor-based micro-affinity purification method to recover peptide fragments for downstream proteomics analysis.

ABSTRACT

The characterization of proteolytic enzymes specificity is a formidable challenge due to the large number of proteins in a proteome, and minute/transient amounts of key substrates. In this work we report on a new platform for proteins screening based on a self-reporting porous Si nanostructure (PSi). A multifunctional PSi biosensor that can both monitor the enzymatic activity of minute samples and allow subsequent retrieval of the entrapped proteolytic products for mass spectrometry analysis is described. The biosensor is constructed by DNA-directed/reversible immobilization of enzymes onto a Fabry–Pérot thin film. We demonstrate high enzymatic activity levels of the immobilized enzymes (more than 80%), while maintaining their specificity. Mild dehybridization conditions allow enzyme recycling and facile surface regeneration for consecutive biosensing analysis. The catalytic activity of the immobilized enzymes is monitored in real time by reflective interferometric Fourier transform spectroscopy. The real-time analysis of minute quantities of enzymes (concentrations at least 1 order of magnitude lower, 0.1 mg mL^{-1}, in comparison to previous reports, 1 mg mL^{-1}), in particular proteases, paves the way for substrate profiling and the identification of cleavage sites. The biosensor configuration is compatible with common proteomic methods and allows for a successful downstream mass spectrometry analysis of the reaction products. The concept illustration (see Figure 1) summarizes the key steps in the assay. First, a minute sample of unknown protein/s is incubated with protease-modified PSi, while on-line optical monitoring of the reaction products is acquired using a simple CCD spectrometer set-up. Later, the entrapped peptides are recovered from the porous matrix for sequence analysis and identification by MS techniques. Given that, to date, the substrate degradome of hundreds of proteases remains unknown, we believe that such a platform will be of practical importance for substrate profiling. It should be emphasized that the presented generic platform can be tailored and applied for the study of different protein classes.

RESULTS OBTAINED TO DATE

The results are summarized in three publications:

1. Shtenberg G., Massad-Ivanir N., Moscovitz O., Engin S., Sharon M., Fruk L., Segal E., *Picking Up the Pieces: A Generic Porous Si Biosensor for Probing the Proteolytic Products of Enzymes*, Analytical Chemistry, 85, 1951-1956 (2013).

2. Shtenberg G., Massad-Ivanir N., Moscovitz O., Engin S., Sharon M., Fruk L., Segal E., *Biosensor based on DNA directed immobilization of enzymes into optically sensitive porous Si*, MRS Proceedings, 1569, 2013.

3. Shtenberg G., Massad-Ivanir N., Engin S., Sharon M., Fruk L., Segal E., *DNA-Directed Immobilization of Horseradish Peroxidase into Porous SiO2 Optical Transducers*, Nanoscale Res. Lett., 7(1), 443 (2012).

FIGURES

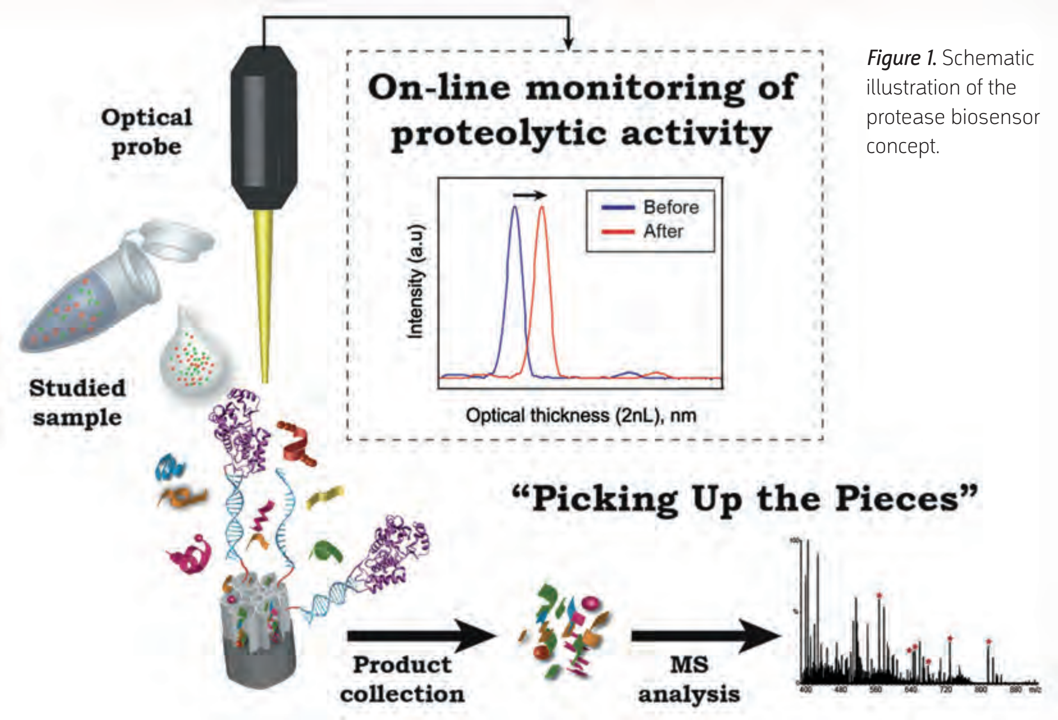


Figure 1. Schematic illustration of the protease biosensor concept.

FACILITIES

Electron Microscopy Center of Soft Matter (Faculty of Chemical Engineering)
Life Sciences and Engineering Infrastructure Unit

nevet

**multidisciplinary
research
collaboration
between Karlsruhe-
Weizmann-Technion**

PROJECT

Nano Oxide Perovskites with Enhanced Surface Exchange Kinetics

Launch year:	2009
Principal investigators:	Prof. Yoed Tsur - *Technion IIT, Department of Chemical Engineering* Prof. Igor Lubomirsky - *WIS* Ellen Ivers Tiffée and Claus Feldmann - *CFN*
Participating students:	1

SCIENTIFIC GOAL

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

ABSTRACT

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

RESULTS OBTAINED TO DATE

1. Synthesis of nano-sized powders with controlled size, has been done by combustion synthesis at Tsur's lab.
2. Characterization of the of the powders was done by size analysis, XRD, and SEM at the Technion.
3. Deposition of thin films on a suitable oxygen electrolyte gadolinia doped ceria-GDC has been done at CFN.
4. Investigation of the mechanical properties of the films and utilizing this knowledge for micro-machining of the films into self-supported structures for device prototypes has been performed in the WIS by Lubomirsky's group.
5. Measurements of impedance spectroscopy (IS) were carried out at the Ivers-Tiffée lab at CFN.
6. The analysis of the IS measurements has been performed in parallel at Ivers-Tiffée's and Tsur's labs, by two different analysis techniques. This also served to countercheck two novel analysis techniques for IS results based on evolutionary programming (Technion) and the distribution of relaxation times (CFN). This is, perhaps, the most important outcome of the current research for us, since it helped us clear some minor bugs in our program and to confirm that it works very accurately.

FACILITIES

XRD, light scattering

PROJECT

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

Launch year:	2009
Principal investigators:	Prof. Hendrik Hölscher - *Karlsruhe Institute of Technology (KIT), Institute for Microstructures* Prof. Oded Gottlieb - *Technion IIT, Dept. of Mechanical Engineering*
Participating students:	1 PhD student, 1 MSc student and 1 postdoctoral research associate

SCIENTIFIC GOAL

The main objective of this collaboration was to develop, validate, and analyze a continuum-based dynamical systems model for a hybrid scanning probe that would enable simultaneous imaging and force detection.

ABSTRACT

We investigate the nonlinear dynamics of a hybrid micro-cantilever for non-contact scanning probe microscopy both asymptotically and numerically in the weakly and strongly nonlinear regimes. We derive an initial-boundary-value problem for a hybrid multiple field sensor which is then reduced to a low-order dynamical system [1]. We employ a model-based asymptotic technique to validate the concept of a non-uniform step-like heterogeneity in the cantilever longitudinal direction *(Fig.1)* by comparison with documented experiments [2]. The analysis yields conditions for both 3:1 and 2:1 internal resonances that govern quasiperiodic energy transfer between the first and second structural bending modes of the hybrid sensor *(Fig. 2)*. Thus, quasiperiodic micro-cantilever response below a jump-to-contact orbital stability threshold *(Fig.3)* can enable multiple function sensing, and possible increased accuracy of time-varying forces via single frequency base excitation [3]. We then examine the robustness of the proposed internal-resonance based sensing technique to an extended model for an atomic force microscope (AFM) that simultaneously incorporates a controlled scan process [4]. Numerical integration of a three mode system reveal existence of non-stationary *(Fig.4)* chaotic-like dynamics for operation in a high vacuum environment. These results correspond to combination resonances that incorporate multiple frequency components which if properly decomposed may enable simultaneous multi-functional sensing of target samples with increased resolution.

RESULTS OBTAINED TO DATE

[1] Gottlieb, O, Hornstein S. and Holscher, H., *"Nonlinear dynamics and internal resonance based design of hybrid scanning probes for simultaneous imaging and force detection"*, Proc. IUTAM Symposium on Nonlinear Dynamics for Advanced Technologies and Engineering Design, 1-2, Aberdeen, UK, July 26-30, 2010.

[2] Hacker E., Saffury, J. and Gottlieb O., *"Nonlinear dynamics of hybrid cantilevers for scanning probe microscopy"*, Proc. 8th EUROMECH Solid Mechanics Conf., Graz, ESMC, p.1-2, July 9-13, 2012.

[3] Hacker, E. and Gottlieb, O., *"Internal resonance based sensing in non-contact atomic force microscopy"*, Applied Physics Letters, 101, 053106, 1-5, 2012.

[4] Hornstein S. and Gottlieb O., *"Nonlinear multimode dynamics and internal resonances of the scan process in non-contact atomic force microscopy"*. J. Applied Physics, 112, 074314, 1-16, 2012.

FIGURES

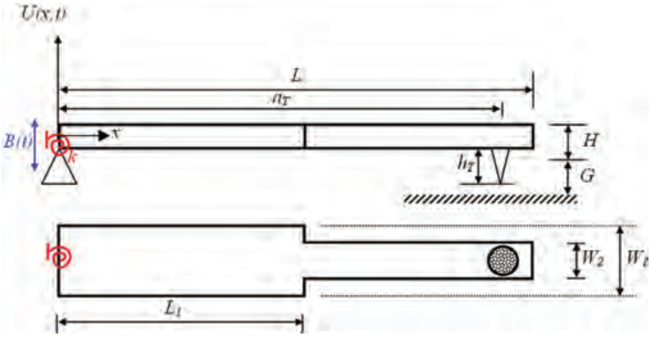


Figure 1. Definition sketch of a hybrid two-field AFM cantilever sensor (side and top views).

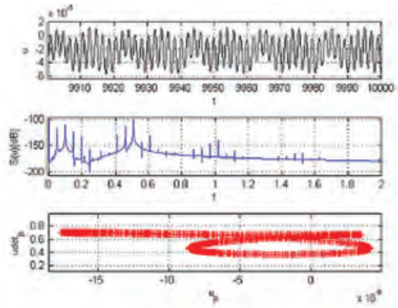


Figure 2. Quasiperiodic double-mode tip response of a hybrid two-field AFM operating in air near a 3:1 internal resonance (time history, power spectra and Poincare' map).

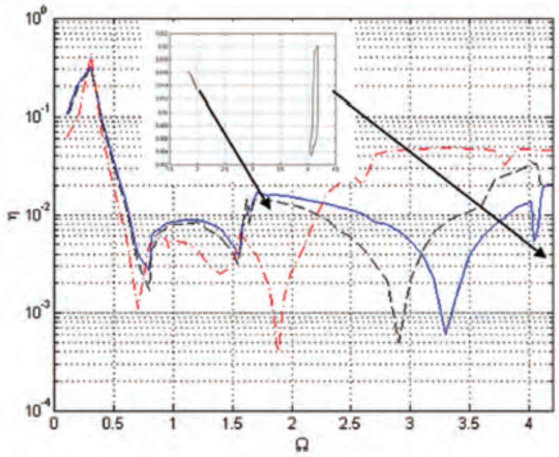


Figure 3. Jump-to-contact orbital stability thresholds for a hybrid AFM sensor (arrows denote regions of quasiperiodic response).

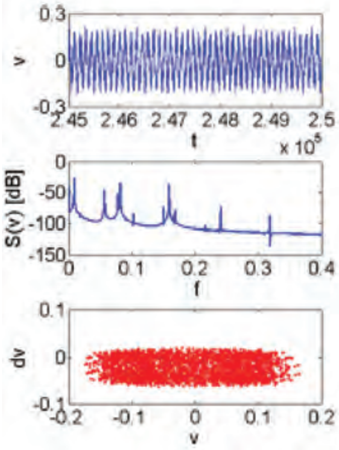


Figure 4. Non-stationary chaotic like triple-mode AFM tip response in vacuum near a 3:1 internal resonance (time history, power spectra and Poincare' map).

FACILITIES

XRD
Light scattering

PROJECT

Radiative Electron-Plasmon Interaction in Nanometrically Modified Metal Films

Launch year:	2009
Principal investigators:	**Prof. Dagmar Gerthsen** - *Karlsruhe Institute of Technology (KIT), Laboratory for Electron Microscopy,* **Dr. Hagai Cohen** - *The Weizmann Institute of Science, Department of Chemical Research Support* **Prof. Tsofar Maniv** - *Technion IIT, Schulich Faculty of Chemistry*
Participating students:	3

SCIENTIFIC GOAL

In this joint research we have been investigating key fundamental questions in the emerging field of photonics-plasmonics of subwavelength metallic structures by means of a swift, focused electron beam. We use electron energy loss spectroscopy (EELS) with a focused electron beam in the transmission electron microscope (STEM) as a complementary method to the standard far-and near-field optical probes, which is capable of probing both far-and near-electromagnetic field components on a subnanometer scale within micrno and submicron holes in metal films and outside small metallic particles.

As a long-term goal we strive for a bottom-up understanding of the mechanisms leading to the recently discovered phenomena of extraordinary optical transmission (EOT) through subwavelength apertures in metal films. This has been done by exploiting the efficient coupling of an electron beam to localized surface plasmon resonances and its remarkable capability, confirmed in our recent experiments, of directly exciting radiative waveguide resonances inside subwavelength cavities. As EOT through slit-arrays has shown much richer phenomenology than EOT through a single isolated slit we have been focusing in the current stage of the research on extending our methodology to systems of several neighboring slits.

ABSTRACT

Electromagnetic far- and near-field excitations of rectangular microholes in gold films are investigated by means of a focused electron beam. Radiative cavity modes, well below the surface plasmon (SP) frequency, are detected at exceptionally large distances from metal surfaces and are shown to be strongly enhanced at near-field regions of selected slit walls due to hybridization with metal-supported SP polaritons. The proposed enhancement mechanism of such hybridized modes, found here

to preserve the cutoff frequencies and symmetry characteristics of the pure waveguide modes, sheds light on the intriguing phenomenon of extraordinary optical transmission through subwavelength apertures in metallic films. Application of the same approach to slit arrays has revealed how EEL signals induced by cavity standing waves are dramatically enhanced, due to inter-slit coupling, the latter realized via the SPPs propagating on the film surface.

RESULTS OBTAINED TO DATE

A recent report on direct excitations of radiative cavity modes by a focused electron beam in single (sub)micrometer slits in thin Au films has shown remarkable similarities with the striking phenomenon of extraordinary optical transmission (EOT). Specifically, it was found that the detected cavity standing waves were strongly enhanced at near-field regions of selected slit walls due to their hybridization with surface plasmon polaritons (SPPs). A similar hybridization mechanism between cavity modes and SPPs was proposed recently in theoretical studies to yield EOT of light through subwavelength apertures in metallic films. Due to its high spatial resolution, scanning transmission electron microscopy (STEM) in combination with electron energy loss spectroscopy (EELS) is well suited for mapping the electrical field in (sub)micrometer slits and thus studying the hybridization between SPP- and vacuum-supported cavity modes. In the present work we reveal how EEL signals induced by cavity standing waves are strongly enhanced in slit arrays, due to inter-slit coupling, the latter realized via the SPPs propagating on the film surface.

Single slits with 180 nm x 900 nm size and slit arrays with different slit distances were prepared by focused-ion-beam milling. STEM-EELS was performed in an FEI Titan 80-300 microscope equipped with a Wien-type filter monochromator and a high-resolution Gatan Tridiem HR 865 imaging filter.

Low-energy signals were detected in single slits which are associated with the funda-mental mode of cavity standing waves with an energy of 0.5 eV and its higher harmo-nics. Slit arrays show a remarkable enhancement of the intensity of the cavity standing waves compared to single slits. The strong dependence of the intensity of the cavity standing waves on the slit distance is illustrated by the EEL spectra in Fig.1 where the fundamental mode at 0.5 eV is strongly enhanced for the smallest slit distance. We note that the 2nd harmonic at 1.0 eV is missing for symmetry reasons since the electron beam was positioned halfway between the narrow slit-walls (see the white crosses in the inset of *Fig.1*). Depending on the electron-beam position higher harmonics up to 12th can be excited.

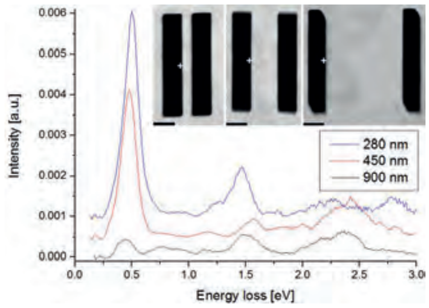


Figure 1. EEL spectra with loss intensity normalized with respect to the zero-loss intensity taken close to the separating metal bar in double-slit systems with different pitch values of 280, 450, and 900 nm. Inset: STEM images of three double-slit systems. Dark regions correspond to the slits. The white cross marks the position where the spectra were taken. The scale bar denotes 200 nm.

FACILITIES

Karlsruhe: An FEI Titan^3 80-300 microscope equipped with a Wien-type filter monochromator and a high-resolution Gatan Tridiem HR 865 imaging filter and focused-ion-beam milling with an FEI 400 STEM.

Technion: An FEI Titan 80-300 kV FEG-S/TEM. Focused-ion-beam milling performed at the FIB center.

PROJECT

Spatially Resolved Study of Nonlinearity in Superconducting Resonators

Launch year:	2009
Principal investigators:	Prof. Alexey Ustinov, *Department of Physics, Karlsruhe* Prof. Eyal Buks, *Department of Electrical Engineering, Technion IIT*
Participating students:	4

SCIENTIFIC GOAL

Studying nonlinearity in superconducting resonators.

ABSTRACT

Nonlinearity strongly affects the dynamics of superconducting planar devices. The wide range of applications of these devices has motivated an intensive research in this field. However, in many cases the underlying mechanisms have not been conclusively determined, and the experimentally observed behaviour has not been fully explained. Recent proposals to employ superconducting resonators for quantum data processing made the need to achieve a better understanding of these effects and their possible applications even more urgent. The current research aims at revealing the underlying mechanisms responsible for nonlinearity in superconducting thin films.

RESULTS OBTAINED TO DATE

Spatially resolved mapping of the response of a superconducting nanowire single photon detector (SNSPD) has been measured as a function of temperature. This experiment has been performed in the Technion lab during a visit of Philipp Jung, a member of the Karlsruhe group who has fabricated the SNSPD under study. Nonlinearity was investigated in superconducting resonators made of aluminum [1], and niobium or niobium-nitride [2-7]. Strong nonlinearity has been achieved by integrating weak links into the superconducting resonators of two types, nanobridges [3,7] and superconducting quantum interference devices (SQUIDs) [1,2-6]. A variety of nonlinearity-induced effects have been investigated including self-excited oscillations [1-3,7], intermode coupling [4], metastability [5,6] and intermittency [3]. Several applications based on superconducting nonlinear resonators have been developed including low-noise amplifiers [1] and sensitive detectors of electron spin resonance [7].

FIGURES

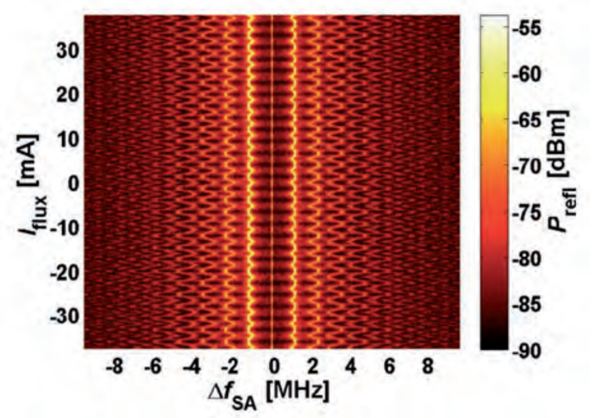


Figure 1. The dependence on magnetic flux of self-excited oscillation in a superconducting resonator with an integrated SQUID [2].

[1] Intermodulation and parametric amplification in a superconducting stripline resonator integrated with a dc-SQUID, Baleegh Abdo, Oren Suchoi, Eran Segev, Oleg Shtempluck, Miles Blencowe and Eyal Buks, Euro. Phys. Lett. 85, 68001 (2009).

[2] Self-oscillations in a superconducting stripline resonator integrated with a DC-SQUID, Eran Segev, Oren Suchoi, Oleg Shtempluck, and Eyal Buks, Appl. Phys. Lett. 95, 152509 (2009).

[3] Noise Induced Intermittency in a Superconducting Microwave Resonator, Gil Bachar, Eran Segev, Oleg Shtempluck, Steven W. Shaw and Eyal Buks, Euro. Phys. Lett. 89, 17003 (2010).

[4] Intermode Dephasing in a Superconducting Stripline Resonator, Oren Suchoi, Baleegh Abdo, Eran Segev, Oleg Shtempluck, Miles Blencowe and Eyal Buks, Phys. Rev. B 81, 174525 (2010).

[5] Metastability in a nano-bridge based hysteretic DC-SQUID embedded in superconducting microwave resonator, Eran Segev, Oren Suchoi, Oleg Shtempluck, Fei Xue and Eyal Buks, Phys. Rev. B 83, 104507 (2011).

[6] Hysteresis and intermittency in a nano-bridge based suspended DC-SQUID, Eran Segev, Oren Suchoi, Oleg Shtempluck, Fei Xue, Eyal Buks, Appl. Phys. Lett. 98, 52504 (2011).

[7] Nonlinear Induction Detection of Electron Spin Resonance, Gil Bachar, Oren Suchoi, Oleg Shtempluck, Aharon Blank, Eyal Buks, Appl. Phys. Lett. 101, 22602 (2012).

FACILITIES

MNFU

nevet

multidisciplinary research collaboration within Technion

PROJECT

Electrospun nanofibers encapsulating whole bacterial cells as an artificialbiofilm in a continuous fixed bed bioreactor for water treatment: Atrazine removal as a case study

Launch year: 2010

Principal investigators:

Prof. Michal Green - *Technion IIT, Faculty of Civil and Environmental Eng.*
Prof. Eyal Zussman - *Technion IIT, Faculty of Mechanical Engineering*

Participating students: 3

SCIENTIFIC GOAL

The objective of this research project is to develop a method for water treatment based on encapsulation of whole bacterial cell in electrospun polymeric nanotubes.

ABSTRACT

Bacterial cell encapsulation studies in soluble microtubes, although demonstrating potential for live cell encapsulation, have limited use for treating polluted water. Encapsulation of live bacterial cell using durable insoluble fibers must first overcome the potential cytotoxic effect of the organic solvents used in the insoluble polymer solution to the microbial cells. Core-shell nanotubes technology may offer the suitable solution since in the single-step co-electrospinning process, the potentially toxic organic phase consists of water- insoluble polymer (the outer shell solution) is separated from the aqueous phase (the core solution). To date, this co-spun microtube technology has been applied for pure enzyme encapsulation. Encapsulation of whole cells in electrospun polymeric nanotubes for water treatment is the focus of this proposal. Electrospun nanotubes encapsulating *Pseudomonas sp.* ADP cells as an artificial biofilm in a continuous fixed bed bioreactor for atrazine (herbicide) removal from polluted water, has been studied.

RESULTS OBTAINED TO DATE

- *P.*ADP cells were successfully incorporated in a core solution of polyethylene oxide (PEO) dissolved in water and spun with an outer shell solution made of polycaprolactone (PCL) and polyethylene glycol (PEG) dissolved in a chloroform and dimethylformamide (DMF). The encapsulated cells lost much of their atrazine removal activity upon encapsulation demonstrating only 15-30% atrazine degradation ability after 24hr under resting conditions. However, their removal activity could have been restored by the amendment of nutrients.

- The percentage of atrazine degrading cells upon encapsulation was estimated to be no more than 3%, calculated as the fraction of the degradation rate of free cells suspension at zero order. Shear and tensional pressures as well as the rapid evaporation upon electrospinning may have lead to a decrease in cell viability.

- Results indicated that the encapsulated cells activity could be recovered following a recovery time under growth conditions that was proven to be related to cell proliferation inside the microtubes.

- The ability of encapsulated *P.*ADP cells to sustain their atrazine removal without the addition of an external carbon source was shown in repeated batches under non-growth conditions and also in a fixed bed continuous reactor containing plastic carriers wrapped with core-shell electrospun nanotubes encapsulating *Pseudomonas sp.* ADP cells as an artificial biofilm.

FIGURES

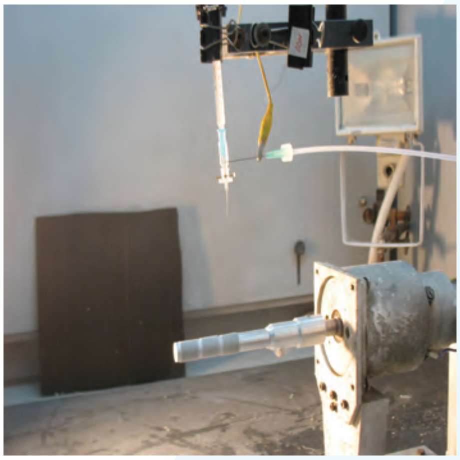


Figure 1. Electrospun System

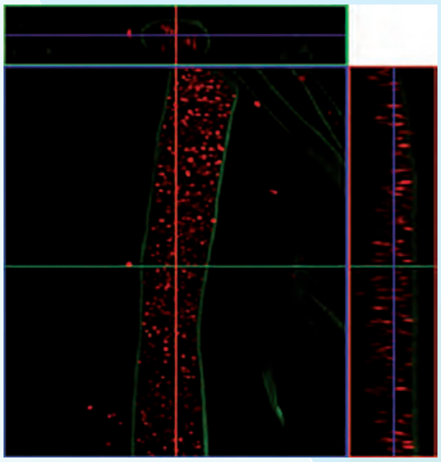


Figure 2. A florescent image of P. ADP embedded in electrospun microtube

FACILITIES

Confocal LSM 510 META Zeiss, Confocal Leica DM 5500Q, fluorescence microscope, Zeizz Axioskop 40, Phenom^{TM} electron microscope

PROJECT

The role of small grains in stability of nanocrystalline thin films

Launch year:	2010
Principal investigators:	Prof. Eugen Rabkin - *Technion IIT, Faculty of Materials Science and Eng.* Prof. Amy Novick-Cohen - *Technion IIT, Department of Mathematics*
Participating students:	2

SCIENTIFIC GOAL

Our aim in this project was to understand how factors such as grain geometry, surface diffusivity, relative grain boundary energy, and grain boundary mobility control the kinetics of surface topography evolution in the vicinity of small shrinking grains during grain growth in thin polycrystalline films. We hypothesized that pinholes which lead to the onset of film agglomeration are formed in direct proximity to certain of these small grains due to acceleration of the grooving process. The technological significance of the project is in gaining an understanding of the role of small grains in pinhole formation, in order to attain the ablity to prolong the lifetime of thin nanocrystalline films.

ABSTRACT

Stability of thin nanocrystalline films at elevated temperatures is often determined by formation of surface depressions (grooves) along grain boundaries and their triple junctions. Film agglomeration leads to deterioration of the film properties (i.e. loss of electrical conductivity) and represents a serious limitation in the design of various nano-devices. We hypothesize that the nucleation of a first pinhole, or pit, which signals the beginning of film breakdown into the array of isolated particles, occurs in the vicinity of certain small rectangular or triangular grains. Such grains are always present in thin films undergoing grain growth. The problem of grooving in a system of grain boundaries and triple junctions which move under the action of capillary forces is challenging and has received little attention in the literature. This project represents a concerted effort of two groups with different research backgrounds (Prof. Rabkin's group from the Dept. of Materials Science & Engineering and Prof. Novick-Cohen's group from the Dept. of Mathematics) to achieve a comprehensive understanding of the factors controlling film stability. The ultimate goal is to understand how various relevant parameters of the system (grain boundary mobility, surface diffusion coefficient, ratio of grain boundary, surface free energies, as well as film geometry) control stability of the film, and to determine parametric conditions optimizing film lifetime.

RESULTS OBTAINED TO DATE

Electron-beam deposition was used to deposit 100 nm-thick Cu film (4N purity) on c-plane oriented sapphire ((0001) single crystal α-Al_2O_3) substrate. The sample was annealed in a quartz-tube furnace under forming gas flow (Ar-10%H_2, 99.999% pure) at the temperature of 300 °C. We employed an interrupted annealing technique to follow the surface topography evolution of a particular region of the film after consecutive heat treatments (three treatments 10 min each). The measurements of surface topography were performed by AFM (Park Systems XE-70) operating in tapping mode.

A sequence of three AFM images of one and the same region in the film is shown in Fig. 1a-c. The deepest pit formed after the first anneal *(Fig. 1a)* reflects either a collapsed grain, or a small grain whose diameter is comparable to the lateral resolution of AFM (10 nm). This pit significantly deepens after the second anneal, yet it does not reach the substrate at this stage. At least two small grains in the vicinity of the deep pit which were present after the first anneal (marked by blue arrows in Fig. 1a) disappear after the second anneal. One of these grains is consumed by its larger neighbor, while the other one collapses. After the third anneal the deep pit transforms into a hole penetrating the film down to the substrate.

These experimental observations demonstrate that shrinking small grains may or may not produce holes in the film. We developed a mathematical model for surface topography evolution by surface diffusion in the vicinity of small shrinking grains. An idealized 3D system of 3 grains in various triangular geometries was considered. It was supposed that the migration rate of the grain boundaries is proportional to their curvature, while the external surfaces evolve by surface diffusion, i.e. their normal displacement rate scales as the surface Laplacian of curvature. We demonstrated that depending on the initial geometry of the system, small grains can either collapse, or lead to accelerated grooving at the quadruple point and pinhole formation, in qualitative agreement with the experimental observations *(see Fig. 2)*. In the latter case the rate of pinhole growth exceeds that of stationary grain boundaries. We argue that, since the grain growth is a statistical process, shrinking grains whose size and shape is suitable for simultaneous shrinking/hole formation can always develop in thin nanocrystalline films. Thus, we conclude that grain growth in thin films always promotes holes formation and film agglomeration.

FIGURES

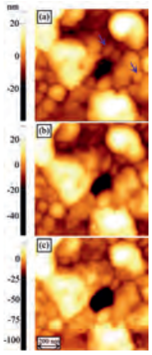


Figure 1. AFM images of a Cu thin film on sapphire after the first (a), second (b), and third (c) consecutive anneal for 10 min at 300 °C. Grains which disappeared after the second anneal without hole formation are marked by blue arrows in (a). The shallow grain transforms into a hole after the second anneal.

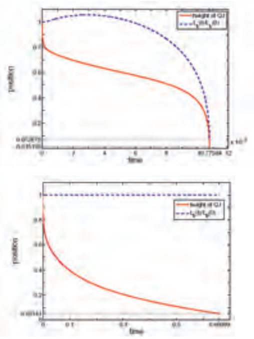


Figure 2. Time dependence of the relative height of the quadruple junction (red) and width of the smallest grain (blue) for a planar tiling with truncated triangular and hexagonal grains (a), and hexagonal grains of equal size (b). The initial volume fraction of the smaller grain is 1% and 33% in cases (a) and (b), respectively.

FACILITIES

The micro- nanofabrication unit at the Department of Electrical Engineering
The “Tamnun” Linux cluster

nevet

multidisciplinary
research
collaboration
within Technion

PROJECT

Using Dielectrophoresis and Nanobeads to Distinguish Stem Cells and Their Differentiated Progeny

Launch year:	2010
Principal investigators:	Prof. Shulamit Levenberg - *Technion IIT, Faculty of Biomedical Engineering* Prof. Gilad Yossifon - *Technion IIT, Faculty of Mechanical Engineering*
Participating students:	2

SCIENTIFIC GOAL

Developing dielectrophoresis-based microfluidic sorting device for characterizing stem cells and their differentiated progeny.

ABSTRACT

The relatively new field of stem cell biology is hampered by a lack of sufficient means to accurately determine the phenotype of cells. Cell-type-specific markers, such as cell surface proteins used for flow cytometry or fluorescence-activated cell sorting, are limited and often recognize multiple members of a stem cell lineage. Here we suggest using a complementary approach that would be less dependent on the identification of particular markers for the subpopulations of cells and would instead measure their overall character. It is based on a dielectrophoresis-based microfluidic sorting device for characterizing stem cells and their differentiated progeny. We intend to investigate which of the cellular nano-characteristics give rise to a shift in its dielectrophoretic (DEP) properties and at which stage it occurs during early embryonic stem-cell differentiation. Furthermore, an innovative multi-stage continuous-flow DEP-based sorting microfluidic device for embryonic stem cells based on their overall cell dielectric characteristics in the first stage and a sequential selective recognition of antigen-coated nano-particle in the second stage will be designed, fabricated and tested. Thus, exploiting the advantages of both techniques. It will be used to sort and analyze stem cell subpopulations to reveal their protein expression profile. In an era where embryonic stem cells are considered one of the most promising therapeutic approaches in cellular biology, this innovative nanotechnology-based technique to identify and sort unique embryonic stem-cell subpopulations can offer superior advantage over traditional methods.

RESULTS OBTAINED TO DATE

Paper published:
L. Rozitsky, A. Fine, D. Dado, S. Nussbaum-Ben-Shaul, S. Levenberg and G. Yossifon, *"Quantifying continuous-flow dielectrophoretic trapping of cells and micro-particles on micro-electrode array"*, Biomed Microdevices 15:859–865 (2013)

FIGURES

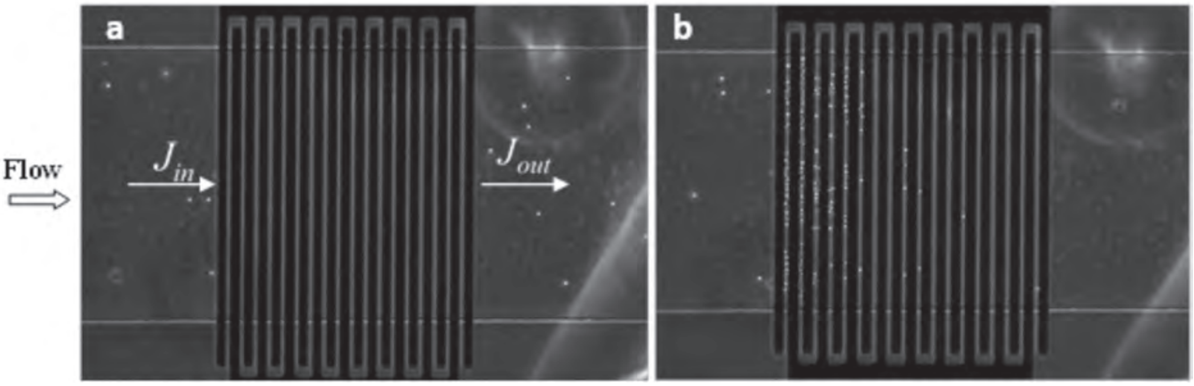


Figure 1. HNDF flowing across the interdigitated electrode array; (a) without electric field; (b) 5Vpp, 1MHZ exhibiting positive dielectrophoresis (p-DEP), which attracts cells to the electrode edges, with ~90% trapping.

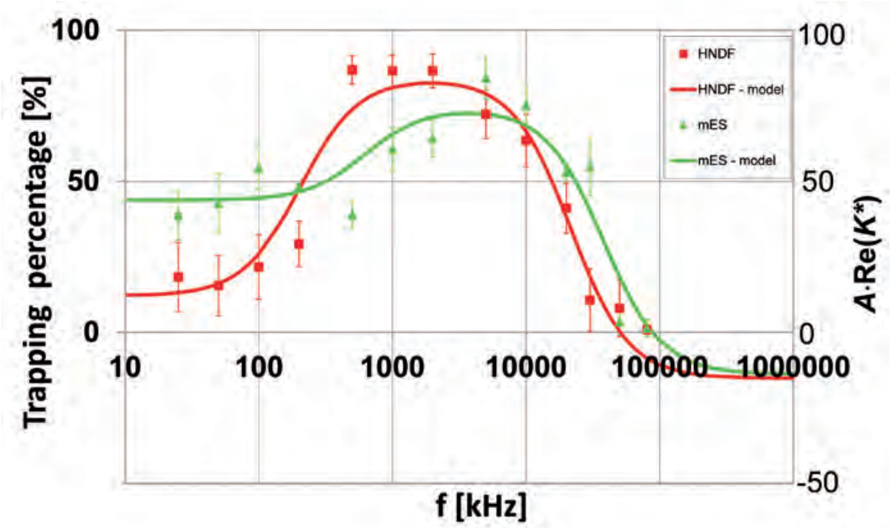


Figure 2. Fitting of the theoretical Clausius–Mossotti (CM) factor (solid lines) to the trapping percentage experimental data (markers; error bars—standard deviation) for various cell types.

FACILITIES

FACS, Microscopes, Clean rooms

PROJECT

Understanding of biomolecules-nanocrystalline interfaces at the molecular level: A key for the design of functional nano-composite materials

Launch year:	2010
Principal investigators:	Prof. Boaz Pokroy - *Technion IIT, Department of Materials Science and Engineering* Prof. Asher Schmidt - *Technion IIT, Schulich Faculty of Chemistry*
Participating students:	1

SCIENTIFIC GOAL

To study the interaction of amino acids on the surface of nanocrystalline calcium carbonate.

ABSTRACT

In the course of biomineralization organisms produce a multitude of biogenic crystals the most common of which is calcium carbonate. One of the most fascination characteristics of these biogenic crystals is the fact that within the crystal structure there are inracrystalline proteins, which lead to lattice strains. In this study we combined high-resolution synchrotron diffraction with solid state NMR and have studied the interaction single amino acids have with a calcium carbonate crystalline host.

RESULTS OBTAINED TO DATE

High-resolution x-ray measurements were conducted at the ID31 powder diffraction beam line at the ESRF. The experiments utilized a synchrotron light in a wavelength of 0.39479729 ± 0.000095 A. The XRD spectra obtained show that the reference sample is composed of the thermodynamically stable calcite phase, whereas the spectra that were obtained for the biomimetic samples contained reflections of the vaterite phase. The XRD spectrum of sample contained the vaterite phase, and was used as a reference for the further analysis. The XRD peaks that were obtained were fitted by using the Fityk software, and were compared to their theoretical peak positions according to the JCPDS. Interestingly, the XRD peaks of the biomimetic samples were all seen to be shifted in relates to their theoretical peak positions. The crystal lattice parameters of the biomimetic crystals, as well as these of the reference vaterite sample were calculated by applying the Reitveld refinement technique Rietveld, performed by the GSAS program. Lattice deformation of $\Delta c/c=2E\text{-}4$ was calculated for the biomimetic sample, that was precipitated in the presence of aspartic acid and $\Delta c/c=2E\text{-}5$ for sample in the presence of glutamic acid. Both biomimetic samples were isochronously annealed in-situ during the high resolution XRD measurement, using a precise blower heating system. Each sample was heated up to 500 °C in steps of 100 °C. Each annealing step lasted 30 minutes, and was followed by an XRD data collection at R.T. For the biomimetic samples, the lattice distortions were seen to relax with temperature, due tintracrystalline molecule destruction.

$CaCO_3$ precipitated in the presence of aspartic and glutamic acids were subjected to 13C and 15N solid state MAS NMR. The NMR study targets to characterize the forming vaterite polymorph and identify the role of the amino acids in directing the crystallization process and polymorph stabilization. In particular the NMR measurements are designed to elucidate whether the amino acids are incorporated within the $CaCO_3$ matrix, what are the structural characteristics of the contacting $CaCO_3$ environments and whether they change upon annealing (mild heating to 100 and 200 C).

Characterization of the occluded amino acids:

- The precipitates contain primarily $CaCO_3$ and small amounts of amino acids – Asp or Glu (n.a. samples).
- Higher quantity of Asp acid than Glu acid (~2-fold; 13C CP n.a. samples) is found occluded within the precipitate.
- 15N CPMAS spectra show peaks with chemical shift consistent with that of the amine/ammonium group. This peak is composed of several unresolved components, indicating the presence of different chemical environments of these species.
- For Asp, the amine/ammonium 15N peak is composed of three main components: ~5 ppm (broad), 14.5 ppm (160 Hz), and 17 ppm (110 Hz). The intensity of the 17 ppm peak increases upon heating, yet the other two peaks remain unchanged. This intensity increase may reflect changing CP dynamics, possibly due to the removal of adjacent water molecules.
- In addition to the amine/ammonium peak the 15N CPMAS spectra of all samples (Asp and Glu) show a peak at 75 ppm which is assigned to carbamate (RNHCOOR/H). This assignment is in accordance with literature reports that at acidic pH (~6), in the presence of HCO_3, amino acids react to yield carbamate.

Characterization of the $CaCO_3$ matrix and its interactions with the amino acids Crystalline $CaCO_3$:

- Vaterite is the major component of the precipitates (13C DEMAS 2400s).
- No molecular proximity of (crystalline) vaterite carbonates to an amine moiety of the amino acids was detected. If such proximity exists, it is below 1% (13C{15N} DE REDOR).
- Following each of the two heating steps (100 and 200 C), the 13C vaterite peaks narrow, reflecting higher structural uniformity, i.e. higher crystalline order (13C DEMAS 2400s).

Interfacial $CaCO_3$:

- 13C CPMAS spectra show broad (140 Hz) carbonate peaks at 169.5 ppm; this extent of heterogeneity is characteristic of disordered environments that maintain the short range order of the neighboring bulk polymorph (e.g. aragonite, calcite); vaterite in this case. The peaks of these ('disordered') carbonates in the CP spectrum originate from the adjacent (< 5Å) hydrogen atoms of entrapped water and amino acid molecules. Such carbonates may occur at exposed or buried interfaces as were identified in biogenic calcium carbonates.

FIGURES

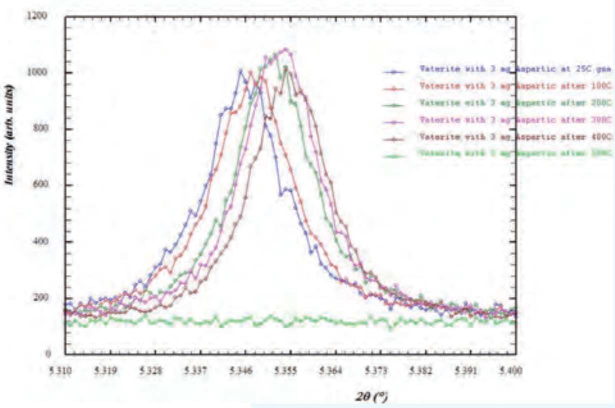


Figure 1. (001) Diffraction peak of biomimetic vaterite grown in the presence of 3mg/ml aspartic acid, taken at a wavelength of 0.3948 Å on the ID31 beamline of the ESRF after different annealing temperatures where applied. It can be seen that the diffraction peak shifts to a higher 2Θangle (lower d-spacing). This indicates shrinkage of the c-lattice parameter. In addition broadening of the diffraction peak is observed. (blue line: room temperature, red line: after 100 deg C for 30 min, olive line: after 200 deg C for 30 min, magenta line: after 300 deg C for 30 min, brown line: after 400 deg C for 30 min, green line: after 500 deg C for 30 min).

FACILITIES

Solid-state NMR

nevet

multidisciplinary research collaboration between Bar-Ilan University-Technion

PROJECT

Brownian motion of chiral nano objects in three dimensions

Launch year:	2010
Principal investigators:	**Prof. Boaz Pokroy** - *Technion IIT, Department of Materials Science and Engineering* **Prof. Eli Sloutskin** - *Bar-Ilan University, Faculty of Physics*
Participating students:	2

SCIENTIFIC GOAL AND ABSTRACT

Brownian motion of spheres is one of the oldest fields in modern physics. However, many of common molecules, viruses and cells have rather complex shapes, such that both the rotational symmetry and the chiral symmetry are broken. Typically, when the diffusion rate of these complex objects is to be estimated, their shape is approximated by that of an ellipsoid, which is a crude approximation. The Brownian motion of chiral objects, such as a simple circular helix, was never quantitatively studied by a direct experimental technique.

RESULTS OBTAINED TO DATE

As a part of our collaboration, supported by Nevet foundation, we employed real-time three-dimensional resonant-laser-scanning confocal microscopy to follow the Brownian motion of a fixed right-handed helically-shaped Leptospira interrogans (LI) bacterium[1], fluorescently-labeled for visibility and density-matched in a D_2O:H_2O mixture to avoid sedimentation and creaming. We extracted from our measurements the translational and the rotational diffusion coefficients of this bacterium (see Figure). We suggested a simple theoretical model, perfectly reproducing the experimental diffusion coefficients, with no tunable parameters. An older theoretical model[2], where edge effects of the diffusing spiral are neglected, significantly underestimates the observed rates of translation. Strikingly, the coiling of LI increases its rotational diffusion coefficient by a factor of 5, compared to a (hypothetical) rectified bacterium of the same contour length. Moreover, the translational diffusion coefficients would have decreased by a factor of ~1.5, if LI were rectified. The live LI bacteria have developed very effective mechanisms of translational motility, which make them able to move in both very viscous soils and liquids of very low viscosity. Yet, their ability to rotate is not very impressive, limiting their chemotactic motility skills. We demonstrate that, at least in a low-viscosity solvent, their poor ability to rotate is compensated by the increased Brownian rotational diffusivity due to the coiling of these species. We believe that our work, leading to a deeper understanding of the hydrodynamics of motion of common helix in a liquid has an importance for the development of racemic separation technologies, biomimetics and bacteriology.

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[1] A. Butenko, E. Mogilko, L. Amitai, B. Pokroy and E. Sloutskin, Langmuir 28, 12941 (2012).

[2] H. Hoshikawa and N. Saitô, Biophys. Chem. 10, 81 (1979).

FIGURES

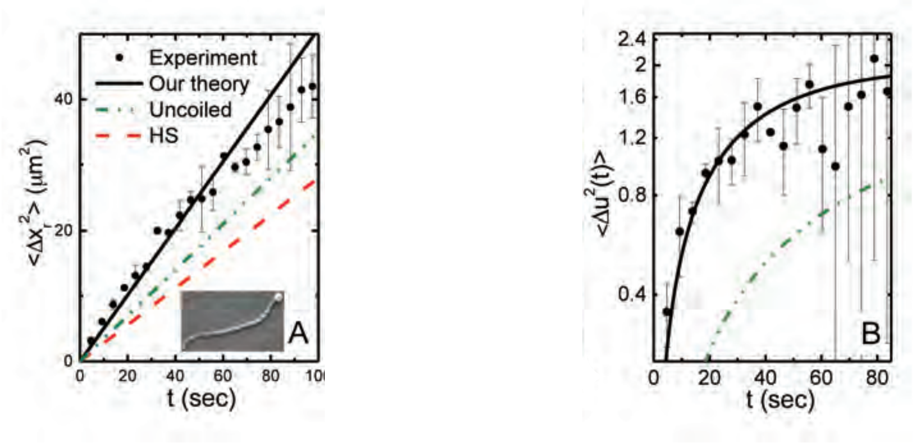


Figure 1. (A) The experimental mean square displacements of the LI bacterium (inset) in the direction of its major axis (solid symbols) are linear in time, exhibiting a normal diffusive behavior. The experimental data are perfectly reproduced by our theoretical model, with no free parameters, while being completely missed by the classical theory by Hoshikawa and Saito (HS) [2] (red dashes). A hypothetical uncoiled bacterium of the same size would have been diffusing slower in the on-axis direction (green dash-dotted line) and its rotational diffusion would have been slowed down, by a dramatic factor of 5, as demonstrated in ***(B)***, where the solid symbols are the mean square displacements of a unit vector, oriented with the long axis of the bacterium. Here, the solid line, passing through the experimental data, is obtained (with no free fitting parameters) from our theoretical model, and the dash-dotted green line describes the hypothetical rotational diffusion of an uncoiled bacterium of the same dimensions.

multidisciplinary research collaboration between Bar-Ilan University-Technion

PROJECT

Combination of a novel biolistic technology and nanostructured hybrids for controlled delivery of anticancer therapeutics

Launch year:	2010
Principal investigators:	Prof. Ester Segal - *Technion IIT, Department of Biotechnology and Food Engineering* Prof. Orit Shefi - *Bar-Ilan University, School of Engineering*
Participating students:	1

SCIENTIFIC GOAL

The objective is to develop a novel methodology for a biolistic delivery therapeutics to target cells at a tissue/cell resolution. Our delivery system employ a pneumatic capillary gene combined with therapeutics-carrying nanoporous Si-based microparticles.

ABSTRACT

A new paradigm for an effective delivery of therapeutics into cancer cells is presented. Degradable porous silicon carriers, which are tailored to carry and release a model anti-cancer drug, are biolistically bombarded into *in-vitro* cancerous targets. We demonstrate the ability to launch these highly porous microparticles by a pneumatic capillary gene gun, which is conventionally used to deliver cargos by heavy metal carriers. By optimizing the gun parameters e.g., the accelerating gas pressure, we have successfully delivered the porous carriers, to reach deep targets and to cross a skin barrier in a highly spatial resolution. Our study reveals significant cytotoxicity towards the target human breast carcinoma cells following the delivery of drug-loaded carriers, while administrating empty particles results in no effect on cell viability. The unique combination of biolistics with the temporal control of payload release from porous carriers presents a powerful and non-conventional platform for designing new therapeutic strategies.

RESULTS OBTAINED TO DATE

The results of this project are summarized in a recent publication in the journal *Scientific Reports* (open access).

http://www.nature.com/srep/2013/130826/srep02499/full/srep02499.html

FIGURES

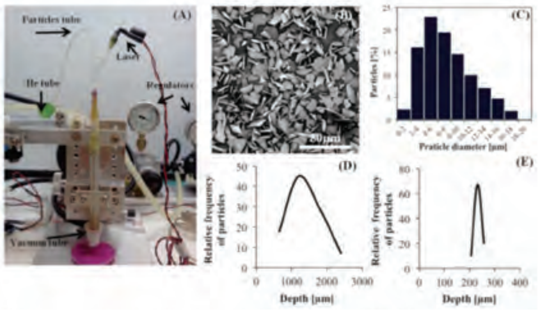


Figure 1. (A) The biolistic setup. Particles are loaded into the 'particles tube' (top left) in parallel to the laser inlet (top right) and are accelerated by controlled pressurized He. In the inner capillary tube the He stream with the particles merges with the gas flowing out the 'He tube'. An active vacuum suction (bottom left) diverts the stream of He from the gun nozzle so only the particles are emerging out of the nozzle and target the sample. (B) HR-SEM micrographs of porous Si microparticles. (C) Particle size distribution of porous Si carriers, showing particles ranging in size from 2 to 18 µm. (D) A typical distribution curve of the number of porous Si particles targeted to 2% agarose gel vs. the penetration depth (the number is normalized to total particles per shot), He pressures of 20/25 psi (particles/He tube)). (E) A typical distribution curve of the number of gold particles (1.6 µm) vs. penetration depth (similar bombardment conditions as in D).

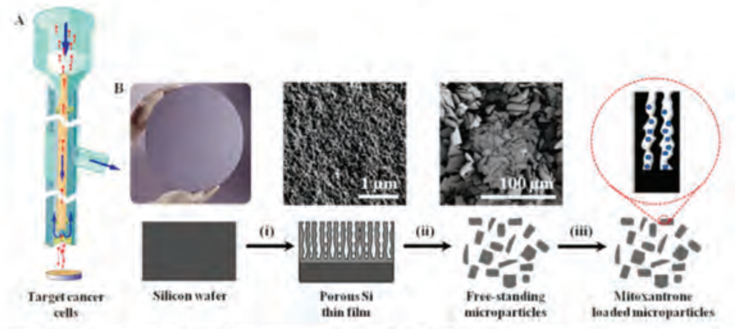


Figure 2. (A) A schematic drawing of the biolistic set up system. (B) A representation of the preparation route of the nanostructured porous Si carriers: (i) Si substrate is subjected to electrochemical etching for 225 s at 15 mA/cm2, followed by (ii) lift-off of the porous layer from the bulk Si and ultrasonication, to produce particles ranging in size from 2 to 18 µm, and (iii) the anti-cancer drug, MTX, is loaded into the particles by physically adsorption.

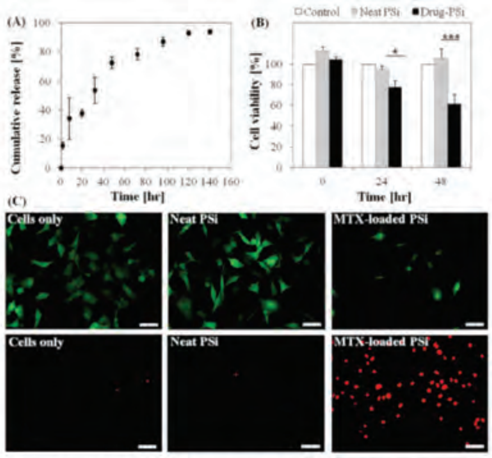


Figure 3. (A) Cumulative percent of drug release from porous Si particles into PBS (pH 7.4, 37°C) as a function of time. MTX release is expressed as percentage of the total MTX loaded. (B) Cell viability experiments over 48h; the normalized percentage of cells, compared to control plates (white bars), following the biolistic delivery of neat PSi (gray bars) and drug-loaded porous Si (black bars) immediately after delivery (0 h), and after 24 and 48h. (n=15). Data are the average percentage ± s.e.m of 4 independent experiments, *$p<0.01$, one-tail t-test. (C) Upper panels: MDA-MB-231/GFP cells 24 h after treatment, GFP Ab labeling *(green)*; *(left)* cells in a control, untreated culture, *(middle)* following delivery of neat PSi particles, and (right) after the delivery of MTX-loaded porous Si particles. Lower panels: PI labeling indicating dead cells *(red)* in *(left)* a control untreated culture, *(middle)* following delivery of neat PSi particles, and *(right)* after the delivery of MTX-loaded PSi particles. Scale bar = 50 µm for upper panels, 100 µm for lower panels.

FACILITIES

Electron Microscopy Center of Soft Matter (Faculty of Chemical Engineering)
Life Sciences and Engineering Infrastructure Unit

PROJECT

Studying DNA – Protein interaction with a novel optical method based on plasmonics nano-structures

Launch year: 2010

Principal investigators:
Prof. Erez Hasman - *Technion IIT, Department of Mechanical Engineering*
Prof. Yuval Garini - *Bar-Ilan University, School of Engineering*

Participating students: Nir Shitrit, Itay Bretner, Yuri Gorodetski, *Technion IIT*

SCIENTIFIC GOAL

Our main goal during this NEVET project was to develop a spin-optics device and to utilize optical spin Hall effect in nanostructure that allows to exert orbital angular momentum to manipulate DNA.

ABSTRACT

Observation of optical spin-Hall effects (OSHEs) manifested by a spin-dependent momentum redirection is presented. The effect occurring solely as a result of the curvature of the coupled localized plasmonic chain is regarded as the *locally isotropic* OSHE, while the *locally anisotropic* OSHE arises from the interaction between the optical spin and the local anisotropy of the plasmonic mode rotating along the chain. A wave-front phase dislocation was observed in a circular curvature, in which the dislocation strength was enhanced by the *locally anisotropic effect.*

RESULTS OBTAINED TO DATE

The human genome contains tens of thousands of genes that are coded along the DNA. These genes can be expressed only due to a large set of important proteins that can process the code and translate it, repair DNA damages, release tension and many more. Garini's group in BIU developed a method for studying DNA – protein interaction based on tethered particle motion (TPM). This method allows one to study the interaction on a single molecule basis with high sensitivity. TPM is based on an optical setup that observes the dynamics and conformations of a short DNA strand (Fig. 1). When proteins interact with the DNA, its structure and conformations are changing and these can be observed and analyzed.

In parallel, Hasman's group at the Technion developed unique nanoscale structures that perform a space-variant polarization manipulation accompanied with geometric phase *(spinoptics).* These devices are used, among other applications, for experimental research of vectorial singular optics and optical vortex carrying an orbital angular momentum.

We worked on a novel method to study DNA – protein interaction that is based on TPM and a nano-plasmonic device that would allow both to observe the DNA, measure its torsion as and apply on it torque. A nano-rod that is sensitive to light polarization will be attached to the end of the DNA. The polarized light scattering from the rod can be easily observed, and its position and angle can be detected with a precision that is better than 10 nm and 10^0. Moreover, by using the polarization properties of plasmonics nanostrucutre, torsional forces can be applied on the rod. These are important for studying a large set of proteins such as helicase and topoisomerase that rotates the DNA during its interaction with it. Understanding these mechanisms is therefore crucial and can lead to important biomedical applications.

Our main goal during this NEVET project was to develop a spin-optics device and to utilize optical spin Hall effect in nanostructure that allows to exert orbital angular momentum to manipulate DNA.

The spin Hall effect is a basic phenomenon arising from the spin-orbit coupling of electrons. The optical spin Hall effect (OSHE) – beam displacement and momentum shift due to the optical spin (polarization helicity) – was recently presented in propagating polarized light, in a plasmonic topological defect, and in a thermal antenna lattice. The effect was attributed to the optical spin-orbit interaction occurring when the light passes through an anisotropic and inhomogeneous medium.

Here, we present and experimentally observe the optical spin Hall effects in coupled localized plasmonic chains manifested by a spin-dependent momentum redirection. A straight chain of anisotropic nanoantennas whose local orientation varies along the chain axis was fabricated. Due to the collective interaction of the localized mode within the periodic plasmonic chain a spin-dependent beam deflection, with an opposite spin state relative to the incident beam (spin-flip), was observed in the momentum space. This effect is regarded as the *locally anisotropic* optical spin Hall effect (OSHE-LA) and it arises due to the interaction between the optical spin and the rotating anisotropic nanoantennas.

In light of these results one can address the question: Is it possible to observe the OSHE with isotropic nanoantennas? We demonstrated a similar spin Hall momentum deviation with isotropic antennas. This effect is regarded as the *locally isotropic* optical spin Hall effect (OSHE-LI) and it results from the interaction between the optical spin and the plasmonic *chain curvature*.

When the structure symmetry, or more explicitly the chain path, is circular, the corresponding conservation rule is for the angular momentum (AM). The AM of an optical beam can have two components: an intrinsic component associated with the handedness of the optical spin, and an extrinsic (orbital) component associated with its spatial structure. The OSHE-LI and OSHE-LA were observed in circular chains with isotropic nanoantennas and rotating anisotropic nanoantennas with an integer-fold rotation, respectively. The scattered spin-flip components were measured and a characteristic singular beam is clearly seen in the images which is a signature of orbital AM. The observed orbital AM in circular symmetry is a manifestation of a spiral phase front which is directly linked to the azymuthal spin Hall momentum deviation. Using the twin vortex sources interference method, we experimentally demonstrated that the orbital AM of the spin-flip component equals to twice of the incident spin for the OSHE-LI, and an integer-fold magnification is obtained for the OSHE-LA.

In summary, we observed the optical spin Hall effect in plasmonic coupled localized mode chains. Compared to the OSHE-LI in circular symmetry, the OSHE-LA provides an additional degree of freedom for optical AM generation, which may be utilized for spin-dependent plasmonic vortex driven nanomotors. The spin of photons may provide an additional degree of freedom in nanoscale photonics leading to a new branch in optics – spinoptics.

FIGURES

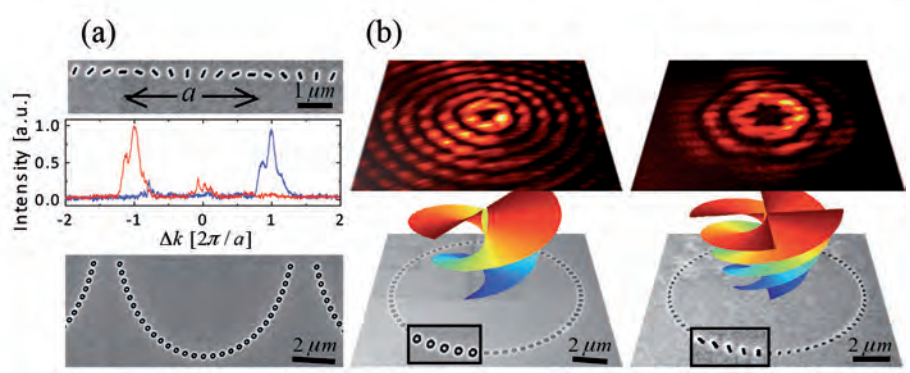


Figure 1. ***(a)*** The scanning electron microscope (SEM) image of a chain in which the orientation of the nanorods (anisotropic nanoantennas) varies linearly along the chain axis with a period of *a*, and the measured spin-dependent momentum deviation Δk for the OSHE-LA. The red and blue lines stand for incident right-handed (spin up) and left-handed (spin down) circularly polarized light, respectively. Bottom, the SEM image of a curved chain consisting of coaxial apertures (isotropic nanoantennas); the designed local orientation of the curved chain results in a similar spin Hall momentum deviation.

(b) The OSHE-LI and OSHE-LA for circular chains. The measured far-field intensity distribution of the spin-flip component scattered from a circular chain of coaxial apertures ***(left)*** and rotating nanorods with a double rotation rate ***(right)***; bottom, SEM images of the chains. The spin Hall momentum deviation is accompanied by a spiral phase-front with an orbital AM per photon of $2\hbar$ and $4\hbar$, for the OSHE-LI and OSHE-LA, respectively.

FACILITIES

Nanolithograpic process, etching, thin film coatings, SEM imaging, Focused Ion Beam (FEI Strata 400s dual beam system, Ga , 30 keV, 48 pA)

Nanoscience & Nanotechnology research at Technion

Nano-Photonics

Nanophotonics for advanced light-detection and sensing

Nano- Electronics

Nanoenergy

Nano-Mechanics & fluidics

Nano-Materials

NanoMed

PROJECT

Nonvolatile Memories Based on Metal Nano Particles

Launch year: 2011

Principal investigators:

Prof. Gadi Eisenstein - *Technion IIT, Electrical Engineering dept.*
Prof. Joseph Salzman - *Technion IIT, Electrical Engineering dept.*
Prof. Wayne Kaplan - *Technion IIT, Materials Science and Engineering dept.*

Participating students: 3

SCIENTIFIC GOAL

Controllability of the memory properties via optimization of the metal nano particles and the dielectric films.

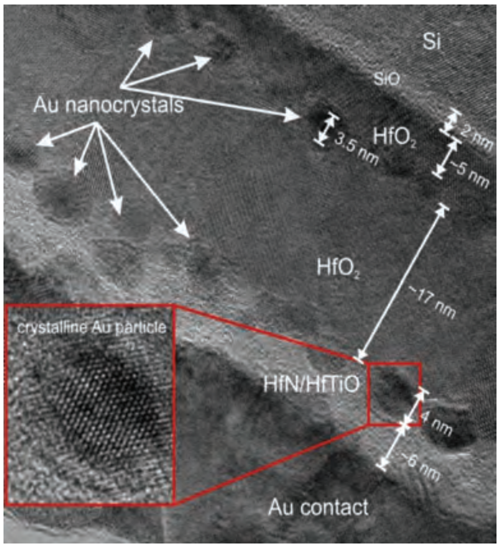
ABSTRACT

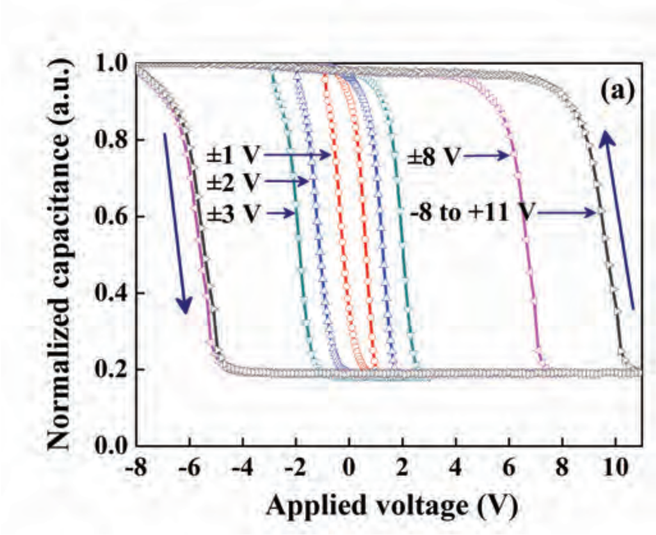
This research deals with controlled fabrication of metal nano particles and to correlate their properties to electrical characteristics of memory cells. The combination of high power analytical tools to characterize the metal nano particles and the dielectric films, and the special detailed electrical measurements performed on the completed devices, are a powerful approach which have led to many results.

RESULTS OBTAINED TO DATE

We have demonstrated several generations of memory cells while progressing in the understanding of the de-wetting mechanism which is responsible for the formation of the nano particles. Very large hysteresis loops were obtained with moderate drive voltages and long term (extrapolated to 10 years) retention properties were observed. The group has published 6 papers.

FIGURES





FACILITIES

MNFU, Electron microscopy center at the Materials Science and Engineering department

PROJECT

Detection of photons emitted from molecular nano-magnets

Launch year: 2011

Principal investigators:
Prof. Amit Keren - *Technion IIT, Faculty of Physics*
Prof. Sahar Rahav - *Technion IIT, Shulich Faculty of Chemistry*

Participating students: 1

SCIENTIFIC GOAL

Detection of photons emitted from molecular nano-magnets.

ABSTRACT

Photons emitted by transition between the discrete spin levels of molecular nano-magnets might obey the elementary condition for Dicke's super-radiance, namely, the wavelength is similar to the sample size. Super radiance is characterized by emission of short intense pulses of light when the molecule undergoes a transition from an excited state to the ground state. We investigated this possibility in the Fe_8 molecule where magnetization jumps are known to occur at discrete magnetic field values. We found by accident energy bursts each time the molecule undergoes a magnetization jump, confirming their quantum nature. A series of tests indicated that photons carry out the energy, and that indeed these photons obey the elementary conditions for super-radiance. We were able to deduce the photon energy from the known spin Hamiltonian of the Fe8 molecule. But, we were not able to measure the photon energy directly, or to confirm the super-radiance nature of the emission. This is the focus of the present "Nevet" proposal. Our aim in this new research direction is to determine the energy of photons emitted from nano-magnets and their angular distribution. This experimental observation will be contrasted with theoretical calculations based on super-radiance predictions.

RESULTS OBTAINED TO DATE

An experiment was constructed and we have indications of photon detection. More experiments are required to increase the confidence and test experiments have to be performed to rule out other sources of radiation.

FIGURES

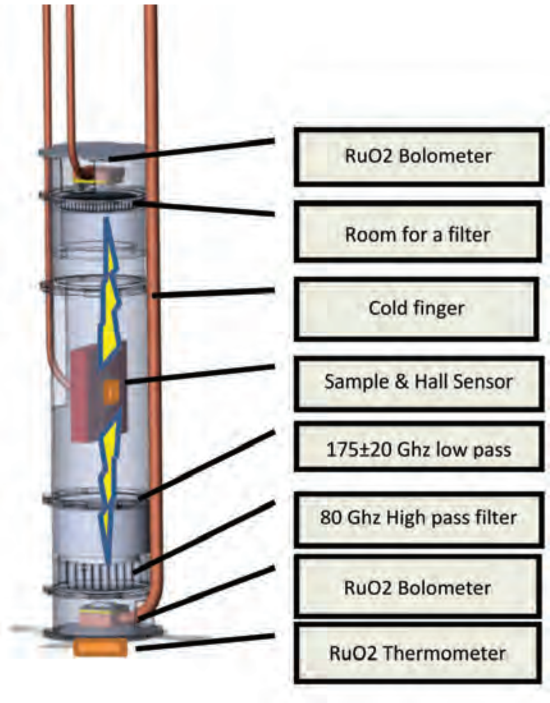


Figure 1. A sketch of the experimental apparatus. The yellow ribbons indicate photons.

Figure 2. A picture of the apparatus.

PROJECT

Nano-liter droplet mixer for early stage RNA transcription analysis in live e-coli cells

Launch year:	2011
Principal investigators:	Prof. Shulamit Levenberg - *Technion IIT, Faculty of Biomedical Engineering* Prof. Amit Meller - *Technion IIT, Faculty of Biomedical Engineering*
Participating students:	3

SCIENTIFIC GOAL

Using Nano-liter droplet mixer for early stage RNA transcription analysis in live e-coli cells.

ABSTRACT

Unlike DNA or proteins, the early stages of mRNA dynamics after its synthesis in the native cellular environment is poorly understood. To date the ability to directly visualize the spatiotemporal organization mRNA in live cells remains challenging primarily due to the lack of efficient low background mRNA labeling methods, and the ability to precisely control the onset of transcription. Recently Prof. Meller's group utilized mRNA-triggered protein complementation of green fluorescent protein (GFP) to critically improve its labeling in live E. coli cells. Using genetic engineering it was possible to externally trigger mRNA transcription and monitor its evolution over time. The increased sensitivity allowed us to observe an unexpected mRNA spatiotemporal patterns which signify mRNA organization in the live cells. However, our system did not allow the measurement of mRNA kinetics at its early stages of transcription, and in particular close to its onset. Notably, this limitation is not due to optical background, but rather is associated with the lack of system to precisely manipulate the cells' environment. This proposal is designed to remove this limitation by introducing a new microfluidic platform developed recently in Prof. Levenberg's group to initiate a biochemical reaction isolated in nanoliter volume droplets with elaborate control over reaction composition. The microfluidic platform offers the advantage of monitoring reaction kinetics seconds after its initiation, and thus can provide a unique opportunity to monitor and investigate mRNA transcription kinetics during one of the most biologically interesting periods; namely its onset.

RESULTS OBTAINED TO DATE

Paper submitted: *Nanodroplet array for multiplexed single-cell assays*

Shemesh J, Ben Arye T, Avesar J, Kang J.H, Fine A, Super M, Meller M, Ingber D.E and Levenberg S.

Stationary nanoliter droplet array with a substrate of choice for single adherent/non-adherent cell incubation and analysis. PNAS. In press (2014).

FIGURES

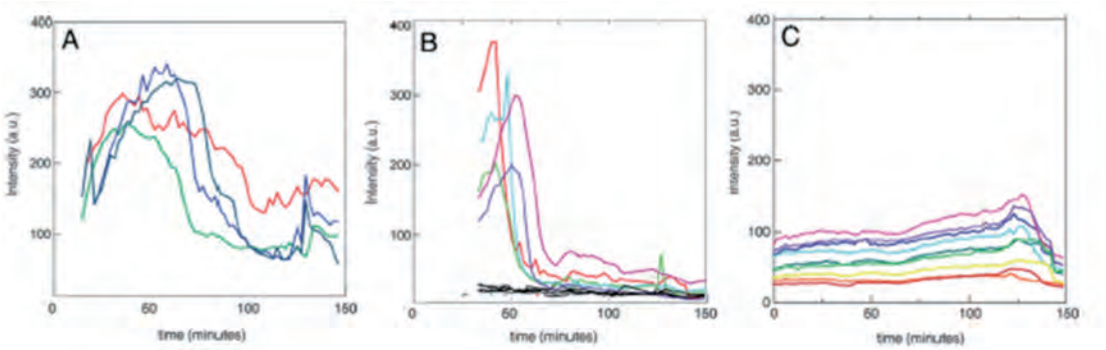


Figure 1. RNA kinetics in single E. coli cells upon induction with ATc. (A,B) Time course of total fluorescence in individual E. coli cells in two representative experiments. The t=0 time is defined as the moment of ATc addition to cells. Measurements are taken at 2-min intervals. The initial delay (15-20 min) is a technical limitation resulting from the handling of cells and the microscope. The droplet-based microfluidic system is expected to overcome this difficulty and detect early stages of transcription. (C) Control measurements using cells with expression of full-size EGFP.

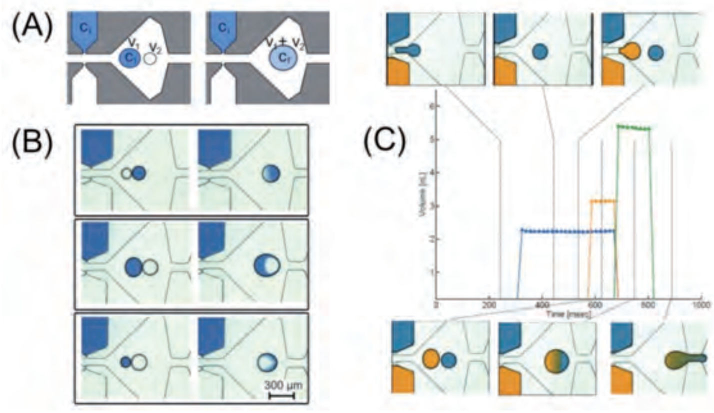


Figure 2. Schematic diagram of the device to control a droplet's composition. (A) Oil is flowing on the main (horizontal) channel, while two droplet generators (vertical channels) contain aqueous phases. Direction of the droplet flow is to the right. Two snapshots of the merging process are shown: before (left) and after (right) merging occurs. The dilution factor is calculated by the volumetric ratio of the two generated droplets. (B) micrograph showing three different merging events before (left column) and after (right column) merging. The volume, timing and order of the droplets are fully controlled by a piezoelectric actuator. (C) detection system based on real-time CCD-camera image analysis measures each of the initial droplet's (blue/orange) volumes as to deliver a final droplet with predefined volume and composition. As can be seen visually , mixing occurs rapidly in a time scales of seconds.

FACILITIES

Clean rooms, Microscopy

PROJECT

Understanding ssDNA sorting of chiral single-walled carbon nanotubes using molecular simulation

Launch year:	2011
Principal investigators:	Prof. Simcha Srebnik - *Technion IIT, Department of Chemical Engineering* Prof. Yachin Cohen - *Technion IIT, Department of Chemical Engineering*
Participating students:	2

SCIENTIFIC GOAL

Our primary objective is to reveal the origin of the sequence-dependent assembly of ssDNA on SWNTs, using scattering experiments and coarse-grained computer simulations.

ABSTRACT

The natural hybridization between complementary single-stranded DNA (ssDNA) chains can be used to organize material on the nanoscale, such as DNA scaffolding, self-assembly of colloidal crystals, and recently the sorting of single-walled carbon nanotubes (SWNTs). This fascinating registry between ssDNA and SWNTs and the ability for the first time to separate SWNTs with the same diameter but different chirality has prompted computational studies that aim to elucidate the interactions on the molecular level. We investigate how the properties of the DNA/SWNT complex are affected by changes in DNA sequence.

We concentrate on two ssDNA sequences (T_{12} and $(GT)_6$) and their dispersion of SWNTs approximately 1 nm in diameter. We analyze the dispersions using SANS, cryo-TEM, and coarse-grained molecular model.

RESULTS OBTAINED TO DATE

Aqueous dispersions of SWNT/ssDNA at 1:1 wt. ratio were prepared by sonication followed by centrifugation and extraction to remove amorphous CNT and precipitation catalyst, yielding black homogenous stable dispersions. Absorbance spectra of the dispersions revealed higher SWNT concentration in the T_{12} dispersion *(Fig. 1)*.

SANS experiments of SWNT-T_{12} and SWNT-(GT)6 were conducted at 100% D_2O, and after subtraction of background scattering from the ssDNA solutions show similar structural information for both complexes (Fig. 2). At very low angles the intensity seems to fit a q^{-1} power law relation to the scattering vector q, as expected for elongated structures.

Cryo-TEM imaging (Fig. 3) of the solutions revealed a large number of isolated and bundled dispersed SWNTs. These images suggest that $(GT)_6$ disperses the SWNTs to individual tubes to a greater extent than T_{12}, whose images show a greater tendency towards SWNT bundles. This result supports the absorption spectra that show higher concentration of dispersed SWNTs by T$_{12}$, i.e., more tubes are wrapped by a single ssDNA chain.

A coarse-grained model of the system was developed, using a parametrized 3-site model for the ssDNA bases and a smooth cylindrical surface representing the SWNT. As with the experiments, the model revealed differences between the heteropolymer and the homopolymer sequences. Simulations suggest that T12 absorbs in a more ordered conformation than (GT)$_6$. The bases of T$_{12}$ appear stacked both with the CNT and among themselves (Fig. 4), while (GT)$_6$ reveals no preferred orientation of the bases. On the other hand, (GT)$_6$ shows greater sensitivity towards the diameter of the tube, which might explain its ability to separate tubes towards individual ones. T$_{12}$ does not distinguish between bundles of SWNTs and individuals, allowing for a greater concentration of SWNTs in the dispersion, while (GT)$_6$ conformation is diameter dependent.

FIGURES

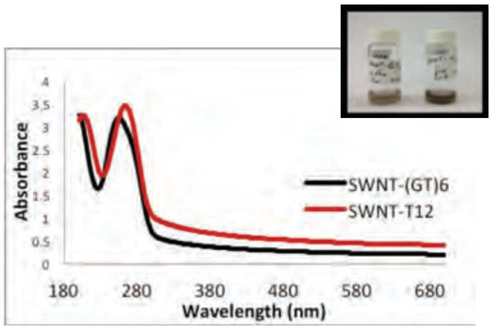


Figure 1. Absorbance spectra of SWNTs/(T)$_{12}$ *(red)* and SWNTs/(GT)$_6$ *(black)*. Inset shows photo of SWNTs/(GT)$_6$ *(left)* & SWNTs/(T)$_{12}$ *(right)*.

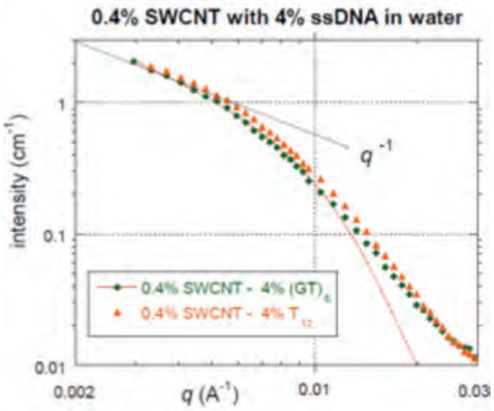


Figure 2. SANS patterns from 0.4% (wt.) SWCNT dispersions with 4% (wt.) ssDNA in 100% D2O, after background subtraction.

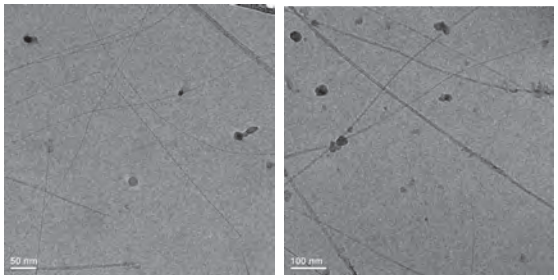


Figure 3. Cryo-TEM images of 0.4% SWCNT dispersion with 0.4% T$_{12}$ *(left)* and (GT)$_6$ *(right)*.

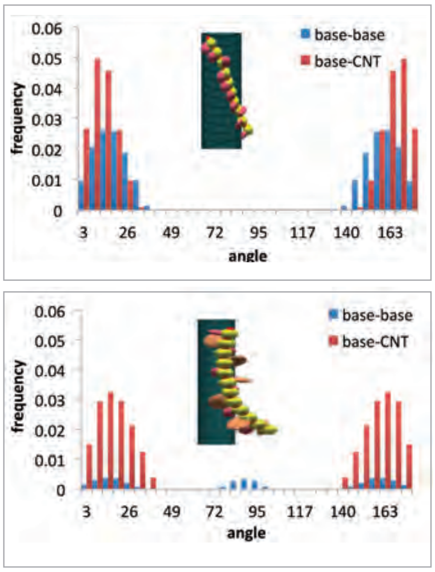


Figure 4. Simulation snapshots of flexible *(top)* vs. rigid *(bottom)* chains adsorbed to a cylindrical surface.

FACILITIES

TAMNUN – 1824 core lynux computing cluster

Gandalf – 24 core lynux server, Computational Polymer Physics Lab

Small-angle neutron scattering (SANS) at the KWS-2 Beamline of the Jülich Center for Neutron Science (JCNS) Outstation at the FRM II Reactor, Forschungs-Neutronenquelle Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Germany

PROJECT

Nanoscale magnetic ice - growth and characterization

Launch year: 2011

Principal investigators: Prof. Gil Alexandrowicz - *Technion IIT, Shulich Faculty of Chemistry*
Prof. Emil Polturak - *Technion IIT, Faculty of Physics*

Participating students: 2

SCIENTIFIC GOAL

Establishing a controlled procedure for delivering nuclear spin magnetization onto a surface using a molecular beam of ortho water and studying the magnetization lifetime of the deposited thin surface layers.

ABSTRACT

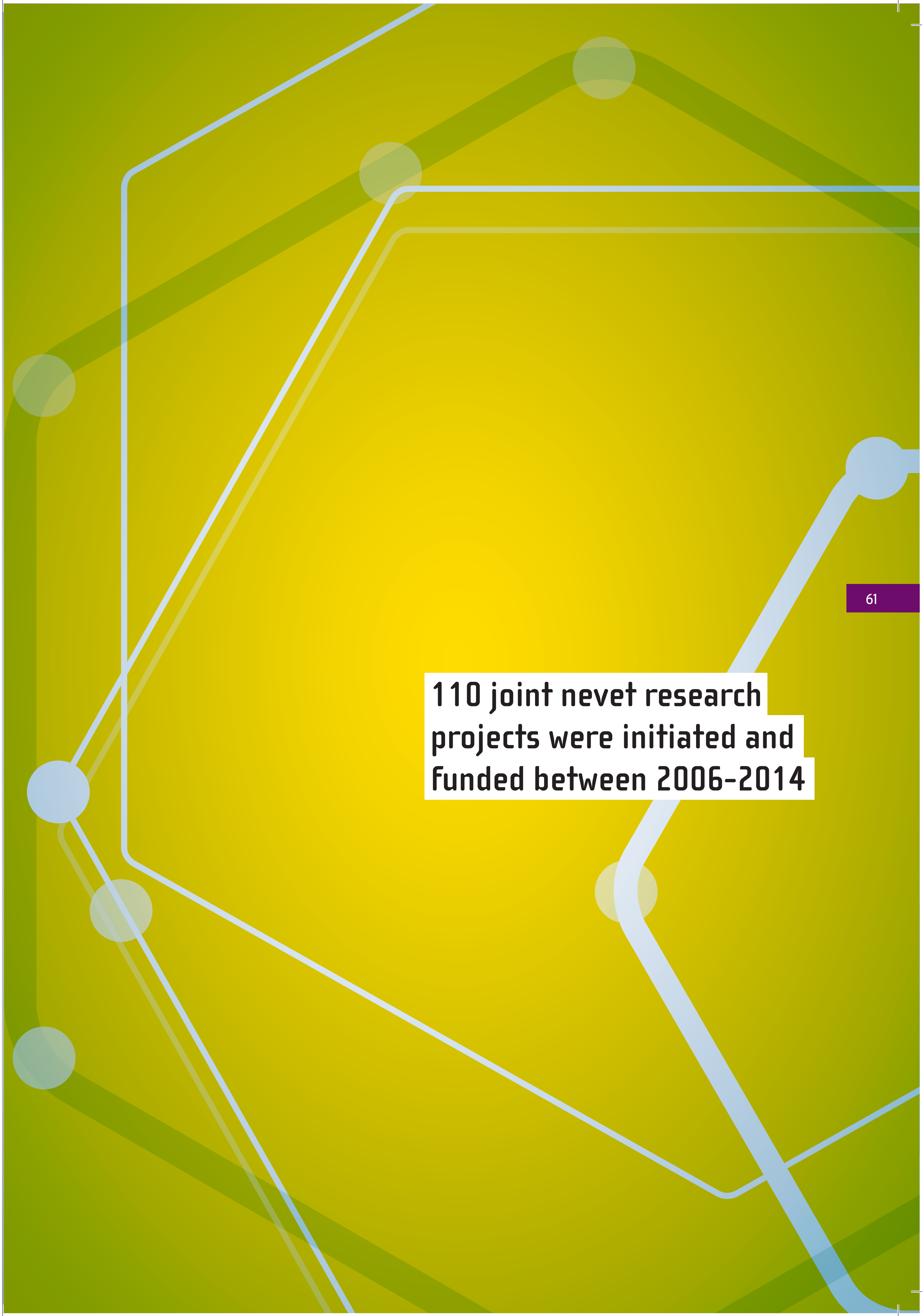
We propose to use a unique spin-selected molecular beam of water molecules in order to grow and characterize ultra-thin spin-polarized layers of water. These nano-scale “magnetic ice” structures represent a novel form of solid water where all the protons are initially in a pure nuclear spin state. We intend to study the spin polarization lifetime of these water structures under different physical conditions, providing rare experimental data of spin transfer mechanisms at surfaces. Studying the spin polarization lifetimes of these hyper-polarized surface systems may serve as a crucial step towards enhancing the sensitivity of proton NMR experiments and extending their applicability to surface systems with nanometer and even sub-nanometer thickness.

RESULTS OBTAINED TO DATE

Using magnetic focusing in a supersonic jet, a beam of “normal” H_2O molecules seeded in a Krypton carrier gas was shown to provide a source of water molecules that is highly enhanced in the ortho-H_2O (o-H_2O) nuclear spin isomer over the high temperature equilibrium 3:1 ortho:para ratio. Water from the magnetically focused beam was isolated and stored within a Kr matrix at 13K whereby the amplitude and lifetime of this strong nuclear spin polarisation were quantified spectroscopically. These results were recently published in Phys. Rev. A 86, 062710 (2012).

FACILITIES

The work was performed in our lab



110 joint nevet research projects were initiated and funded between 2006–2014

multidisciplinary
research
collaboration
within Technion

PROJECT

Atomic layer deposition of TiO_2 and ZnO onto and into polythiophene films: hybrids for photocurrent generation

Launch year:	2011
Principal investigators:	Prof. Gitti Frey - *Technion IIT, Department of Materials Science and Engineering* Prof. Boaz Pokroy - *Technion IIT, Department of Materials Science and Engineering*
Participating students:	1 student, 1 lab engineer

SCIENTIFIC GOAL

Developing low temperature ALD of metal oxides into highly porous and high surface-to-volume ratio polymer substrates.

ABSTRACT

In the latter years many attempts have been made to produce hybrid photovoltaic devices to replace the expensive conventional silicon-based photovoltaic devices. Despite extensive studies of these materials and devices there are as yet some cardinal open questions such as the discrepancy between the models predicting spontaneous (organic) charge generation at hybrid interfaces with suitable band misalignment, and the actual poor device performance. Herein we suggest revisiting this fundamental subject and investigating the mechanism of charge generation at conjugated polymer-metal oxide interfaces. More specifically, we propose to determine the correlation between the interfacial properties such as proximities, composition and interactions, with the exciton dissociation process. We suggest combing both PI's different, but complementing expertises to try and answer these important scientific questions by developing low temperature ALD into highly porous and high surface to volume ratio polymer substrates, as well as high resolution structural characterization of the organic/inorganic interface. These well-defined hybrid structures will allow investigating exciton dissociation at conjugated polymer-metal oxide interfaces prepared by ALD.

RESULTS OBTAINED TO DATE

We have studied the ALD of TiO_2 from a TTIP precursor into the surface of two conjugated polymers, MEH-PPV and P3HT, as a function of deposition temperature: 130, 200 and 300°C. XPS and HRSEM analysis revealed the presence of TiO_2 on the surface of P3HT, but not on MEH-PPV. Moreover, the HRSEM images showed TiO_2 islands but not full coverage of the polymer surface. Generally the amount of TiO_2 on the surface increases with temperature showing higher density of islands on the surface. Our overall conclusion was that indeed ALD can be used to deposit metal oxide on conjugated polymers; however the conditions such as temperature, humidity and polymer surface chemistry must be controlled.

FIGURES

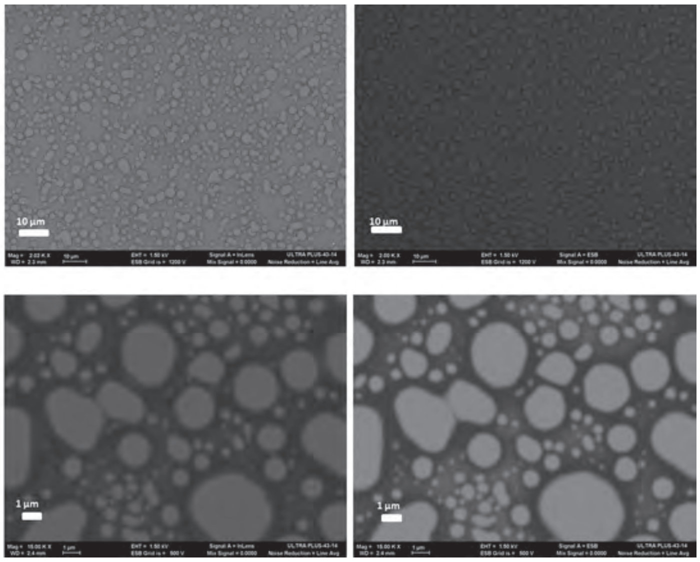


Figure 1. backscattered (left), and secondary (right) HRSEM top view images of TiO_2 islands (bright domains) on P3HT (dark background) deposited at 130 °C (top row) and 300 °C (bottom row).

FACILITIES

ALD system (Pokroy lab)
Spectrophotometer (Frey lab)
Scanning Electron Microscope (MIKA)
Elipsometer (PV lab)
XPS (Solid State Institute)

PROJECT

Optical Detection of Bacteria via Peptide-Mimetic Antimicrobial Compounds Tethered to Nanostructured Porous Si Hybrids

Launch year:	2011
Principal investigators:	Prof. Ester Segal - *Technion IIT, Department of Biotechnology and Food Eng.* Prof. Amram Mor - *Technion IIT, Department of Biotechnology and Food Eng.*
Participating students:	2

SCIENTIFIC GOAL

The main aim of this project is to develop a label-free optical biosensing platform for rapid and quantitative bacteria detection. The biosensor is based on a nanostructured porous Si (PSi) scaffold, which is used as the optical transducer, conjugated with peptide-mimetic antimicrobial compounds (as the receptor entities).

ABSTRACT

The development of robust and portable biosensors for rapid detection of pathogenic bacteria could have a profound impact in many areas ranging from water quality monitoring to pharmaceutical applications. The proposed project aims to address limitations associated with current detection methods, which are either laborious and/or time consuming and lack the ability to detect microorganisms in "real-time" and outside the laboratory environment.

A label-free biosensor based on the integration of a synthetic peptide-mimetic capture probe with a nanostructured PSi optical transducer is designed and constructed. Synthetic peptide-mimetic copolymers, termed OAQs, are a novel group of antimicrobial compounds, composed of oligomers (O) of acylated (A) charged residues (Q). Herein, a specific OAQ (oligomers of acylated lysines) sequence, termed as $K\text{-}7\alpha_{12}$, is synthesized and conjugated to the PSi. Exposure of these OAQ modified-PSi to the target bacteria will result in a "direct-bacteria-capture" onto the biosensor surface. These binding events induce predictable changes in the reflectivity spectra of the biosensor and can be continuously monitored using a simple photoelectric device.

OAQs offer several key advantages over antibodies, in terms of cost-effective development process, high environmental stability and performance. Exposure of these OAQ modified-hybrids to the target bacteria will result in a "direct-bacteria-capture" onto the biosensor surface. These binding events induce predictable changes in the reflectivity spectra of the biosensor and can be continuously monitored using a simple photoelectric device. The suggested biosensing concept offers significant advantages in comparison to existing technologies in terms of speed, sensitivity, and cost of measurement, as well as simplicity, and portability of the system. Thus, we expect that knowledge gained in this preliminary study will aid the rational design of improved biosensors.

RESULTS OBTAINED TO DATE

Porous Si films are fabricated by anodization followed by thermal oxidation and silanization, to introduce thiol groups onto oxide surface. Next, the peptide K-7α_{12} is immobilized onto the surface via the terminal carboxyl group using carboimide chemistry. The attachment of the peptide to the PSi is confirmed by ATR-FTIR spectroscopy and confocal microscopy, using fluorescein-labeled peptides.

The peptide-immobilized PSi biosensors are exposed pre-sonicated *E. coli* O416 suspensions at different concentrations. The optical reflectivity spectrum of the PSi nanostructure displays Fabry–Pérot fringes characteristic of thin-film interference, enabling direct, real-time observation of bacteria attachment within minutes. The optical reflectivity changes observed are proportional to the bacteria concentration; i.e., smaller changes in intensity for lower bacteria concentrations. After biosensing experiments, the PSi are studied by high-resolution scanning electron microscopy in order to confirm that the intensity changes result from bound species. Indeed, the bacteria cells debris are found to be bound to the biosensors surface. Figure 1 depicts a single intact bacteria cell captured onto the PSi biosensor surface. The current limit of detection of the system is 10^3 CFU mL^{-1} within several minutes.

FIGURES

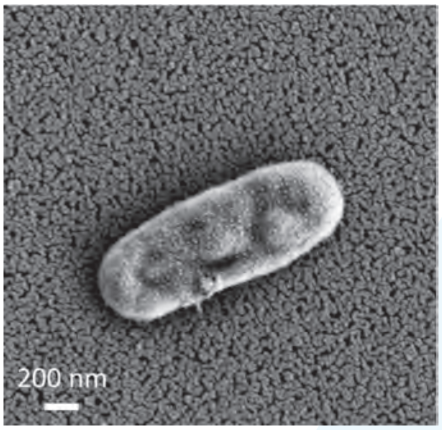


Figure 1. High-resolution scanning electron micrograph of an *E. coli* cell captured on the surface of a porous Si optical transducer.

FACILITIES

Electron Microscopy Center of Soft Matter (Faculty of Chemical Engineering)
Life Sciences and Engineering Infrastructure Unit

PROJECT

Quantitative study of nanoparticles targeted to cancer cells using reflectance confocal microscopy *in vivo*

Launch year: 2011

Principal investigators:

Prof. Dvir Yelin - *Technion IIT, Faculty of Biomedical Engineering*
Prof. Rachela Popovtzer - *Bar-Ilan University, Department of Biomedical Engineering*

Participating students: 2

SCIENTIFIC GOAL AND ABSTRACT

Recently, various types of targeted nano-probes have been developed for optical molecular imaging of cancer, including quantum dots, fluorescent particles, and gold nanoparticles. These studies have provided strong evidence that nanoparticles accumulate in vivo on the tumor; however, there are almost no reports regarding the number of nanoparticles that bind per cell, their accumulation rate, as well as their spatial distribution on the cells' surfaces and throughout the tumor. In this research, we propose to use a novel reflectance confocal microscopy apparatus to quantitatively investigate the amount and distribution of gold nanoparticles that selectively target to cancer biomarkers, on a single cell level. This quantitative information is essential, and can significantly affect basic cancer research and its medical applications.

RESULTS OBTAINED TO DATE

Aim 1: An experimental protocol for the optimization of SECM for imaging gold nanoparticle was established. A tissue phantom that mimics the optical properties of tissue labeled with gold nanoparticles was designed and prepared for imaging, having maximum penetration depth into the sample while maintaining sub-cellular 0.8 μm resolution, as well as real-time imaging rates of two frames per second, large field of view, and high signal-to-background ratio. The system's ability to detect various concentrations of nanoparticles, either spheres or rods, was optimized by adjusting its optical components and scanning parameters.

Aim 2: Our mouse model implanted with human squamous cell carcinoma (SCC) head and neck cancer was intravenously injected with immuno-targeted gold nanoparticles. Before and immediately after injection, the tumor region was imaged using our two-photon microscope with a large penetration depth, identifying nanoparticles that were accumulated in the tumor *(Fig. 1)*. Special attention was devoted for identifying the particles diffused through the blood vessels walls and following their distribution within the tumor.

We have found that the injected gold nanoparticles have found their way to the tumor, but their distribution throughout its volume was highly non-uniform; nanoparticles were abundant within several tissue regions *(Fig. 1, top panels)*, while numerous blood vessels throughout the tumor were found filled by gold, with a completely particle-free surrounding tissue *(Fig. 1, lower panels)*. Future research will be dedicated to better quantify and understand these results, and correlate them to known processes of blood perfusion within malignant tissue.

FIGURES

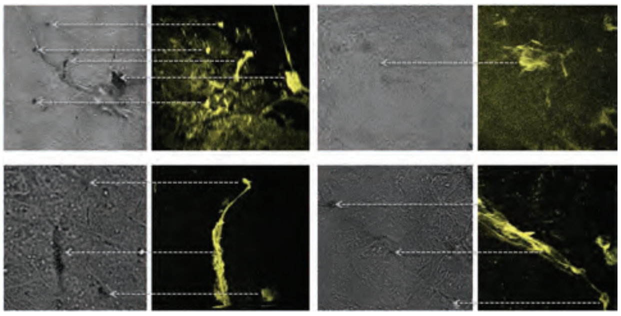


Figure 1. Distribution of gold nanoparticles in a CAM model SW480 cancer tumor. Left panels – bright-field microscopy images. Right panels – two-photon excited fluorescence images. Traces of gold nanoparticles, appear as strong fluorescence signals (false color yellow), are found within blood vessels and at specific areas.

nevet

multidisciplinary research collaboration between Ben-Gurion University-Technion

PROJECT

Photochemical deposition of metallic nanostructures using visible light

Launch year:	2011
Principal investigators:	Prof. Yaron Paz - *Technion IIT, Faculty of Chemical Engineering* Prof. Iris Visoly-Fisher - *Ben Gurion University of the Negev, Department of Chemistry and IKI*
Participating students:	2

SCIENTIFIC GOAL

Nanometer-size islands are often deposited on photocatalytic materials to improve charge separation. The purpose of this program was to study the feasibility of depositing nano-island of silver on TiO_2 overcoated with organic charge-carriers molecules using a combination of photodeposition and electrochemical deposition. In this context it was important to find out what are the effects of bias and light on the structure and morphology of the metallic islands.

ABSTRACT

In this research we used light to control Ag deposition rates and morphology on TiO_2 surfaces. Combining electrochemical deposition and UV illumination was shown to provide such control. Changing the applied potential is known to lead to different Ag nanostructures due to changing the reducing current vs. the diffusion and drift rates. We have found that combining UV illumination with electrodeposition can shift the effective deposition potential by photogeneration of electrons in the TiO_2, which changes the potential profile in the electrolyte adjacent to the TiO_2 surface, hence the charge concentration in the “double layer.” Therefore, control of the morphology was achieved via the deposition potential as well as via the UV illumination, independently and combined. UV control of the deposition further allowed spatial and temporal control of the Ag nanoparticle deposition.

An organic chromophore absorbing in the visible range adsorbed on the visibly transparent semiconductor TiO_2 surface can also serve to reduce the silver metal cations under illumination in the visible range, as opposed to UV illumination. Deposition of Ag nanoparticles on 5,10,15,20 – Tetrakis (4-carboxyphenyl) porphyrin (TCPP) preadsorbed on TiO_2 was detected under illumination in the visible range at wavelengths corresponding to the TCPP absorption peaks, albeit very slowly. The mechanism involved in light control of the deposition was attributed to electron transfer from the photo-excited porphyrins, with competing transfer directions between the reducing Ag particles and the TiO_2 conduction band edge.

RESULTS OBTAINED TO DATE

Bias seemed to play a dominant role on the structure of the nano-islands: large negative potentials led to a dendritic structure, whereas “flowers-like” structures were obtained at lower potentials and nano-spheres were obtained at zero-potential. Exposure to UV light enhanced the deposition rates, however did not alter the morphology of the nano-islands.

While the general scheme of photodeposition involves absorption of light by the photocatalyst, hence, in the case of un-doped TiO_2 is limited to UV light, it was shown that visible light deposition was possible if visible – absorbing molecules are pre-attached to the surface of the photocatalyst. Prolonged illumination resulted in particles at more uniform-size particles, most likely due to competing deposition-dissolution processes resulting from plasmonic absorption by the silver nanoparticles.

FIGURES

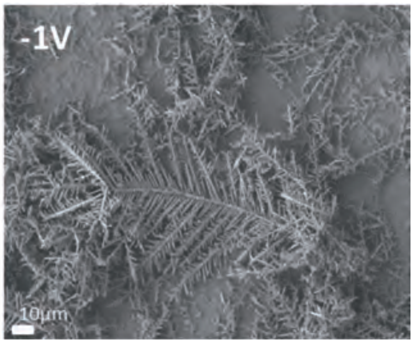


Figure 1. SEM of TiO2 thin film onto which Ag was photodeposited under bias

FACILITIES

Apart from laboratory equipment, shared facilities were used for characterization of the resulting samples, in particular electron microscopy, spectrophotometry and Raman spectroscopy.

PROJECT

Self-organization of bio-inspired active networks on soft interfaces

Launch year: 2011

Principal investigators:

Prof. Kinneret Keren - *Technion IIT, Physics Dept*
Prof. Anne Bernheim - *Ben Gurion University of the Negev, Chemical Engineering Dept*

Participating students: 3

SCIENTIFIC GOAL

Develop synthetic physical model systems to study actin polymerization and force generation on soft interfaces.

ABSTRACT

The cytoskeleton is comprised of an active network of filamentous proteins which gives the cell its mechanical resistance and plays important roles in many cellular processes. The ability of the cytoskeleton to execute a diversity of tasks depends on its ability to self-organize and to constantly remodel itself. Many vital cellular processes, such as cell motility and division, involve cytoskeletal dynamics close to soft surfaces, particularly, fluid membranes. The mechanisms governing cytoskeletal self-organization and dynamics near such surfaces are still largely unexplored. In this project we propose to develop synthetic physical model systems to study actin polymerization on such soft interfaces in a simplified and controlled environment, detached from the complexity of the living cell. We plan to study the effect of curvature, surface tension, as well as the type and composition of the motility machinery on the patterning and self-organization processes.

RESULTS OBTAINED TO DATE

The aim of this project was to study the self-organization of actin networks near soft interfaces. Both groups developed model systems to that end. The Technion team developed a system of water-in-oil emulsions in which the motility supporting machinery is encapsulated within cell-sized droplets surrounded by oil. Actin cortices were grown at the inner interface of water-in-oil emulsions by localizing an amphiphilic actin nucleating promoting factors. The dynamics of actin assembly were studied as a function of the emulsion size and the concentration of actin nucleator.

In parallel, the BGU team developed systems that consist of lipid membranes to which branched actin nucleators localizes. Conjugation of the nucleators was done via specific lipids (e.g., PIP2 Phosphoinositide) and proteins that localize to the membrane. Purified actin and auxiliary proteins were used to initiate the polymerization of the networks on the membrane surface. The structure and dynamics of actin network organization were studied by live confocal imaging.

FIGURES

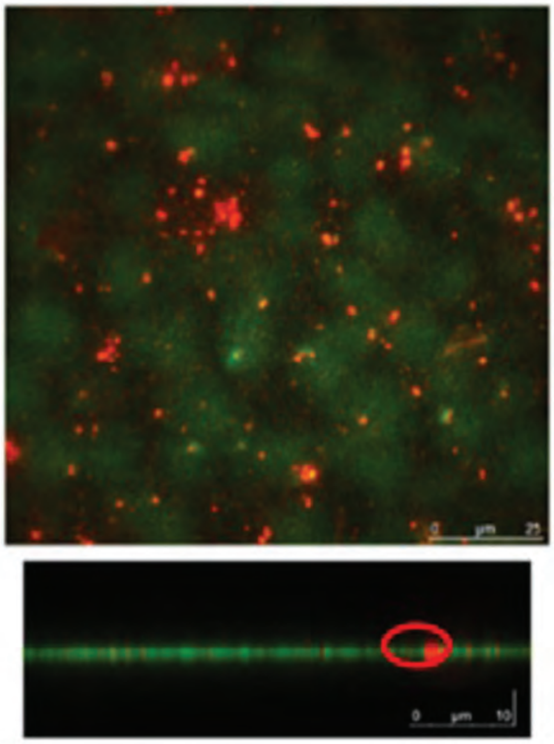


Figure 1. Acto-myosin organization on supported membranes. Confocal images of a supported membrane composed of PIP2 lipids (5% labeled) and an actin network that grows from it. Both a top view (upper panel) and a side view (lower panel) are presented. Islands of actin patches form on the membrane with actin and the labeled lipids localized along the membrane. Actin is in green and the membrane in red.

FACILITIES

Confocal microscope

multidisciplinary research collaboration between Ben-Gurion University-Technion

PROJECT

Exploring ribosomes association with mitochondria by FRET

Launch year:	2011
Principal investigators:	Prof. Yoav Arava - *Technion IIT, Department of Biology* Prof. Daniel Gitler - *Ben Gurion University of the Negev, Department of Physiology and Cell Biology*
Participating students:	3

SCIENTIFIC GOAL

Develop a FRET-based system to detect sites of protein synthesis in vivo, with focus on sites near the mitochondria.

ABSTRACT

An important goal in cellular biology is determination of the functional proximity between various complexes. Specifically, we are interested in determining whether ribosomes are in close proximity to the mitochondria. Such proximity will imply that proteins are synthesized near the mitochondria thereby substantiate a hypothesis to this effect that was suggested 40 years ago, and which was never fully resolved. To address this, we devised a novel in vivo experimental system that is aimed at measuring Fluorescence Resonance Energy Transfer (FRET) between a ribosomal protein and a mitochondrial protein. Detection of FRET, which occurs only at nanometric distances, will imply proximity between these complexes. While FRET was used previously to study proximity between proteins, it was not applied to such large complexes. Within the course of this proposal, we tagged two different ribosomal proteins with a FRET donor (Cerulean) and three different mitochondrial proteins with a FRET acceptor (Venus). The tagged proteins were introduced into yeast cells either singly or at various combinations. All these steps were performed at the Technion Lab. Then, the various yeast strains were grown at the BGU lab, and FRET measurements were performed using a Nikon C1Si spectral confocal microscope. Substantial time was allocated to establish the growth conditions as well as the visualization and detection procedures, because yeast cells are notorious for having significant levels of autofluorescence which can interfere with the quantitative detection of exogenous fluorescence. Furthermore, the small size of these cells necessitated development of suitable immobilization, measurement and quantitation tools. The correct targeting of the constructs was verified using mitochondrial staining, and spectral fluorescence data was collected from the different yeast strains with the tagged proteins and analysis of these results is ongoing.

RESULTS OBTAINED TO DATE

Studying ribosomes proximity to the mitochondria is a broad topic that is studied at the Technion lab from various aspects. Hence, some of the tools that were developed in the course of this research were used for other applications. For example, tagged ribosomal proteins are a valuable tool for any study of translation. As such, grant applications that are not necessarily joint ones had benefited from this research. For example, Arava's lab has recently received a 5-years research grant from the ISF ("Localized translation near the mitochondria: characterization of a novel receptor for ribosomes"). Some concepts and preliminary data of this ISF grant were conceived from the Nevet program.

Work on this project has raised significant interest on mitochondrial function during synaptic transmission in the Gitler lab. This subject is currently being developed for submission of an independent future proposal.

FIGURES

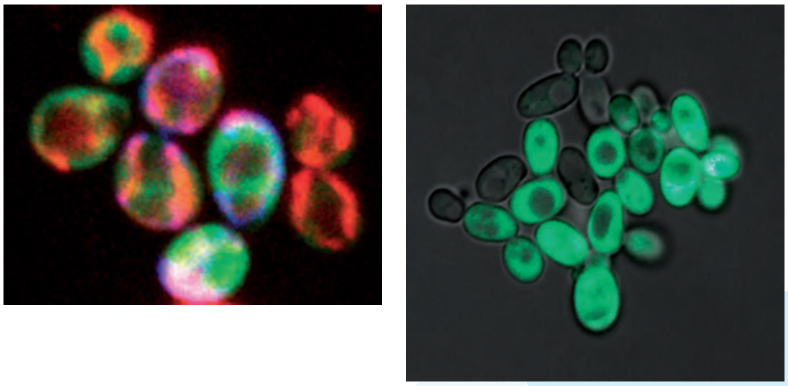


Figure 1. Yeats cells expressing fluorescent proteins: The right figure shows yeast cells expressing fluorescently tagged ribosomal protein, with signals detected throughout the cytoplasm. The left panel presents cells that express both FRET donor and acceptor, fused to ribosomal protein and mitochondria membrane protein, respectively. Colors were modified digitally according to the expression level of the proteins.

multidisciplinary research collaboration within Technion - with Grand Technion Energy Program

PROJECT

Formation of silver coated nickel nanoparticles for inkjet printing

Launch year: 2011

Principal investigators: Prof. Tsur Yoed - *Technion IIT, Faculty of Chemical Engineering*

Participating students: 2

SCIENTIFIC GOAL

Development of silver coated nickel nanoparticles synthesis (of the size of approximately 50 nm or less) for front metallization in PV by ink- jet printing.

ABSTRACT

The use of silver nanoparticles for ink was already successfully performed in the last decade; however, the cost of silver is quite high in comparison to nickel. Therefore, silver-coated nickel nanoparticles might reveal an excellent option. Silver nanoparticles have increased oxidation resistance in comparison to Ni; while this structure can lower the ink cost in comparison to silver nanoparticles based ink.

RESULTS OBTAINED TO DATE

1. The first step in order to synthesize the coated nanoparticles is synthesizing the nano- nickel particles. Various methods have been tested.
   a. The first one was synthesis of Ni nanoparticles by hydrazine reduction. No clear results were obtained. The DLS results did not show a clear trend probably due to particle aggregation.
   b. Another synthesis route was tested: synthesis of dodecanethiol monolayer-stabilized nickel nanoparticles. The procedure was attempted both in air atmosphere and in nitrogen. The procedure in nitrogen did not yield any particle formation, thus air atmosphere was chosen for further investigation. The reaction product was two separate layers, one polar layer (black) and one non-polar layer (purple). Typically, the nanoparticles covered with a monolayer of dodecanethiol will remain in the polar layer; hence, the polar layer was recovered using two methods. One is by using a mixture of toluene and ethanol and dissolving the organic layer in it. The second method is by drawing the polar layer with a syringe and filtering it with a centrifuge running at 9000 rpm, then dispersing the remaining particles in toluene and running it through a sonicator.
2. The next step of the research was to form silver coating over the nickel particles. The aspiration is to use only 2 mol% silver. Silver acetate solution was added to the solution formed in the previous part of the experiment, and stirred. The polar layer from this product was drawn and filtered. The particles received were then dispersed in toluene and sonicated.

FIGURES

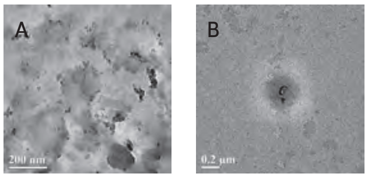


Figure 1 A. TEM images of dodecanethiol monolayer-stabilized nickel nanoparticles in air. The particles are filtered by the first method. Most of the particles are not mono-dispersed, they are organized in aggregates each sized approximately 60 nm.

Figure 1 B. Some of the particles are well dispersed.

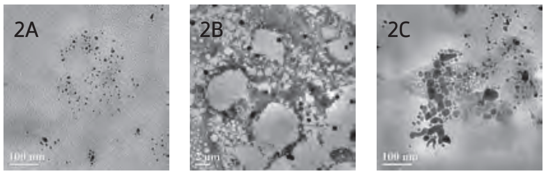


Figure 2 A. TEM images of dodecanethiol monolayer-stabilized nickel nanoparticles in air. The particles are filtered by the second method. The particles that were filtered are 5-15 nm in diameter. They are mostly well dispersed.

Figure 2 B&C. There are also much bigger particles sized approximately 0.75 micron

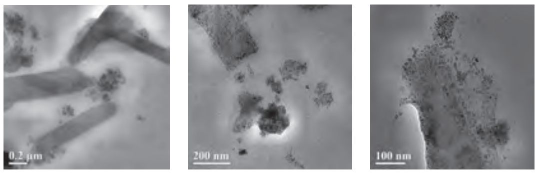


Figure 3. TEM images of the coated particles produced. Some of the particles are spheres of about 10 nm as were the nickel particles in the last part of the experiment and some are rod-like of about 10 nm long. The particles form aggregates that are shaped in different geometric figures.

FACILITIES

DLS, TEM

PROJECT

ITO-TiO_2 Nanostructures En-Route for Highly Efficient Dye Sensitized Solar Cells

Launch year: 2011

Principal investigators: Prof. Yaron Paz - *Technion IIT, Department of Chemical Engineering*

Participating students: 1

SCIENTIFIC GOAL

Since their discovery in 1991, Dye Sensitized Solar Cells (DSSCs) have attracted rapidly growing interest due to their relatively high efficiency and low cost. For these devices to operate successfully, it is important to find ways to suppress interface recombination, and to maintain vectorial transfer of electrons from the sensitizer to the wide band-gap semiconductor (TiO_2 for most cases). The large distance that electrons must diffuse through in order to get to the collecting electrode is known to have a deleterious effect on solar cell efficiency, because it increases the odds that the electrons might reach the surface and reduce the electrolyte, or otherwise will be trapped within the matrix. For this reason it was proposed to synthesize a bicontinuous layer on top of the conductive substrate, comprising of a mixture of TiO_2 nanoparticles and indium tin oxide (ITO) nanoparticles, on top of a densely-packed ITO sintered film (Figure 1). The basic idea was to mix ITO particles and TiO_2 nanoparticles at relative concentrations that are slightly above the percolation threshold of both constituents. In this fashion, a continuous phase of ITO would deliver the electrons to the front of the electrode, while maintaining most of the volume for the dye-coated TiO_2. In addition to that, it was proposed to use chemisorbed calixarenes as a means for preventing the aggregation of the dye on the TiO_2 surface.

ABSTRACT

Pastes made of various types of titanium dioxide and indium tin oxide nanoparticles were prepared at different weight ratios. These pastes served for the preparation of electrodes on ITO-coated glass. Unfortunately, the conductivity was by far lower than expected. The reasoning had to do with adhesion difficulties. With respect to the calixarenes it was found that these groups were very stable on the TiO_2 surface, a property that is encouraging for future application.

RESULTS OBTAINED TO DATE

Pastes made of various types of titanium dioxide and indium tin oxide nanoparticles were prepared at different weight ratios. These pastes served for the preparation of electrodes on ITO-coated glass, using Dr.'s Blade technique. The electrodes went through a heat treatment process at elevated temperature and were characterized. The conductivity between the ITO surface and the mixed layer was measured as a function of composition and type *(Figure 2)*. The conductivity was found to be nil, unless the weight percentage was as high as 90%. This value was app. 6 times higher than what could have expected based on percolation considerations.

A close examination revealed that the reason was due to poor adherence. Several attempts were made to improve adhesion. These included altering the carrier medium (solvent), surface treatment to increase the number of polar OH groups on the surface, using nanoparticles of antimony tin oxide (ATO) instead of indium tim oxide, varying the heat treatment conditions, introducing an intermediate layer by spin- coating and by liquid phase deposition.

With respect to the possibility of using chemisorbed calixarenes to prevent dye aggregation of the TiO_2 particles, 1-C NMR results showed that the chemisorbed calixarenes had very high stability against photoinduced degradation. This paves the route for using these compounds not only in the context of solar cells but also as part of photocatalytic devices.

FIGURES

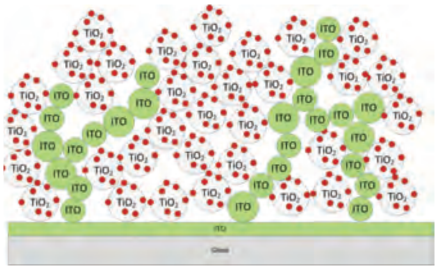


Figure 1. A bicontinuous layer on top of the conductive substrate, comprising of a mixture of TiO_2 nanoparticles and ITO nanoparticles, on top of a densely-packed ITO sintered film.

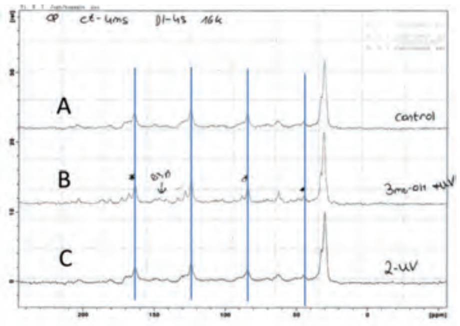


Figure 3. NMR of Calixarene attached to TiO_2. A- Control, B- following exposure to UV light in the presence of methanol C- following exposure to UV.

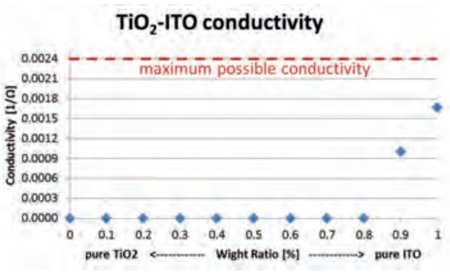


Figure 2. Conductivity vs. ITO weight ratio.

FACILITIES

SEM, AFM, NMR

multidisciplinary research collaboration between RBNI-Grand Technion Energy Program

PROJECT

Tunable Chromophores for Dye Sensitized Solar Cells

Launch year:	2011
Principal investigators:	Prof. Zeev Gross - *Technion IIT, Schulich Faculty of Chemistry*
Participating students:	1

SCIENTIFIC GOAL

One main goal of this research is to determine the underlying principles governing the efficiencies of corrole-based photovoltaic cells. The advantage of the new dyes (for DSSC) is the synthetic control of desired properties by means of organic and inorganic chemistry. This enables a delicate control of binding modes to the metal oxides and a tuning of the photochemical and photophysical properties of the dye, thus allowing for systematic investigations.

ABSTRACT

Our research focuses on the preparation of advanced chromophores for dye sensitized solar cells that will perform better than existing ones, for the following reasons: better coverage of the solar spectrum, better conjugation of the metal-oxide binding groups with the chromophore, larger long-term photo-stability, and hypothesis-driven slowdown of undesired (efficiency-lowering) pathways.

RESULTS OBTAINED TO DATE

We have decided to prepare metallocorroles with long-lived and emissive excited states, in line with the following guidelines: a) the central metal should be a light non-transition metal, whose corrole complexes have very high emission quantum yields; b) the heavy atom substituents required for encouraging ISC should be located on the corrole periphery; c) the compound should be amenable to further chemical modification as to allow future applications. The adopted methodology was iodination of **1-Al**, because a) iodine is the heaviest easily introduced atomic substituent; b) iodination should be more selective than bromination (which nearly always affords octabrominated metallocorroles); and c) C-I bonds are ideal synthons. Our expectations for the resulting molecule (**4-Al**) were completely fulfilled: iodination did not proceed further than four iodides per corrole, all four C-I bonds were formed on one pole of the molecule, and the complex displayed unique photophysical properties. The luminescence of **4-Al** revealed both short- and long-lived components; and its long-lived phosphorescence (>200 µs, under N_2, Θ_{max} = 820 nm) was apparent even at room temperature. In yet unpublished work, the same methodology was applied on the complex with Ga as central metal (**1-Ga**). After few minor changes in the synthetic pathway, iodination of **1-Ga** selectively gave the same type of product (**4-Ga**) with interesting photophysical characteristics. The emission maxima of **4-Ga** are slightly red-shifted (by 8-10 nm) relative to **4-Al** and its phosphorescence lifetime is even longer (>300 μs).

After the success working with N-iodosuccinimide (NIS) we decided to check iodination by simpler reagent. One hour of reflux in toluene with molecular iodine and few drops of pyridine provided only one product in each case, different from those described previously. They were characterized as the tris-iodinated Ga and Al corroles (**3-Ga** and **3-Al**, respectively), based on ^{1}H-NMR spectroscopy (one singlet) and X-ray crystallography. The photophysical properties of these complexes are under investigation in our lab. Ongoing efforts are devoted to C-I replacement by functional groups that will induce binding to metal oxides such as TiO_2, for applications in energy.

Another synthetic approach is the iodination of already functionalized corroles, with emphasis on amphiphilic derivatives, whose synthesis is well established. The formylation by the Vielsmeier reagent provided mono-formylated corrole (**6-Ga**), which is reacted with malonic acid to form products with both extended conjugation and a di-carboxylic moiety (**9-Ga**). Preliminary results confirmed the applicability of this approach for both the iodinated and non-iodinated Ga formyl-corroles.

FIGURES

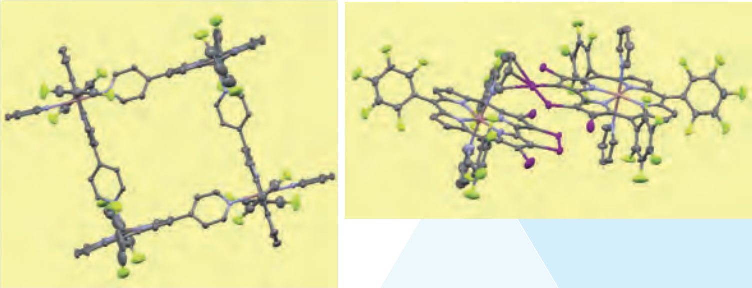
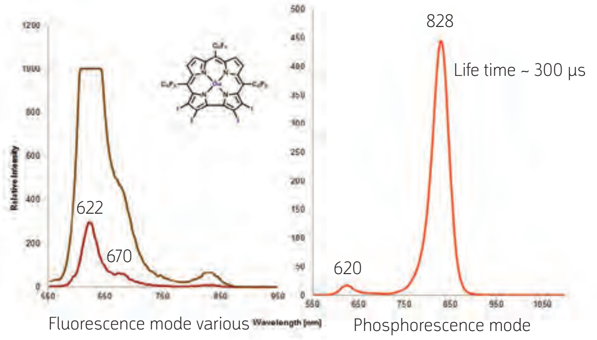


Figure 1. Molecules under Investigation



Fluorescence mode various signal amplifications

Phosphorescence mode (100 μs delay)

This complex displays both short- and long lived excited states

Figure 2. Emission Spectrum of **4-Ga** (toluene, N_2, RT)

FACILITIES

We used during the research all the equipments needed for routine synthetic work which also includes a 2-cabinet glovebox, vacuum systems, 2 spectrophotometers, 1 CD (circular dichroism), 1 fluorometer, 2 GC, 2 HPLC, two FT-IR's, five NMR's (^{1}H, ^{13}C, ^{19}F, and ^{31}P 500 MHz, broad band 400 MHz, ^{1}H, ^{13}C, ^{19}F, and ^{31}P 300 MHz, ^{1}H and ^{13}C 200 MHz, ^{1}H, ^{13}C, ^{19}F, and ^{31}P 200 MHz), EPR (with N_2 and He cooling systems), MS (GC/MS, high resolution, ES, MALDI-TOF, and FAB), X-ray crystallographic facilities, and all needed electrochemical facilities (CV, bulk, spectroelectrochemistry).

PROJECT

Photon spliting for efficiency enhancement of Photovoltaics

Launch year:	2011
Principal investigators:	Prof. Carmel Rotschild - *Technion IIT, Faculty of Mechanical engineering*
Participating students:	Nimrod Kruger - *MSc student*

SCIENTIFIC GOAL

Our research goal is to pave the way for efficiency enhancement of Si solar cell devices by successfully presenting wide band transition and splitting of energetic photon to low energy, Si bandgap fitted, photons.

ABSTRACT

Finding an efficient method for splitting energetic photons for the purpose of solar PV's is a challenge many years in research, but up to now no efficient energy transfer in the optical path, detectable externally, was presented. The success of producing two Si bandgap fitting photons for each high energy photon arriving from the sun can boost the efficiency of a given PV by 7%, even above the Shockley Queisser limit.

We hope to present in this study two breakthroughs in the effort to overcome this challenge. The first is by finding a highly efficient energy transfer medium suitable for the occurrence of photon splitting in the desired wavelengths.

The materials commonly known to fit the requirements are the Tb^{3+} -Yb^{3+} couple. The Tb^{3+} acts as a donor that absorbs photons at 485nm, while the Yb^{3+} serves as an acceptor with a single NIR emission at 1020 nm, perfectly matching the band-gap of Si solar cells. The Pr^{3+} is also known to replace the Tb^{3+} as a donor, with a similar absorption line. Most mediums doped with these materials do not present high emission in the NIR, usually due to quenching of the Yb^{3+}.

We identified a crystal, potassium yttrium tungstate - KYW, with good optical properties and low quenching effect when doped with Yb^{3+}. We hope that by co-doping this crystal with the donor-acceptor materials we will be able to show high efficiency photon splitting. We expect to see high efficiency of photon splitting by measuring quantum efficiency (QE) that is higher than 100%.

The second aspect of our research that will enhance the efficiency of any photon splitting device we create is the use of organic fluorescent materials and cascaded energy transfer. The combination of organic sensitizes at high concentration and a final emitter at low concentration, all deposited as a coating layer of a luminescent solar concentrator (LSC) are chosen as a basis of demonstrating our idea.

Organic sensitizers, few microns thick and placed of a LSC device, absorb solar photons between 330nm-460nm, and transfer the energy to a final emitter (also deposited on the LSC) through Forester Energy Transfer (FET) with nearly 100% efficiency. The final organic emitter emits with high quantum efficiency at 485nm matched to the inorganic donor (within the crystal).