Final Report for Period: 07/2009 - 06/2010 **Submitted on:** 07/22/2010
Principal Investigator: Tsukruk, Vladimir V. **Award ID:** 0650705
Organization: GA Tech Res Corp - GIT
Submitted By:
Tsukruk, Vladimir - Principal Investigator
Title:
NIRT: Bioinspired Flex Nanomembranes for Multifunctional Microsensors

Project Participants

Senior Personnel

Name: Tsukruk, Vladimir
Worked for more than 160 Hours: Yes
Contribution to Project:

Post-doc

Name: Jiang, Chaoyan
Worked for more than 160 Hours: Yes
Contribution to Project:
Membrane fabrication and studies

Name: Kim, Kisub
Worked for more than 160 Hours: Yes
Contribution to Project:
Synthesis of new nanowires

Name: Kozlovskaya, Veronika
Worked for more than 160 Hours: Yes
Contribution to Project:
film fabrication

Graduate Student

Name: Lin, Yen-Hsi
Worked for more than 160 Hours: Yes
Contribution to Project:
Membrane fabrication and studies

Name: Ho, Peter
Worked for more than 160 Hours: Yes
Contribution to Project:
Flexural measurements of the SWNT membranes

Name: Lilly, Daniel
Worked for more than 160 Hours: Yes
Contribution to Project:
Preparation of nanowires

Name: Bishnu, Khanal
Worked for more than 160 Hours: Yes
Contribution to Project:
synthesis of nanoparticles

Name: Xu, Jun
Worked for more than 160 Hours: Yes
Contribution to Project:
synthesis of polymers

Name: Tucker, Craig
Worked for more than 160 Hours: Yes
Contribution to Project:
microfdabrication of MRMS structures

Name: Hu, Alan
Worked for more than 160 Hours: Yes
Contribution to Project:
microfabrication

Name: Chen, Nannan
Worked for more than 160 Hours: Yes
Contribution to Project:
microfabrication

Name: Goodman, Matt
Worked for more than 160 Hours: Yes
Contribution to Project:

Undergraduate Student

Name: Merrick, Emily
Worked for more than 160 Hours: Yes
Contribution to Project:
Membrane fabrication and studies

Name: Jones, Keith
Worked for more than 160 Hours: Yes
Contribution to Project:
film fabrication

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Northwestern University at Chicago
Improvement of LbL membranes, Prof. P. Messetsmith

Tufts University
LbL films from silk, Prof. D. Kaplan

Agiltron Inc.
Microfabricated substrates for LbL membranes

Louisiana Tech University

Fluorescence polymer synthesis and microfabrication, Prof. Yu. Lvov

Other Collaborators or Contacts

Activities and Findings

Research and Education Activities:

Tsukruk and Lin group fabricated ultrathin, perforated, freely suspended membranes with uniform nanopore size controlled in the range of tens of nanometers. It has been demonstrated that photoluminescence of CdSe/ZnS quantum dots deposited at surfaces can be can be tuned by placing the nanoscale (3-50 nm) LbL polymer film between QDs and a substrate. We have shown that a single monolayer of CdSe/ZnS quantum dots (QDs) encapsulated into a 60 nm LbL film can be released from surfaces as a freely-suspended film.

Tsukruk and Zubarev groups demonstrated that gold nanorods can be incorporated in hydrogel LbL films to construct ultrahin films and core-shell microcapsules with pH-responsive properties caused by reversible swelling-deswelling of the crosslinked matrix.

Tsukruk and Kotov groups fabricated responsive photoluminescent hybrid materials with quantum dots immobilized in organized manner fabricated by spin-assisted layer-by-layer assembly (SA LbL). The strongly interacting polyelectrolytes such as poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) serve for confining CdTe nanoparticles stabilized by thioglycolic acid, while a poly(methacrylic acid) (PMAA) hydrogel matrix presents an elastomeric network with pH-responsive properties. Quantum dot layers were encapsulated inside this hybrid hydrogel matrix.

In Zubarev's group, new polyelectrolyte-functionalized gold nanoparticles have been successfully synthesized and characterized by various techniques, including GPC, NMR, and TEM. In addition, first example of gold nanorods covalently functionalized with PDMS polymer chains has been synthesized and incorporated into polymer matrix (cross-linked PDMS). We developed a new techniques to synthesize and separate gold nanostructures of different shapes and sizes.

Zubarev group developed a new strategy to increase compatibility of metallic nanoparticles and anisotropic solvents. We synthesized thiol-terminated liquid crystalline ligands that were used for functionalization of monodisperse gold nanoparticles. Homogeneous solution of such novel particles in nematic solvents were prepared and their optical, thermal, and electrical properties were studied.

In Lin's group, organic-inorganic nanocomposite, i.e., poly(3-hexylthiophene)-CdSe quantum dot (P3HT-CdSe) was synthesized and characterized. Water soluble CdSe quantum dots, both positively charged and negatively charged were synthesized. Organic-inorganic nanocomposite, i.e., poly(3-hexylthiophene)-CdSe quantum dot (P3HT-CdSe) were investigated at the air-water interface. CdTe nanoscale tetrapods were synthesized, characterized, and studied on the air-water interface. CdSe quantum rods were synthesized with and without a functional ligand for further modification, i.e., making organic-inorganic nanocomposites.

Lin prepared CdTe tetrapods by utilizing multiple Te precursor injections to provide the control over the tetrapod arm width, thereby effectively controlling the tetrapod shape and studied the self-assembly of CdTe tetrapods at the air/water interface using Langmuir-Blodgett (LB) technique

Kotov's group, composite membranes of clay and poly(vinyl alcohol) polymer for FLEX sensors have been designed, prepared and tested. LbL membranes form carbon nanotubes (SWNT) were self-assembled and their electrical properties were evaluated. New QDs have been synthesized to test in LbL films.

Liu's group has designed a MEMS platform for integrating the LbL films in free-suspended state and tested several LbL films with incorporated silver nanowires.

In 2006-2010, 30 peer-reviewed papers reporting scientific results fully or partially supported by this project have been published in archival journals such as Science, Nature Materials, Adv. Mater., Chem. Mater., JACS, and Langmuir. Another 5 manuscripts reporting scientific results fully or partially supported by this project have been submitted to journals, such as Adv. Mater., Chem. Mater., J. Phys Chem., J of Mater Chem.

Six graduate and two undergraduate students along with two post-docs participated in and were partially/fully supported by the project. Three graduate students and two post-docs graduated and moved to various industrial and academic research centers (U. Berkeley, Whirlpool, etc).

65+ presentations have been delivered at national meetings by the co-PIs and their students. Intense exchange of students took place between UIUC, ISU, and UoM.

In 2005-2006, seven different types of new components (conjugated polymer, CdSe quantum dots, CdTe nanowires, silver nanorods, carbon nanotubes, fluorescent-label polyelectrolyte, and polymer-gold nanoparticle hybrids) have been synthesized, characterized, and integrated into LbL films and corresponding freely suspended multilayer nanomembranes. The composition, thickness, and vertical design of nanocomposite LbL membranes varied in a wide range of parameters. The mechanical, optical, and electrical properties of nanoparticle-containing LbL membranes were studied considering potential applications as microsensors.

Strategic research plan for NIRT team has been developed in October 2005 as a result of NIRT Workshop at Iowa State U. which was attended by all co-PIs. Co-PIs made presentations on their current research activities on a morning session open to public and an afternoon session was devoted to brainstorming and tailoring NIRT strategy. Another workshop has been organized in Atlanta in October 2007 to refine directions of research. It has been attended by all Co-PIs and many participated students.

Findings: (See PDF version submitted by PI at the end of the report)

Major findings follow (see also a separate file with selected results attached):

- a reproducible synthetic procedure for the preparation of well-defined PNIPAAM- and PAA-functionalized 5 nm gold nanoparticles has been developed

- conditions for thiol functionalization and coupling of linear PDMS chains to gold nanorods have been identified and bulk polymer nanocomposites containing gold nanorods have been prepared

- an organic-inorganic nanocomposite, i.e., poly(3-hexylthiophene)-CdSe quantum dot (P3HT-CdSe) was synthesized via a mild palladium catalyzed Heck coupling, dispensing with the need for ligand exchange chemistry

- a simple yet novel biphasic ligand exchange method to transfer original hydrophobic CdSe-TOPO QDs into hydrophilic dithiocarbamate functionalized CdSe (D-CdSe) QDs in one step has been developed

- the perfect structure of the polymer ? composite system suitable for FLEX membranes has been identified and the first FLEX devices from clay-composites with PVA polymer have been manufactured

- the LBL membranes for FLEX devices from carbon nanotubes have been prepared. They are the strongest non-fibrous materials from SWNT ever made and completely suitable for FLEX devices

- a new method of incorporation of luminescent magnetic and other nanoparticles in the LBL membranes was developed and reversible loading/release of nanoparticles in the FLEX membranes was achieved

- FLEX membranes were also applied for the development of new strain sensors which demonstrated excellent linearity and reproducibility

- planar array of silver nanorods with high aspect ration (up to 100) were embedded into freely suspended polymeric multilayer membranes. These nanorods can reinforce the nanocomposite with a higher elastic modulus than pure polymer membranes. Moreover, in-plane conductivity can be significantly improved when the volume fraction of silver nanorods over 22.5%.

- an unusual multi-length scale pattern of mechanical instability was found for nanoscale composite film under compressive stress. We demonstrated two concurrent strain-dependent buckling modes under different critical strain. The zig-zag buckling patterns were attributed to the development of the biaxial stress along the boundary lines for micropatterned regions in the nanomembrane.

- the conjugated polyelectrolytes and quantum dots used for LbL assembly provided the unique fluorescence and semiconductive properties of the flexible multilayer membranes which are substrate devenpent.

- the first flexible membrane from SWNT was demonstrated. It is important that the Young modulus of the small membranes was found to be about 10 times higher that that measured on typical samples in bulk tensile strength meter.

- it was demonstrated that optimization of the strength of LBL composite can be achieved by intelligent selection of the polyelectrolytes. Adhesive properties in of many mariene animals are attributed to DOPA-containing polymers which have been introduced in ye LBL assembly with much success. The tensile strength (macroscale) had been improved 2 times.

- a reproducible synthetic procedure for the preparation of well-defined nanorods has been identified and structural parameters that affect the growth of gold nanostructures and their aspect ratio have been explored

- a new method to functionalize gold nanorods by ligand exchange technique has been developed and covalent attachment of polymer chains to gold nanostructures has been achieved and the conditions for the product isolation and purification have been found

- water soluble, negatively charged poly(2,5- methoxy-propyloxysulfonate phenylene vinylene) (MPS-PPV) with different molecular weights has been synthesized using the Gilch polymerization procedure. The absorption and photoluminescence of MPS-PPV have been measured

- pH-responsive LbL films and microcapsules with incorporated gold nanorods and in-situ grown gold nanoparticles have been fabricatred and their reversible significant LSPR response was demonstrated

- an organic-inorganic nanocomposite, i.e., poly(3-hexylthiophene)-CdSe quantum dot (P3HT-CdSe) was studied at the air-water interface, exhibiting complex packing due to the intimately coupled conjugated polymer to the quantum dot core. It was used as the active layer in a photovoltaic device and showed relatively high short-circuit current while having an ultrathin profile of 30 nm.

- nanoscale CdTe tetrapods were synthesized in a one-pot reaction with controllable, variable arm widths, tuned by number of precursor injections, with arm length held constant. Control of the width determined absorption onset. Unique ribbon morphology was observed on the air-water interface.

- CdSe nanorods were synthesized both with and without a functionalized ligand, allowing for further use, both with and without further modification, i.e., attachment of a conjugated polymer, in optoelectronic devices.

- a reproducible synthetic procedure for the preparation of high aspect ratio gold nanorods and their purification has been developed.

- Quantum dot layers encapsulated in PSS-PAH bilayers demonstrated reversible changes in photoluminescent intensity in response to pH variations. Such hybrid quantum dot-containing hydrogel-LbL assemblies provide a way for a novel design of materials with precisely controlled structure and pH-triggered optical properties which might be developed into or pH- or chemical sensors.

-- Analysis of the tetrapod materials yields an arm length of 47.2  5.0 nm, within the length range of the 10-injection sample. However, the width of the 6-injection is determined to be 3.91  0.52 nm, significantly smaller than the 10-injection sample.

-- The increase in the number of injections alters the width of the tetrapods, which controlled the absorption maximum. The synthesis with multiple injections provides a simple and direct way to control the absorption maximum of the nanocrystals.

-- Ribbon-like morphologies of tetrapods occur at the onset of pressure, i.e., 1 mN/m. The formation of ribbons is attributed to the dewetting of the CdTe nanocrystals and the unique tetrapod shape. The deposition at 22 mN/m shows the larger aggregate morphology similar to the deposition at 10 mN/m; however, the aggregates have condensed and thickened, resulting in a denser network-like pattern. At highest surface pressure (i.e., 39 mN/m), these ribbons coalesce into a network structure, yielding a hierarchical structure that has voids on the submicron, tens, and hundreds of micron scale.

- composites of liquid crystals and gold nanoparticles from form highly stable solutions in the nematic liquid crystal 4-cyano-4-n-pentylbiphenyl (5CB) were fabricated. The solubility of these nanoparticles in 5CB was significantly higher than that of conventional alkanethiol-terminated nanoparticles. An 8 nm shift of the surface plasmon resonance was observed when the gold nanoparticles were dissolved in the nematic phase of 5CB, as compared to the isotropic solution in methylene chloride. Good agreement of the experimental surface plasmon resonance shift with Mie calculations using an adjusted dielectric function for a reduced electron mean free path in small nanoparticles confirmed that the gold nanoparticles are solvated by the liquid crystal molecules.

Training and Development:

New bulging setup was developed to facilitate programmable pressure adjustment, automatic interference fringes recording, and fast data processing. Three students were trained on a new fluorescent microscope with point-shot fluorescent spectrometer attachment and on confocal Raman spectrometer. Six students have been trained on TEM, NMR and GPC instruments. Five students were trained on a new set-up with flex measurements of membranes. 6 students and post-docs graduated and continue their research career in academia and industry.

Outreach Activities:

In 2006-2010, the co-PIs and their students made more than 70 oral and poster presentations of results related to the current project at scientific conferences, workshops, and seminars.

Journal Publications

C. Jiang, V. V. Tsukruk, "Freestanding Nanostructures via Layer-by-Layer Assembly", Adv. Mater., p. 829, vol. 18, (2006). Published,

C. Jiang, M. E. McConney, S. Singamaneni, E. Merrick, Y. Chen, J. Zhao, L. Zhang, V. V. Tsukruk, "Thermo-Optical Arrays of Flexible Nanoscale Nanomembranes Freely Suspended over Microfabricated Cavities as IR Microimagers", Chem. Mater., p. ASAP, vol. 18, (2006). Published,

Wang, Y.; Tang, Z.; Podsiadlo, P.; Elkasabi, Y.; Lahann, J.; Kotov, N. A.
, "Mirror-like photoconductive layer-by-layer thin films of Te nanowires: the fusion of semiconductor, metal, and insulator properties", Adv. Mater., p. 518, vol. 18, (2006). Published,

Sinyagin, A. Belov, A. Tang, Z. Kotov. N. A.
, "Monte Carlo Computer Simulation of Chain Formation from Nanoparticles", J. Phys. Chem., p. 7500, vol. 110, (2006). Published,

Guldi, Dirk M.; Rahman, G. M. Aminur; Sgobba, Vito; Kotov, Nicholas A.; Bonifazi, Davide; Prato, Maurizio
, "CNT-CdTe Versatile Donor-Acceptor Nanohybrids", J. Am. Chem. Soc., p. 2315, vol. 128, (2006). Published,

C. Jiang, D. S. Kommireddy, V. V. Tsukruk, "Gradient array of freely suspended nanomembranes", Adv. Funct. Mater., p. 27, vol. 16, (2006). Published,

R. Gunawidjaja, C. Jiang, H. Ko, V. V. Tsukruk, "Free standing 2D arrays of silver nanorods,", Adv. Mater., p. 2895, vol. 18, (2006). Published,

19. C. Jiang, S. Singamaneni, E. Merrick, V. V. Tsukruk, "Complex Buckling Instability Patterns of Nanomembranes with Encapsulated Gold Nanoparticle Arrays", , Nanolett., p. 2254, vol. 6, (2006). Published,

R. Gunawidjaja, H. Ko, C. Jiang, V. V. Tsukruk, "Buckling behavior of highly oriented silver nanowires encapsulated within LbL film", Chem. Mater., p. 2007, vol. 19, (2007). Published,

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Gibson, J.D.; Khanal, B.P.; Zubarev, E.R. Paclitaxel, "Paclitaxel-Functionalized Gold Nanoparticles.", JACS, p. 11653, vol. 129, (2007). Published,

Zimnitsky, D.; Jiang, C.; Xu, J.; Lin, Z.; Tsukruk, V.V., " Substrate- and Time-Dependent Photoluminescence of Quantum Dots Inside the Ultrathin Polymer LbL Film", Langmuir, p. 10176, vol. 23, (2007). Published,

D. Zimnitsky, J. Xu, Z. Lin, V. V. Tsukruk, "Domain and Network Aggregation of CdTe Quantum Rods within Langmuir-Blodgett Monolayers", Nanotechnology, p. 215606, vol. 19, (2008). Published,

D. Zimnitsky, V. V. Shevchenko, V. V. Tsukruk, "Perforated Freely Suspended Layer-by-Layer Nanoscale Membranes", Langmuir, p. 5996, vol. 24, (2008). Published,

17. V. Kozlovskaya, E. Kharlampieva, B. P. Khanal, P. Manna, E. R. Zubarev, V. V. Tsukruk,, "Ultrathin Layer-by-layer Hydrogels with Incorporated Gold Nanorods as pH-Sensitive Optical Materials", Chem. Mater., p. 7474, vol. 20, (2008). Published,

Chang, W.-S.; Slaughter, L. S.; Khanal, B. P.; Manna, P.; Zubarev, E. R.; Link, S., "One-Dimensional Coupling of Gold Nanoparticle Plasmons in Self-Assembled Ring Superstructures", NanoLett., p. 1152, vol. 9, (2009). Published,

Khanal, B. P.; Zubarev, E. R., "Purification of High Aspect Ratio Gold Nanorods: Complete Removal of Platelets", JACS, p. 12634, vol. 130, (2008). Published,

M. Goodman, J. Xu, J. Wang, and Z. Lin, "Semiconductor organic-inorganic nanocomposites at the air/water interface and their photovoltaic performance", Chem. Mater., p. 934, vol. 21, (2009). Published,

E. Kharlampieva, V. Kozlovskaya, J. Chan, J. F. Ankner, V. V. Tsukruk, " Spin-Assisted Layer-by-Layer Assembly: Variation of Stratification as Studied with Neutron Reflectivity", Langmuir, p. 14017, vol. 25, (2009). Published,

E. Kharlampieva, V. Kozlovskaya, O. Zavgorodnya, G. D. Lilly, N. A. Kotov, V. V. Tsukruk, "pH-Responsive Photoluminescent LbL Hydrogels with Confined Quantum Dots,", Soft Matter, p. 800, vol. 6, (2010). Published,

Slaughter, L. S.; Chang, W.-S.; Swanglap, P.; Tcherniak, A.; Khanal, B. P.; Zubarev, E. R.; Link, S., ""Single-Particle Spectroscopy of Gold Nanorods beyond the Quasi-Static Limit: Varying the Width at Constant Aspect Ratio", J. Phys. Chem. C, p. 4934, vol. 114, (2010). Published,

Critchley, K.; Khanal, B. P.; Gorzny, M. L.; Vigderman, L.; Evans, S. D.; Zubarev, E. R.; Kotov, N. A., ""Near-Bulk Conductivity of Gold Nanowires as Nanoscale Interconnects and the Role of Atomically Smooth Interface"", Adv. Mater., p. 2338, vol. 22, (2010). Published,

Books or Other One-time Publications

Web/Internet Site

URL(s):
http://polysurf.mse.iastate.edu/lab/NIRT%20homepage/homepage.html
Description:
General info, current activities, and links to all co-PIs

Homepage example:

NIRT
NSF 05-06832
Chemical and Thermal Systems Division
National Nanotechnology Initiative

NSF Sponsored the Nanoscale Interdisciplinary Research Team

Scope: Collaborative Research on Bioinspired Nanomembranes for Multifunctional Microsensors: synthesis, assembly, and properties of flexible multilayered nanocomposites as a prospective sensing platform for microsensor arrays for thermal, chemical, and biological applications.

Who: Materials scientists from Iowa State, a chemical engineer from U. Michigan, a chemist from Rice U., and an electrical engineer from U. Illinois at UrbanaChampaign.

Other Specific Products

Contributions

Contributions within Discipline:

We demonstrated that ultrathin (thickness down to 20 nm) perforated LbL membranes with tunable nanopore sizes in the range of 20-50 nm can be fabricated using spin-assisted LbL assembly on hydrophobic sacrificial polymeric substrates. The formation of nanopore morphology is caused by the poor wettability of hydrophobic substrates by the polyelectrolytes. The hydrophobic surfaces have never been used for constructive purposes. We suggest that contrary to the common fact that smooth hydrophilic and charged substrates with high surface energy are preferable for the fabrication of homogeneous LbL films, hydrophobic surfaces with low surface energy provide the best opportunity for the fabrication of perforated nanoscale membranes with unique nanoporous morphology.

We showed that separation of QDs from the silicon substrate with the polymer film resulted in the overall increase of the PL intensity. However, the encapsulation between polymeric films leads to significant initial PL enhancement followed by a gradual PL decrease. These changes are accompanied by a significant blue-shift, indicating a fast reduction of the QD nanoparticle dimension. We suggest that the encapsulation of QDs into the polymer film stimulates both photooxidation and photobleaching processes. This acceleration could be related to the presence of water molecules bound to polyelectrolyte matrix in the course of assembly on QD nanoparticles, as well as to the presence of the charged groups serving as additional nucleation sites.

We learn how to control of density and orientation of silver nanorods arrays in the freely suspended multilayer nanomembrane. We found that the density of silver nanorod fillers can be applied to tune mechanical properties as well as electrical behavior of the composite membranes. The in-lane conductivity of nanomembranes with 22.5 v% silver nanorods presented 110-660 S/cm due to the random silver nanorods confined to the two-dimension planar state.

We observed an unusual complex pattern of mechanical instability for nanoscale multilayer composite films under compressive stress. We demonstrated that localized adjustment of mechanical properties can be achieved by micro-printing gold nanoparticle arrays into the thin film. The mechanical differences within the thin film can cause the zig-zag buckling patterns due to the development of the biaxial stress along the boundary line, which can be expanded towards more complex multisclae wrinkles and applied in the fields as micro-fluidic channels.

We developed the synthetic approach for gold nanorods fabrication by seed-mediated method with highly reproducible and scaleable procedure. The key element is the addition of silver salt ($AgNO_3$) and CTAB surfactant to promote the one-dimensional growth of gold structures. TEM analysis shows that there is at least 95 % of rods versus spherical nanostructures. Esterification under mild conditions (DIPC/DPTS) was found to be a highly efficient method for covalent attachment of various carboxyl-terminated polymers. The method gives high yield and very high grafting density (1.3 chains/nm2). Self-assembly was observed for gold nanorods functionalized with polystyrene and polybutadiene chains.

We prepared water soluble, negatively charged poly(2,5- methoxy-propyloxysulfonate phenylene vinylene) (MPS-PPV) which can be exploited for LbL assembly with different molecular weights using the Gilch reaction.

Overall, a whole new class of freely standing flexible LbL nanocomposites with a vaiet of reinforcing nanostructures ranging from metal nanoparticles to semiconducting tetrapods have been designed, fabricated, and characterized in terms of their microstructure, mechanical and optical properties and demonstrated to be promising for emerging applications.

Contributions to Other Disciplines:

We developed a MEMS based device that will be integrated with LbL films for ultra-sensitive detection of displacement and pressure. This device would have greater sensitivity than traditional MEMS sensors due to the ultra low membrane thickness.

The potential applications of the perforated nanomembranes with properly modified surfaces include the efficient separation of large biomolecules, nanoparticles, carbon nanotubes, and quantum dots with high selectivity. Suspending these perforated LbL membranes over microfabricated microscopic hole arrays in a manner similar to that employed for microthermal imagers88 can lead to the fabrication of intriguing sieve arrays with hierarchical multiscale micro- and nanoporous structures.

The strongest Flex LbL clay composites ever prepared with some mechanical parameters similar to steel have been developed and the perfect stress transfer on the composites with high loading of clay has been demonstrated.

First demonstration of optical sensitive flexible nanoscale composite membranes over microfabicated cavities as the application of Infrared microimagers.

Ability of functionalizing gold nanorods with self-assembling block copolymers brings a new means in directed assembly and nanofabrication of inorganic nanostructures.

Overall, freely standing flexible nanocomposite structures were demonstrated to be applicable in a variety of sensing and structural applications.

Contributions to Human Resource Development:

In PI's group, YenHsi Lin, received PhD and became a Researcher at Whirlpool Research Center, MI, July 2007; HyunHyub Ko received PhD and became a post-doc at U. Berkeley in May 2008; Dr. Chaoyang Jiang moved to the faculty of U. South Dakota in July 2007, Dr. Dmitry Zimnitsky became a Researcher at KCI, TX, February 2008, M. McConney received NRC post-doctoral fellowship and moved to AFRL, and Eugenia Kharlampieva became a professor at U. Alabama in 2010.

Jun Xu, a graduate student from Lin's group, earned Ph.D. degree and moved to Pixelligent Technologies LLC, College Park, MD as a research scientist M. Goodman received MS degree and will be enrolled in PhD program at UIUC.

SEVEN UNDERGRADUATE STUDENTS PARTICIPATED IN SUMMER AND ACADEMIC YEAR RESEARCH GAINING INVALUABLE RESEARCH EXPERIENCE.

Contributions to Resources for Research and Education:

Strong and visible collaboration among four academic institutions and across four different departments is an excellent role model for interdisciplinary approach for solving complex problems. NIRT workshops (2005, 2007) were well-attended and served as a venue for a number of graduate students from different departments (~20) to get 'first-hand' information on recent nanotechnology developments.

Contributions Beyond Science and Engineering:

New materials with simple and easy synthetic routine opens the way toward obtaining robust and flexible nanoscale membranes in a sharp contrast with current approaches.

Conference Proceedings

Categories for which nothing is reported:

Any Book

Any Product

Any Conference

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. Illinois UC; Eugene R. Zubarev, Rice U.

Major Research Accomplishments, 2006-2010

Educational achievements and related professional activities, 2006-2008

30 refereed papers have been published including high-impact journals such as *Science, Nature Materials, Adv. Mater., JACS, NanoLett., Langmuir, etc*

Students and post-docs on the project:

YenHsi Lin *received PhD and became a Researcher at Whirlpool, MI, July 2007*

Chaoyang Jiang *moved to the faculty of U. South Dakota, July 2007*

HyunHyub Ko *received PhD and became a post-doc at U. Berkeley, May 2008*

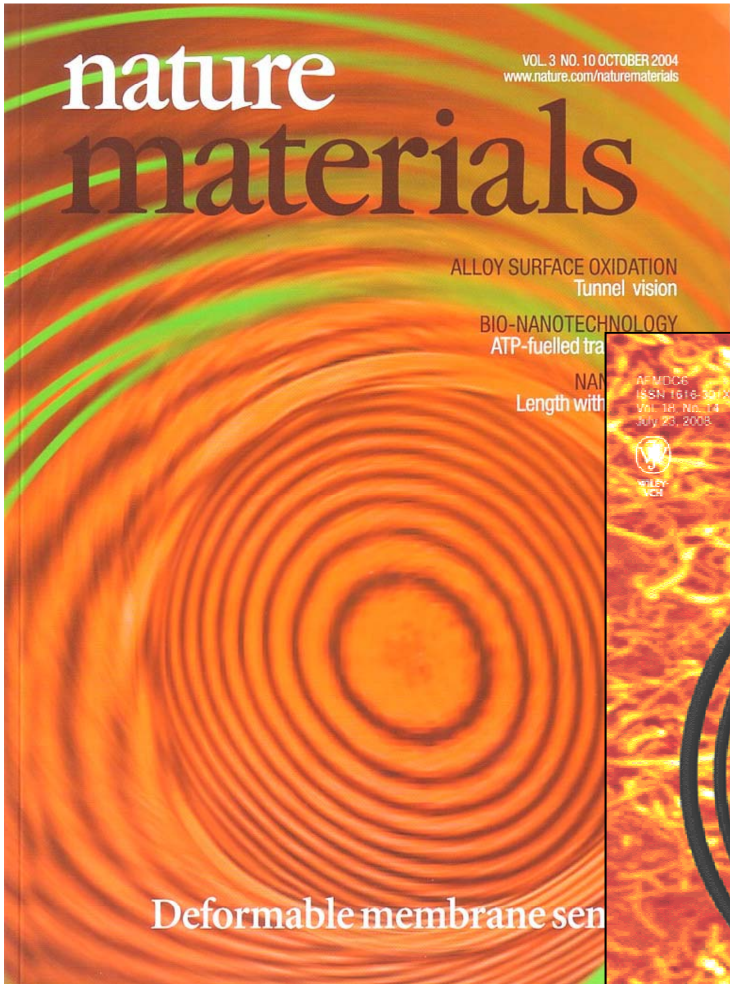
Dmitry Zimnitsky *became a Researcher at KCI, TX, February 2008*

Jun Xu *received PhD and became a Researcher at Pixelligent Technologies, MD, January 2008*

Eugenia Kharlampieva*, became a faculty member at U. Alabama, July 2010*

***Langmuir* (Feature Article and Cover), *24*, 5996, 2008**

Free-standing flex nanocomposites



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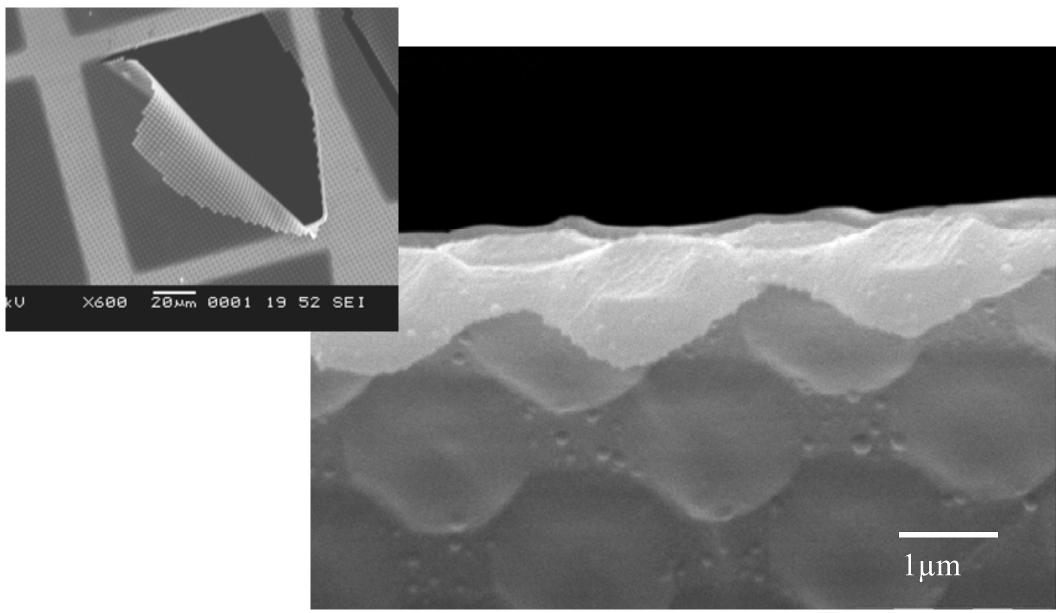
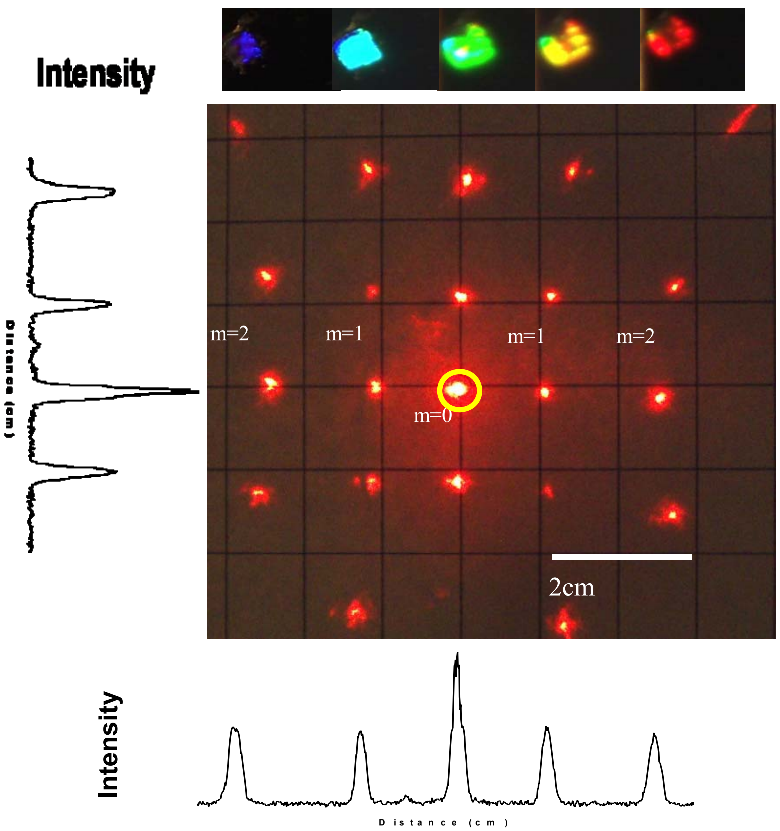
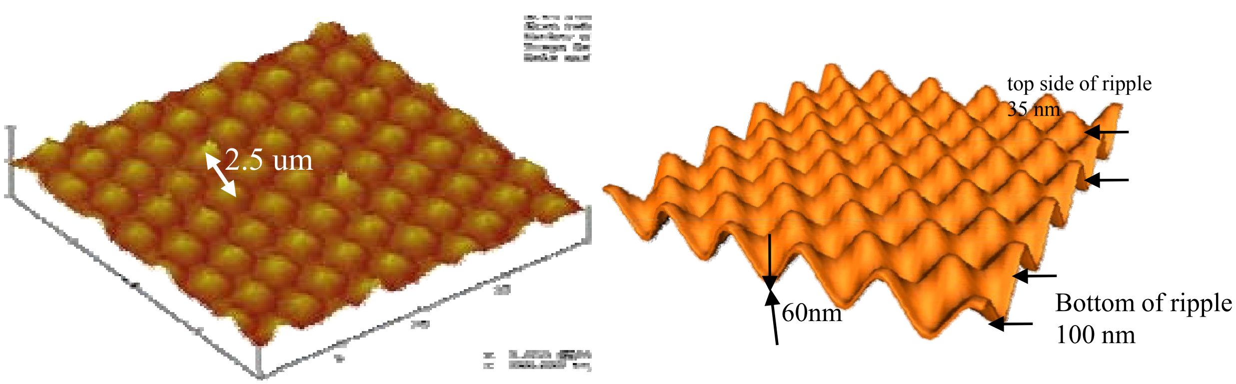
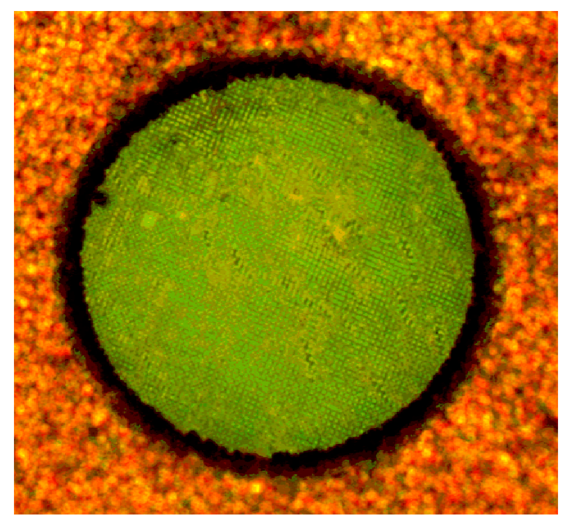
Structural colors with sculptured nanomembranes









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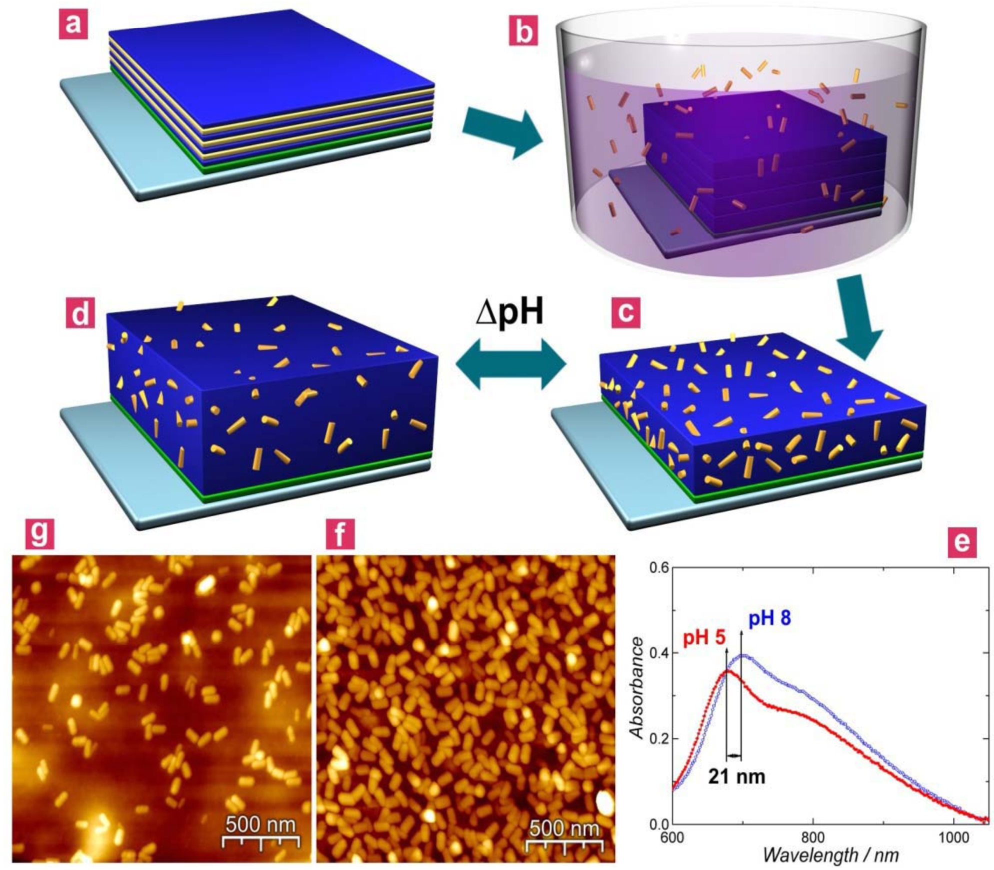
Adv. Mater., 2007, *19*, 3827

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. Illinois UC; Eugene R. Zubarev, Rice U.

Major Research Accomplishments, 2006-2010

We report ultrathin pH-responsive plasmonic membranes of [poly(methacrylic acid)-gold nanorods]20 (PMAA-Au NRs)20 with gold nanorods embedded into swollen cross-linked LbL hydrogels. In contrast to the most of known pH responsive materials which rely on pH-triggered change in the intensity of photoluminescence or plasmon bands, the responsive structures suggested here exhibit a significant pH-triggered shift in easily detectable, strong plasmon resonance band. We show that a pH-induced de-swelling of the LbL hydrogel film in the pH change from 8 to 5 causes a dramatic blue-shift of the longitudinal plasmon peak by 21 nm due to the increased side-by-side interactions of adjacent gold nanorods.



Incorporation of gold nanorods into hydrogel LbL film and their LSPR response to variable pH

Tsukruk, et al., *Chem. Mater.*, 2008, *20*, 7474

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. Illinois UC; Eugene R. Zubarev, Rice U.

Major Research Accomplishments, 2006-2010

Our research is focused on design and development of ultrathin (< 100 nm) flex nanomembranes acting as thermal, acoustic, chemical and gas sensors with a primary inorganic nanoparticle sensing layer encapsulated between nanoscale LbL polyelectrolyte films. Among recent results, we fabricated ultrathin, perforated, freely suspended membranes with uniform nanopore size controlled in the range of tens of nanometers (Fig.1). We demonstrate that nanopore formation is caused by the partial dewetting of polyelectrolyte layers during LbL deposition on the hydrophobic surfaces (Fig.2). The nanoscale thickness of perforated membranes with a high concentration of nanopores might allow higher rates of transport facilitating fast ultrafine separation.

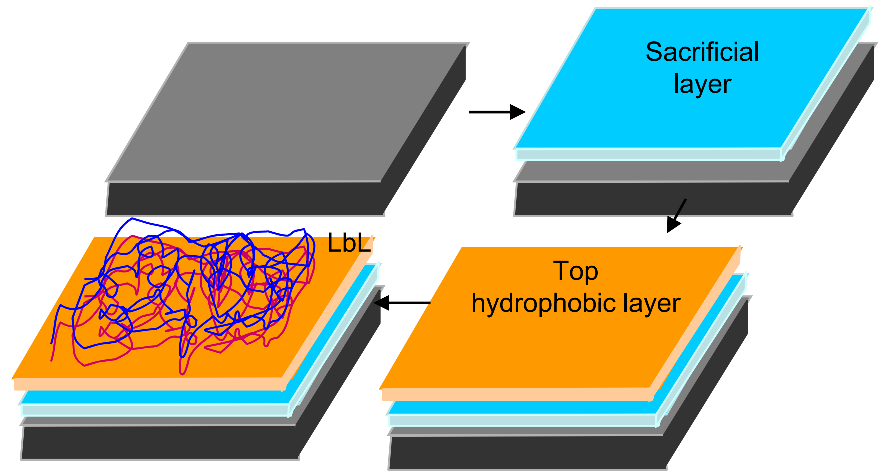


Fig.1. Deposition of a sacrificial and top hydrophobic layers for fabrication of perforated LbL membranes.

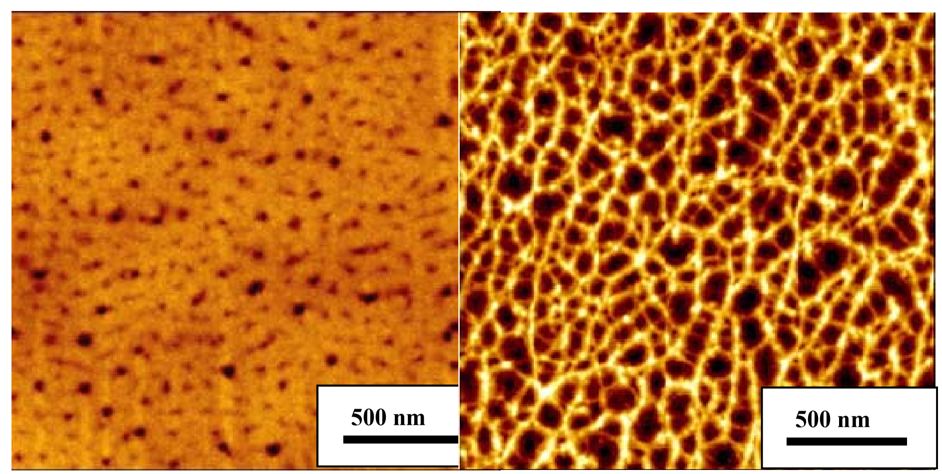


Fig.2. AFM images of the (a) top and bottom sides of the freely suspended (PAH-PSS)$_{15}$ membrane.

Tsukruk, et al., *Langmuir, 24, 5996,* 2008

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. Illinois UC; Eugene R. Zubarev, Rice U.

Major Research Accomplishments, 2006-2010

We demonstrate that photoluminescence of CdSe/ZnS quantum dots (QDs) deposited at surfaces can be can be tuned by placing the nanoscale (3-50 nm) LbL polymer film between QDs and a substrate (Fig.3). Such QDs encapsulation into the LbL film results in a dramatic initial increase in the photoemission intensity due to the accelerated photooxidation process. Such enhanced photoemission of encapsulated QDS enables fabrication of ultrathin, flexible, QD-polymer films, with improved light emitting properties.

Z. Lin, V. V. Tsukruk, et al. *Langmuir* 2007, 23, 4509.

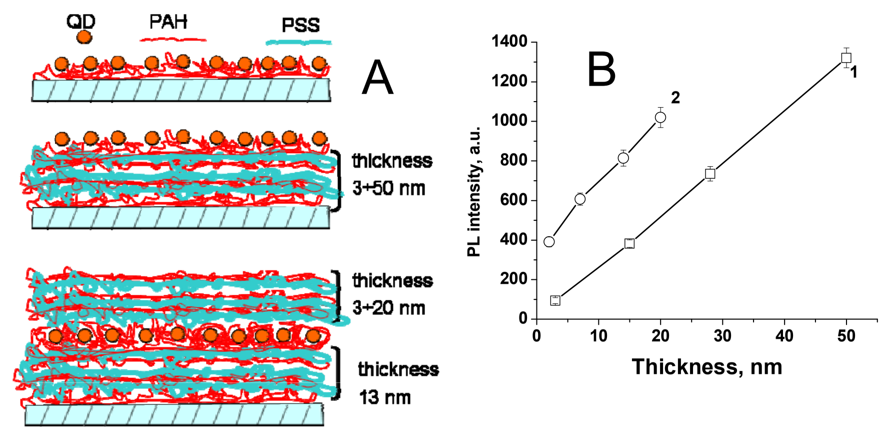


Fig.3. (A) Different types of QDs-LbL film organization. (B) The PL intensity vs film thickness (1) between QDs and Si surface and (2) above QD monolayer.

We showed that a single monolayer of CdSe/ZnS quantum dots (QDs) encapsulated into a 60 nm free-suspended LbL film exhibits the manifold increase of photoluminescencence intensity when freely suspended over the cylindrical cavities (Fig. 4). Such drastic enhancement in PL is mostly due to elimination of the surface quenching enhanced by optical reflection. We suggest that a significant increase of PL intensity of QD monolayers suspended over the microfabricated array can be useful for diagnostic and sensing.

Z. Lin, V. V. Tsukruk et al. *Langmuir* 2007, 23, 10176.

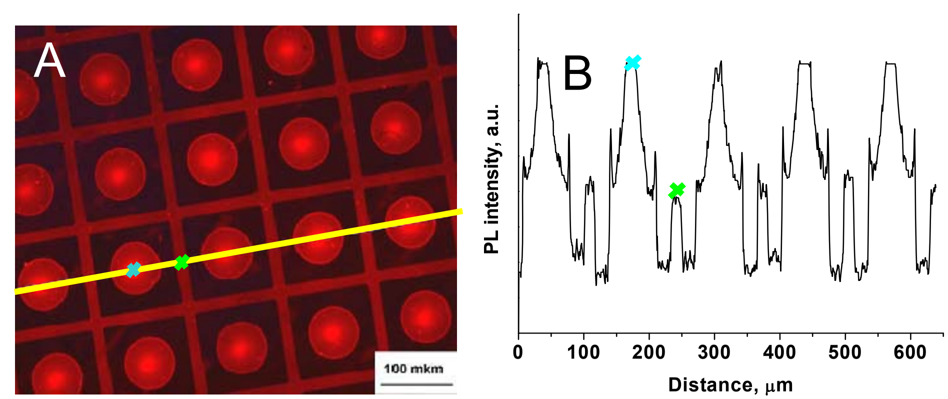
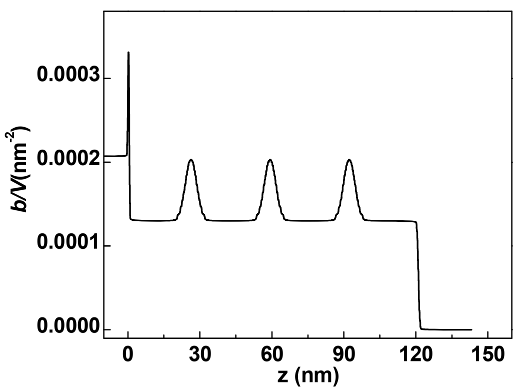
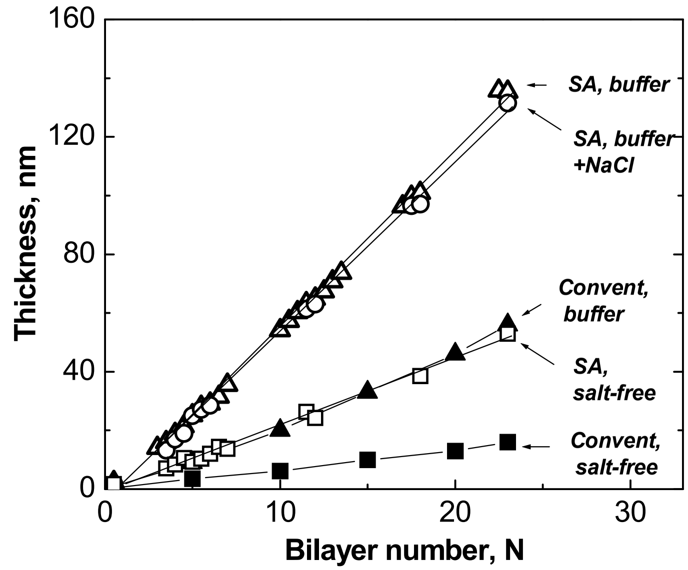
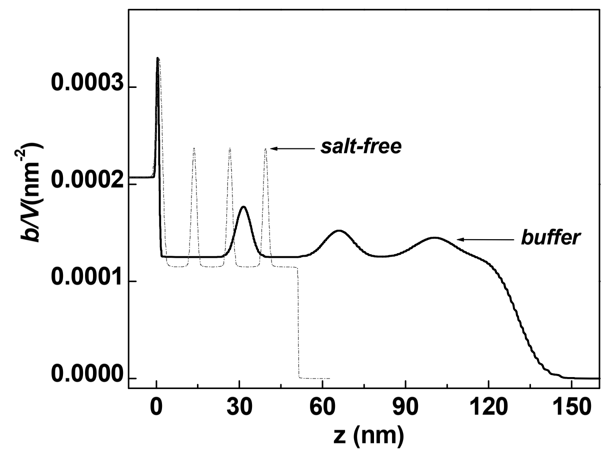


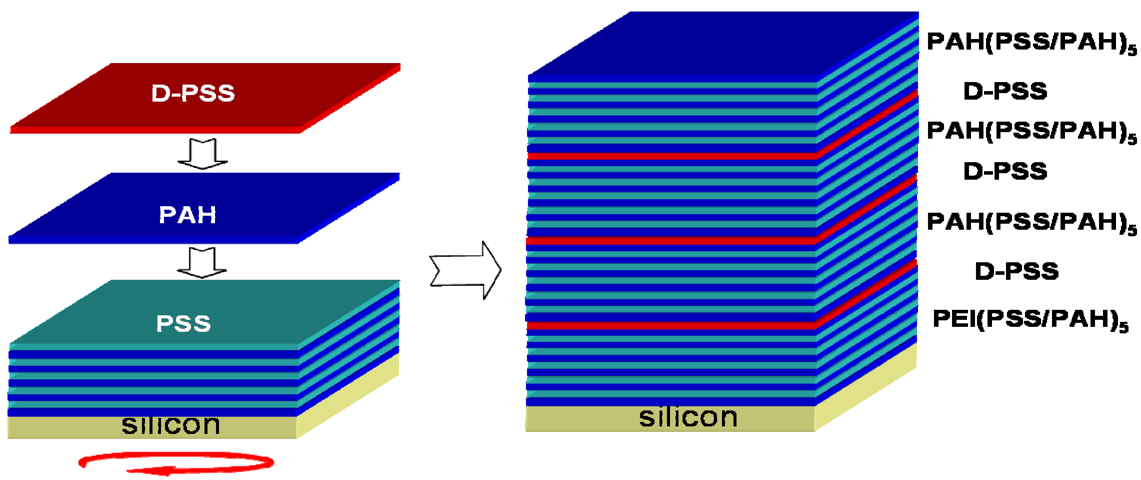
Fig. 4. A fluorescent image of a 9(PSS/PAH)QDs9(PSS/PAH) film freely suspended over microscopic cavities of a microfabricated silicon wafer (A). The PL intensity across the yellow line (B).

Neutron reflectivity of LbL films







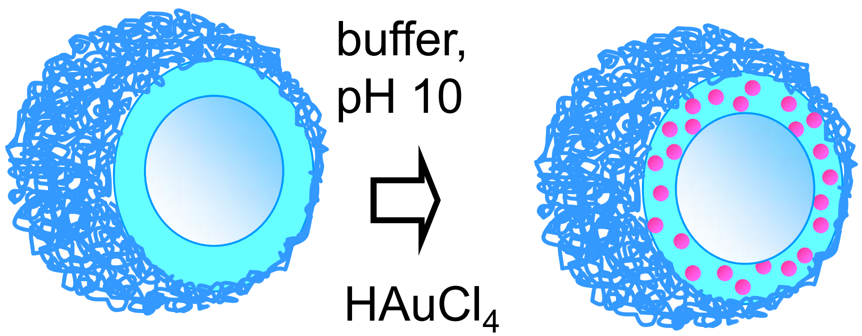


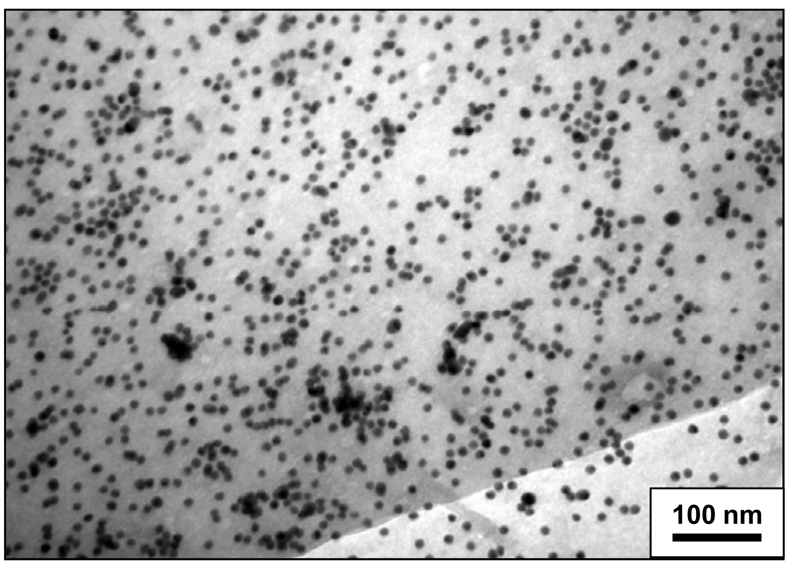
Langmuir. **2009**, *25, 14017*

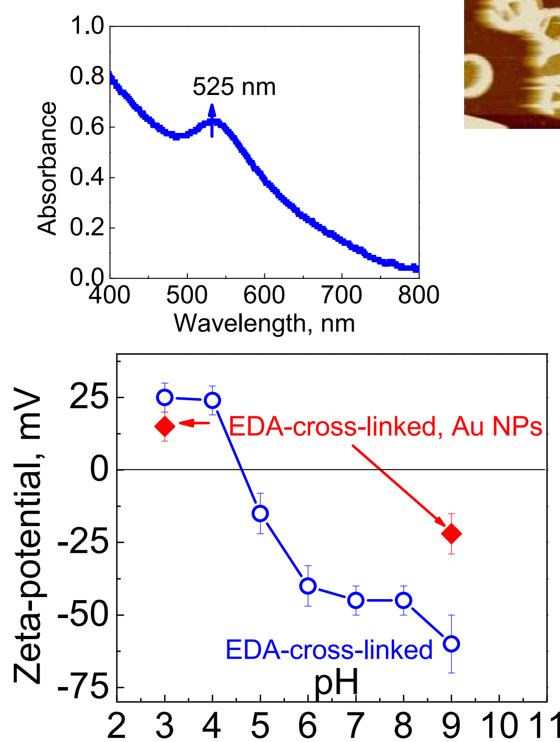
PEI[(PSS-PAH)5/*d*PSS/PAH]3(PSS/PAH)5

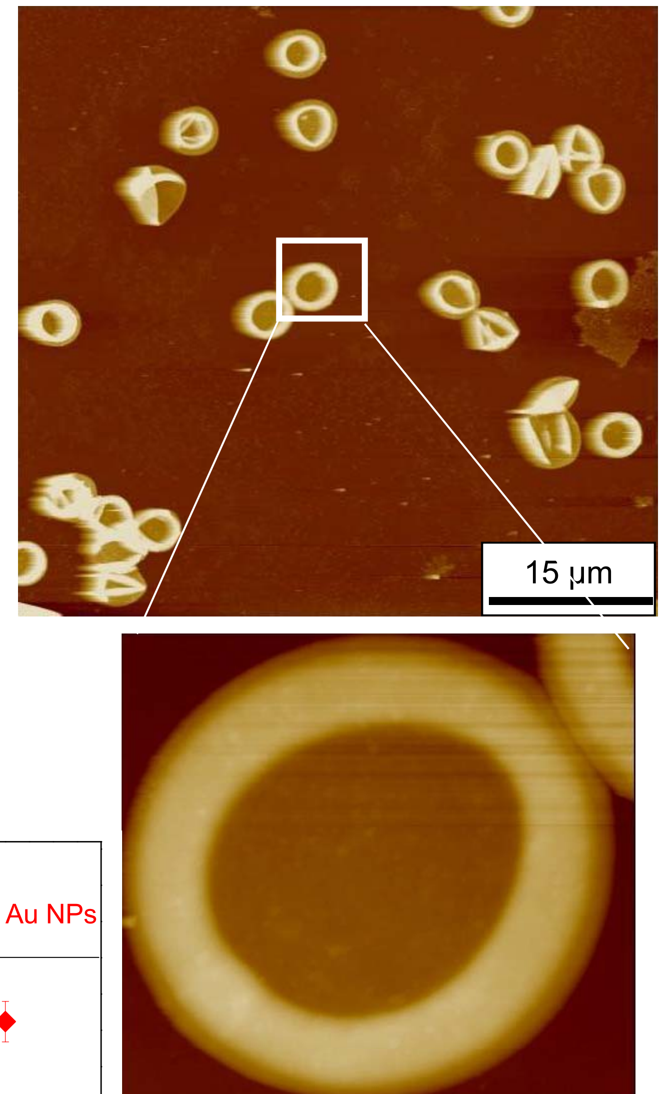
Free-standing PMAA LbL-derived hydrogels

Au-(PMAA)$_{40}$









***Chem. Mater.* 2009, *21*, 2158**

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. illinois UC; Eugene R. Zubarev, Rice U.

Major Research Accomplishments, 2006-2010

We developed the ways to synthesize water-soluble QDs through functionalization of their surface with polar ligands. We demonstrated that water-soluble dithiocarbamate-functionalized CdSe quantum dots (QDs) can be synthesized via a simple biphasic route (Fig.5). Optical images of emission under UV excitation at the wavelength of 365 nm, demonstrate the transformation of hydrophobic CdSe-TOPO QDs from chloroform phase (Fig.5A) into hydrophilic dithiocarbamate-CdSe QDs in water (Fig.5B) after the biphasic ligand exchange (C) at room temperature.

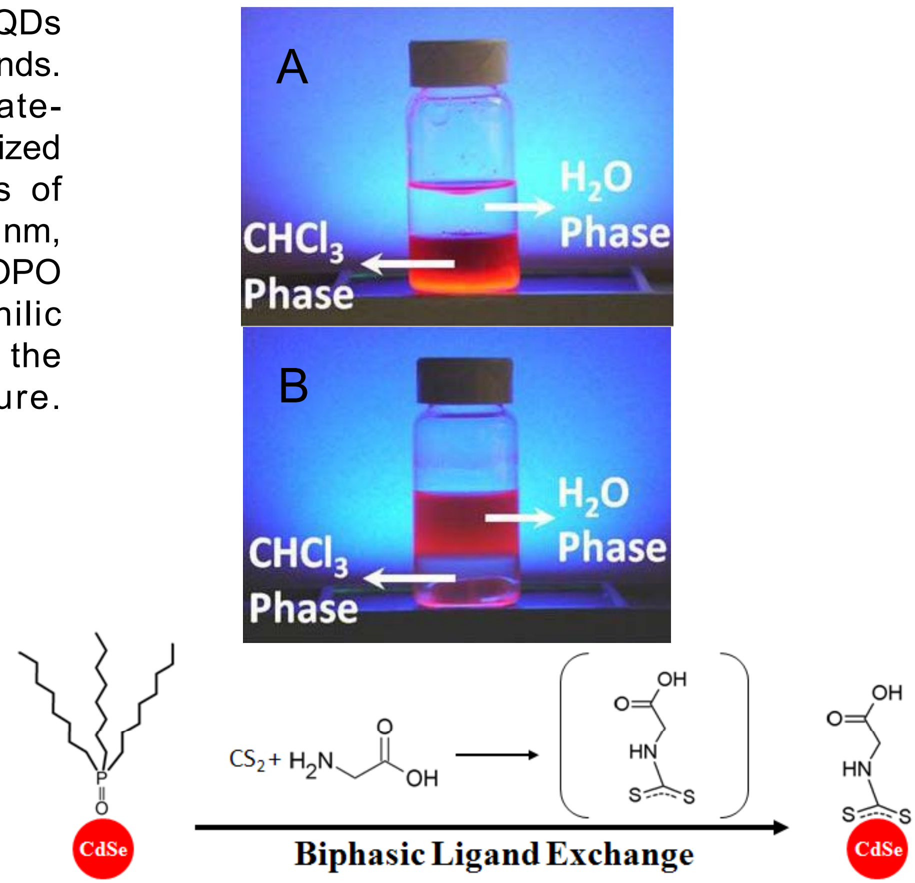


Fig.5. Digital images of CdSe-TOPO in chloroform (A), and after their functionalization with dithiocarbamate as D-CdSe in water (B).

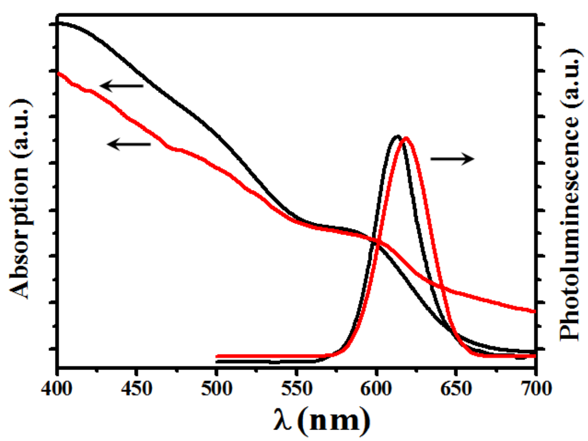


Fig.6. Absoprtion and photoluminescence (PL, Ex:365 nm) spectra of CdSe-TOPO in chloroform (black), and of dithiocarbamate-CdSe in water (red).

Z. Lin et. al. *J. Mater. Chem.*, 2008

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. Illinois UC; Eugene R. Zubarev, Rice U.

Major Research Accomplishments, 2006-2010

We synthesized functionalized quantum dots for the use as a central sensing layer in LbL polymer films (Fig.7). We show that compared to the original photoluminescence (PL) of dithiocarbamate-CdSe in ethanol (Fig. 8, black curve), a 65% reduction in PL (Fig. 8, red curve) after 2 h stirring and a 94% reduction in PL (Fig. 8, blue curve) after 24 h stirring were observed.

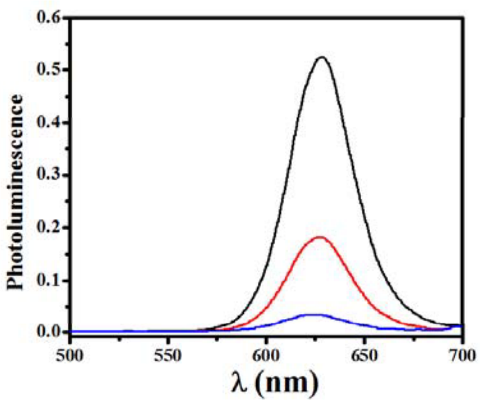


Fig. 8. The PL spectra of the mixture of dithiocarbamate-CdSe and TiO_2 nanoparticles during the different stirring periods.

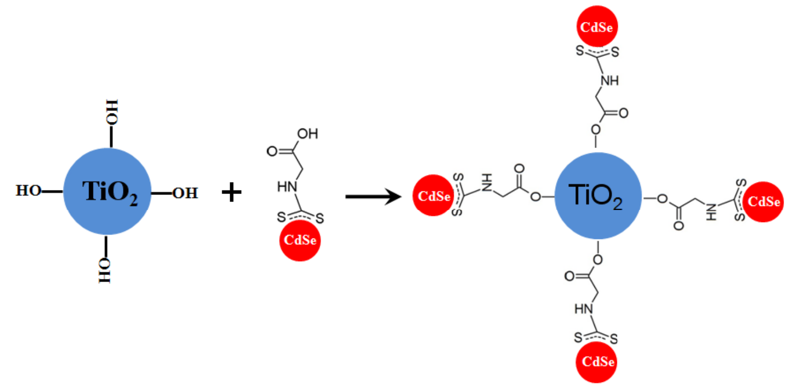


Fig.7. Scheme of covalent linkage of dithiocarbamate-functionalized CdSe QDs to native hydroxyl terminated TiO_2 nanoparticles

Direct integration of CdSe QDs with conjugated polymers was achieved via coupling of [(4-bromophenyl)methyl]dioctylphosphine oxide (DOPO-Br)-functionalized CdSe QDs (D = 3.5 nm) with vinyl terminated P3HT (Fig.9.)

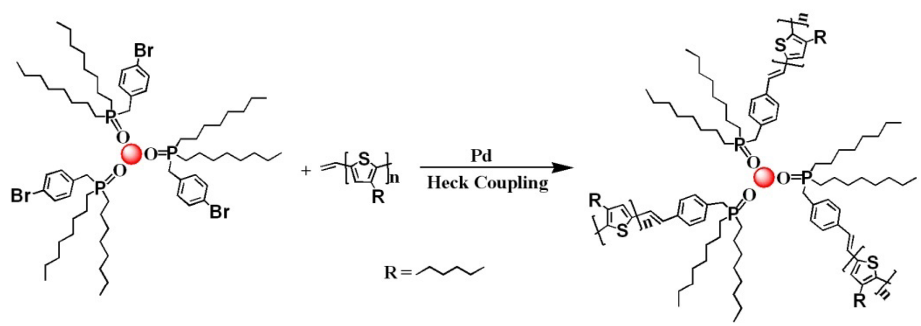


Fig. 9. Coupling of DOPO-Br-CdSe QDs with a vinyl terminated polythiophene derivative (P3HT)

Z. Lin, *Chem. Eur. J.*, 2008

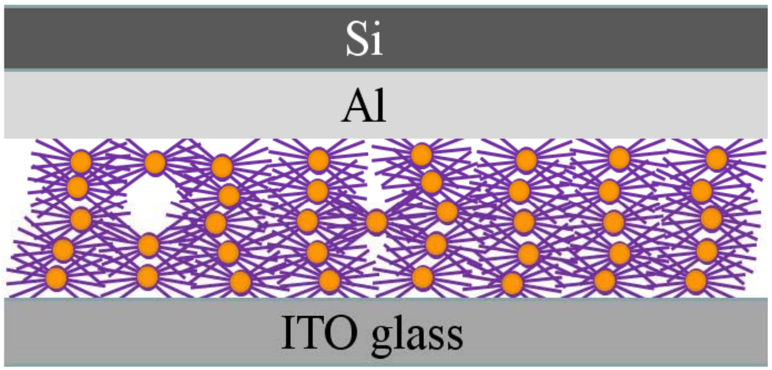
Z. Lin et al *JACS*, 129, 9486 (2007)

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. Illinois UC; Eugene R. Zubarev, Rice U.

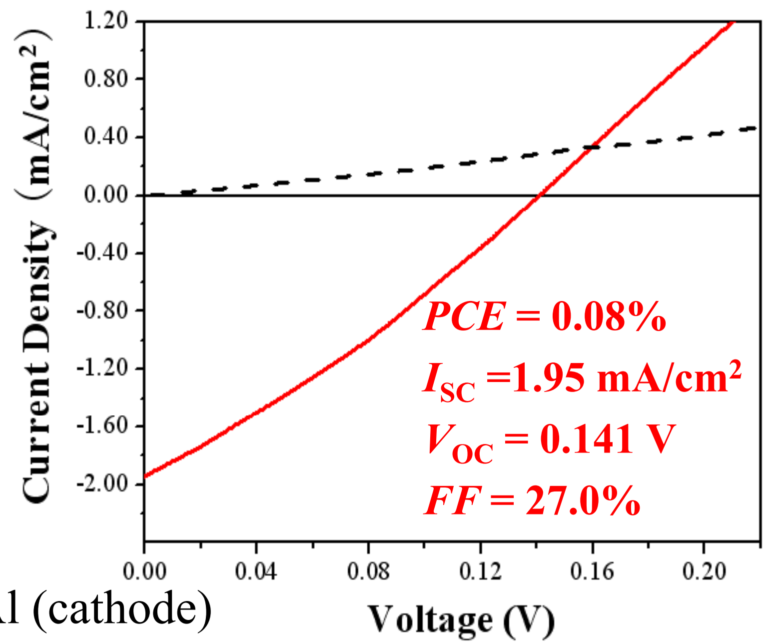
Major Research Accomplishments, 2006-2010

(a)



A 30-nm thick photovoltaic device fabricated from **5 LB deposition cycles**.
Film thickness = **30 nm**.

(b)



- Contact between multilayer (active layer) and Al (cathode)
- 30-nm thick active layer resulted in low light absorption
- *n*-type CdSe QDs were in contact with hole conducting ITO (anode)
  - • LB depositions on Al-Si; • poor performance from Al_2O_3
- Lack of PEDOT/PSS (h^+ injecting) due to solubility in water subphase

$$FF = \frac{I_{max}V_{max}}{I_{SC}V_{OC}}$$

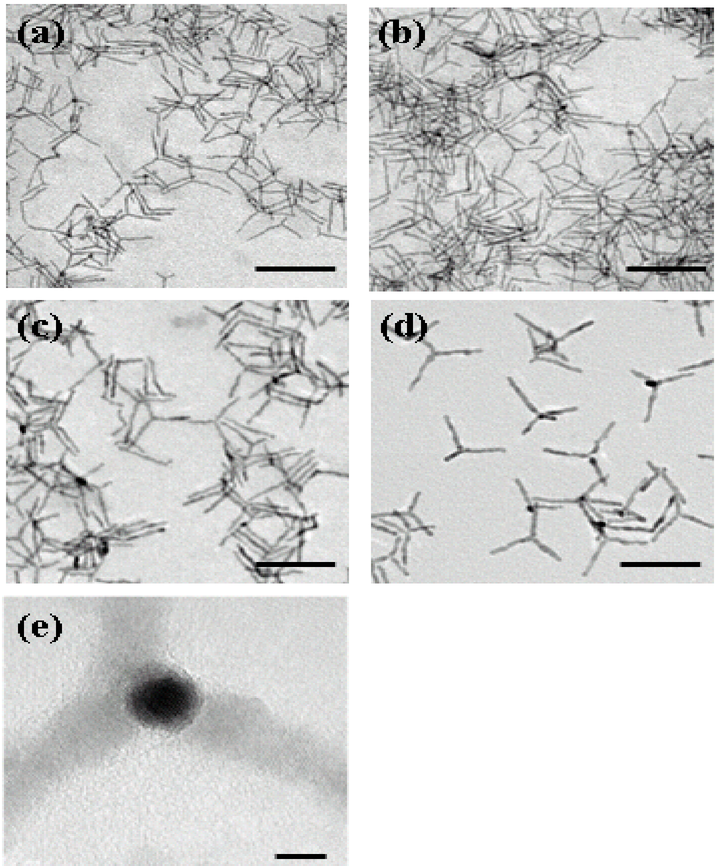
$$PCE = \frac{I_{SC} \cdot V_{OC} \cdot FF}{P_{inc}}$$

Goodman, M. et al, *Chem. Mater.* **21**, 934 (2009)

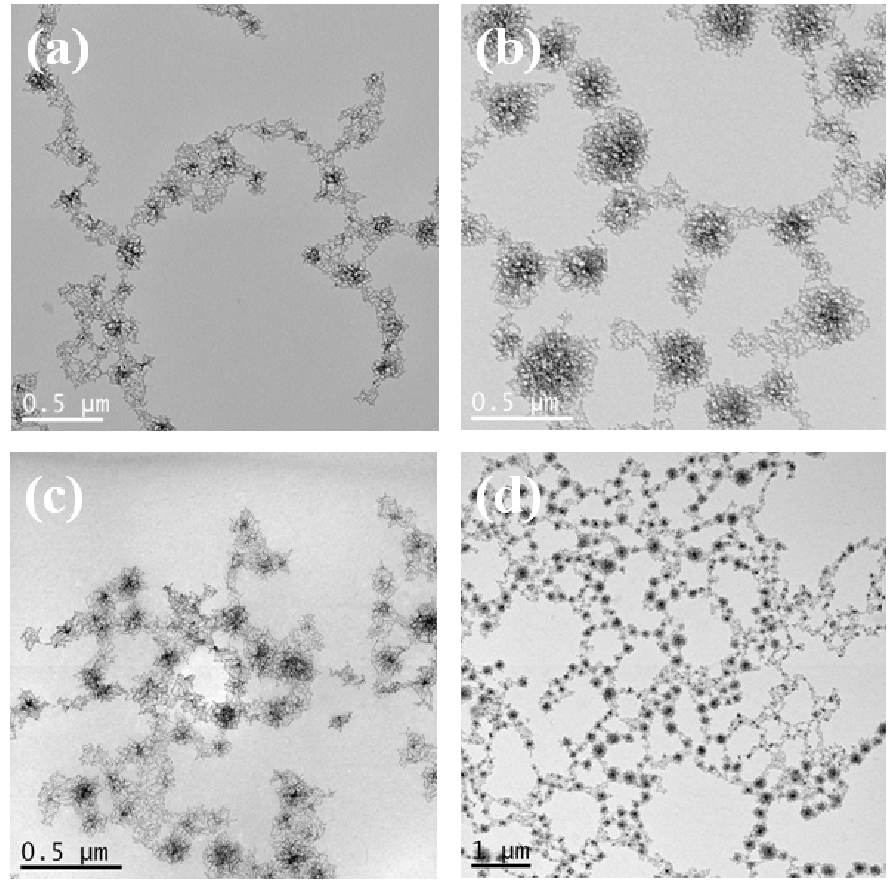
Ongoing work

- **QD/CP–QD solar cells** to form a better percolation for charge transport
- **CP–QR in vertically oriented nanoporous arrays that bridge between two electrodes**

Self-Assembly of CdTe Tetrapods into Network Monolayers at the Air/Water Interface



CdTe tetrapods synthesized via multiple injections of Te-TOP in one reaction with aliquots taken after various number of injections: (a) 4 injections, (b) 6 injections, (c) 8 injections, and (d) 10 injections. (e) Close up of a single tetrapod from (d). Scale bars are 100 nm in (a)-(d), and 5 nm in (e).



Large scale TEM images obtained at pressures of (a) π = 1 mN/m, (b) π = 10 mN/m, (c) π = 22 mN/m, and (d) π = 39 mN/m.

M. Goodman et al, ***ACS Nano***, **4** 2043 (2010)

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. Illinois UC; Eugene R. Zubarev, Rice U.

Major Research Accomplishments, 2006-2010

We synthesized gold particles (5 nm) functionalized with polyacrylic acid (PAA) or poly-N-isopropylacrylamide (PNIPAM) chains (Fig.10A) via two-phase synthesis of dodecanethiol-terminated gold nanoparticles.
We demonstrate that annealing the particles in neat alkanethiol at elevated temperatures reduces the size distribution of the particles due to digestive ripening, which allows their colloidal crystallization with a long range hexagonal order (Fig.10B). As the size of environmentally sensitive PAA or PNIPAM arms is comparable with the particle diameter, changes in pH or temperature, respectively, are expected to affect the optical properties of the polymer layer-by-layer films containing the gold nanoparticles as a sensing layer.

We suggested novel nanocomposites of gold nanorods covalently functionalized with PDMS chains (Fig.10C). These hybrid nanorods were easily dispersed and cross-linked in PDMS pre-polymer. Importantly, no phase separation occurred during the cross-linking of the PDMS matrix. Such composite materials show almost the same position of the longitudinal plasmon indicating the absence of aggregation. Optical and mechanical properties of the novel composites are under investigation.

E. Zubarev et al. *JACS*, 2007, 129, 11653.

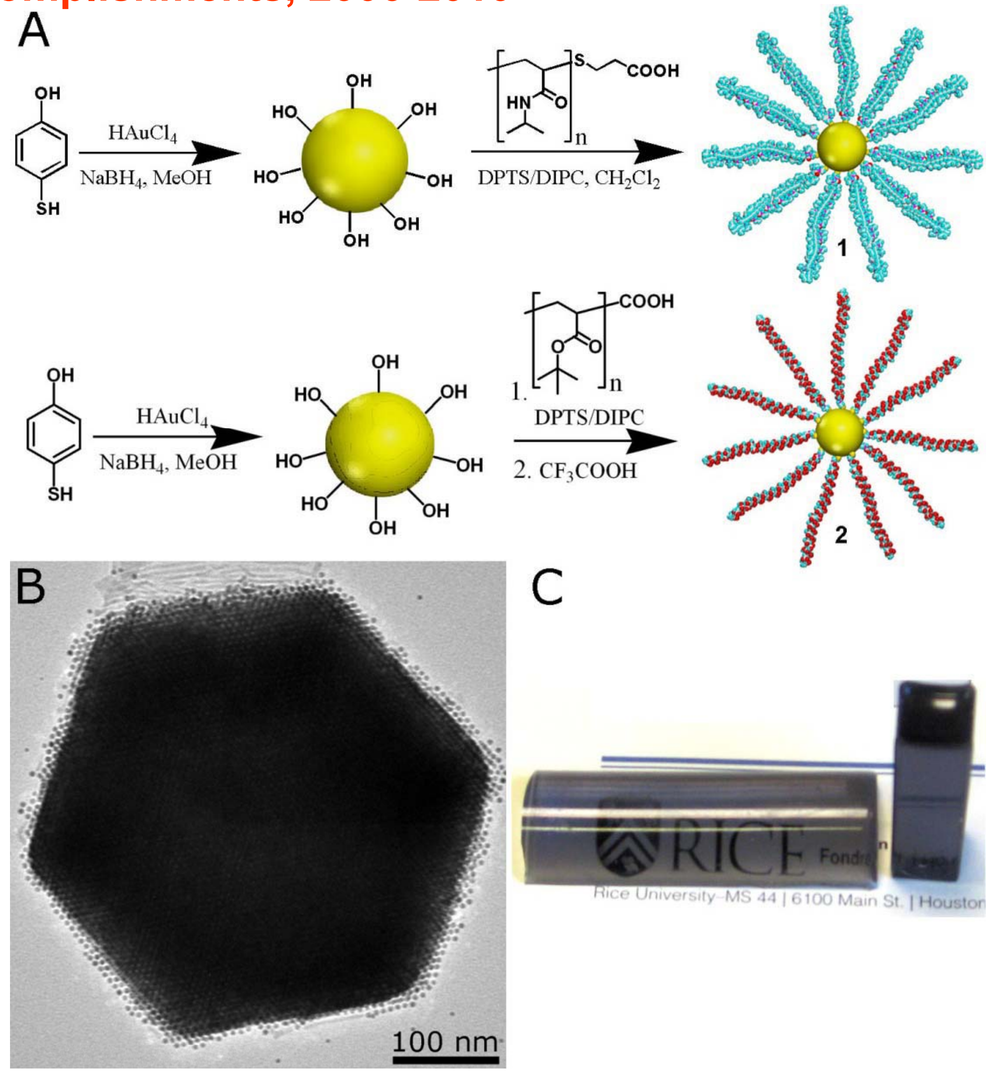


Fig. 10. Synthesis of Au NPs with polyelectrolyte chains (A); TEM image of colloidal single crystal formed by 5nm gold NPs (B); PDMS doped with gold NRs functionalized with linear PDMS chains (C).

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Major Research Accomplishments, 2008-2010

Results: Because physical and chemical properties of nanostructures strongly depend on their shape, it is of great importance to find either synthetic or separation techniques that can produce objects of a particular shape in a pure state. We recently described a solution to a long standing problem of separating 2D platelets from 1D nanorods coated by cationic surfactant CTAB. The key aspect of our approach relies on the partial dissolution of faceted platelets with Au(III)/CTAB complex that transforms them into smaller nanodisks. Due to the reduction in size, the 2D structures become fully soluble in water and can be separated from the nanorods that undergo slow precipitation. In addition, the isolated nanodisks can be converted back into initial faceted platelets upon treatment with Au(I)/ascorbic acid mixture. As a result of these simple procedures, a seemingly inseparable mixture of rods, platelets, and spheres is converted into nearly pure individual components.

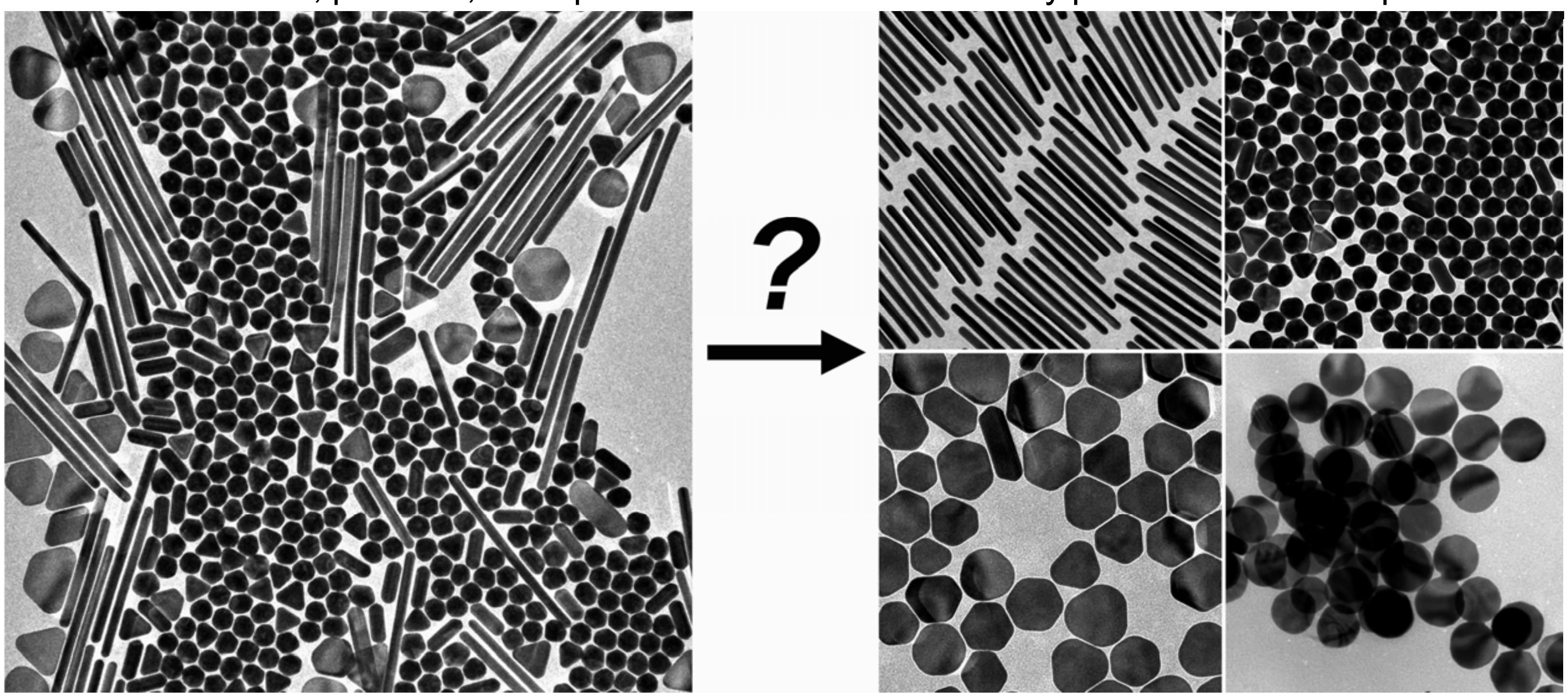


Fig. 1. TEM images of as-synthesized mixture of gold nanostructures (left) and individual components after the separation.

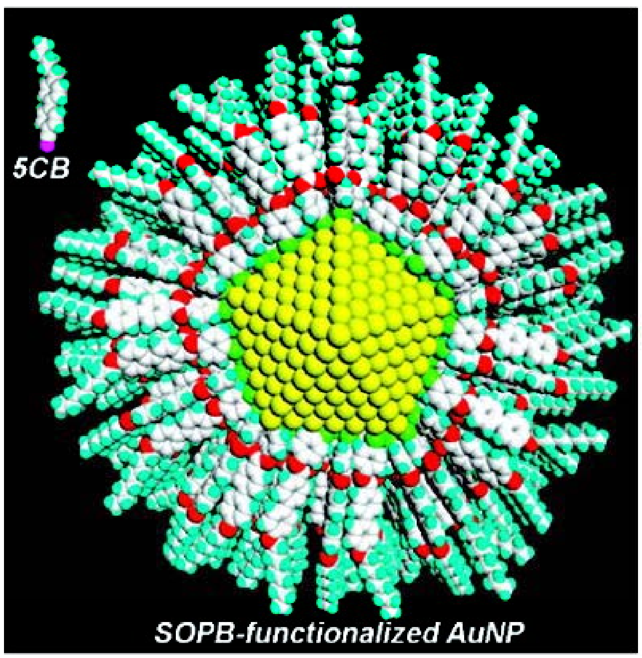
Zubarev et al. *JACS* **2008**, *130,* 12634.

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

Vladimir V. Tsukruk, Georgia Tech; Zhiqun Lin, Iowa State U.; Nick Kotov, U. Michigan; Chang Liu, U. Illinois UC; Eugene R. Zubarev, Rice U.

Major Research Accomplishments, 2006-2010

Results: We report on the plasmonic properties of 6 nm gold nanoparticles that form highly stable solutions in the nematic liquid crystal 4-cyano-4-*n*-pentylbiphenyl (5CB). The nanoparticles were covalently functionalized with 4-sulfanylphenyl-4-[4-(octyloxy)phenyl]benzoate, which resembles the structure of the 5CB molecules. The solubility of these nanoparticles in 5CB was significantly higher than that of conventional alkanethiol-terminated nanoparticles. An 8 nm shift of the surface plasmon resonance was observed when the gold nanoparticles were dissolved in the nematic phase of 5CB, as compared to the isotropic solution in methylene chloride. Good agreement of the experimental surface plasmon resonance shift with Mie calculations using an adjusted dielectric function for a reduced electron mean free path in small nanoparticles confirmed that the gold nanoparticles are solvated by the liquid crystal molecules. The stability of this composite was verified by repeated temperature cycling between the isotropic and nematic phases. We also investigated the nematic-to-isotropic phase transition temperature and the threshold voltage for the Freedericksz transition in gold-nanoparticle-doped and undoped liquid crystal devices.



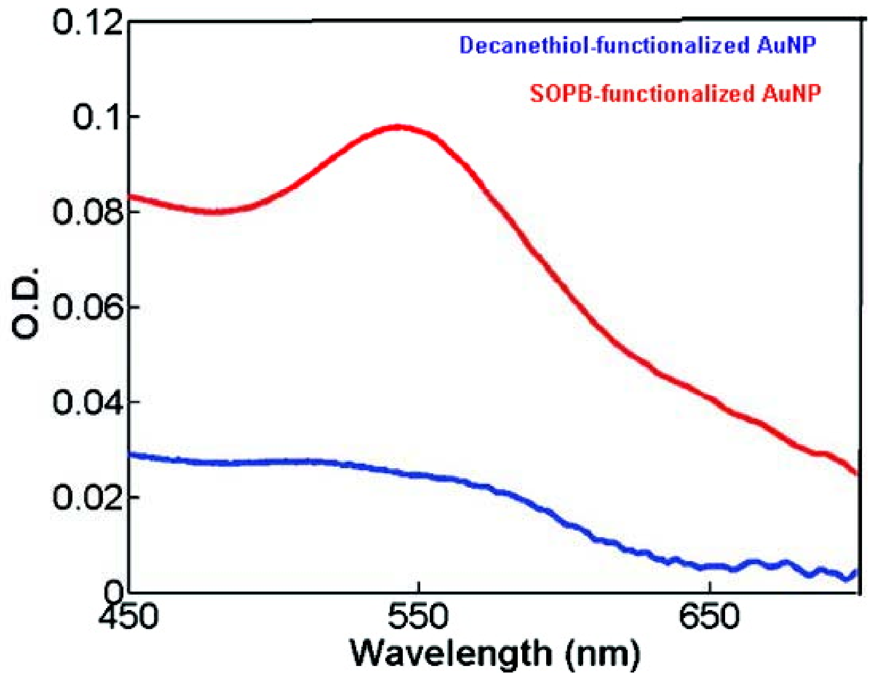


Fig. 1. Molecular graphics representation of liqud crystal functionalized gold nanoparticles (left) and their UV-vis spectra in nematic solvent (right).

CBET-0650705, NIRT: Bioinspired nanomembranes for multifunctional sensors

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Major Research Accomplishments, 2006-2010

We designed and developed ultra-strong and tough polymeric nanocomposites via LbL. We demonstrate that a nanocomposite composed of ~ 50 vol.% of well organized and dispersed nanosheets of the montmorillonite (Fig. 11) has E' ~260 GPa, which have received substantial interest in the development of reinforced polymeric composites. These results encouraged a generation of a new class of biomimmetic materials and ultra-strong nanocomposites at very high loadings of the reinforcing nanoparticles. We show that use of a macroscopically stronger polycation, a biomimmetic polymer with highly adhesive groups, along with covalent and ionic cross-linking of the polymeric matrix increases the load transfer between the polymer and the filler. Ideal load transfer was realized for high load composites, which leads to the development of a clay nanocomposite with record-high strength and stiffness with tensile strength of 480 MPa, Young modulus of 125 GP, ultimate strain of 0.33 ± 0.04 (Fig. 12).

N. A. Kotov et al. *Science* 2007, 318, 80.

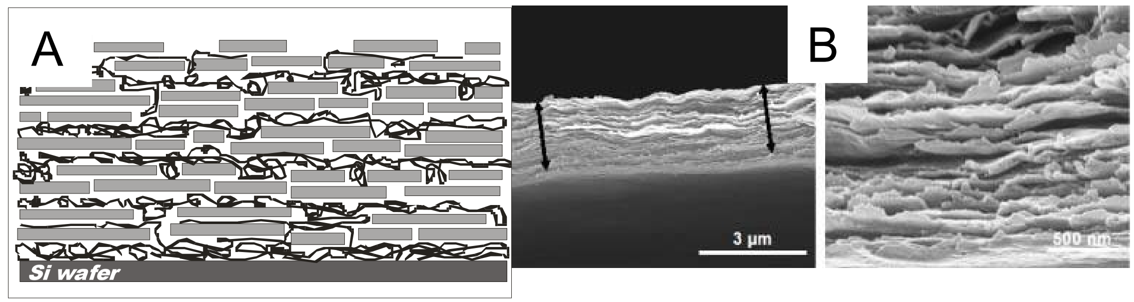

Fig. 11. LbL self-assembled nanocomposite films (A). SEM images of a cross-section of the free-standing poly(vinyl alcohol)-clay film shows well defined, stratified architecture.

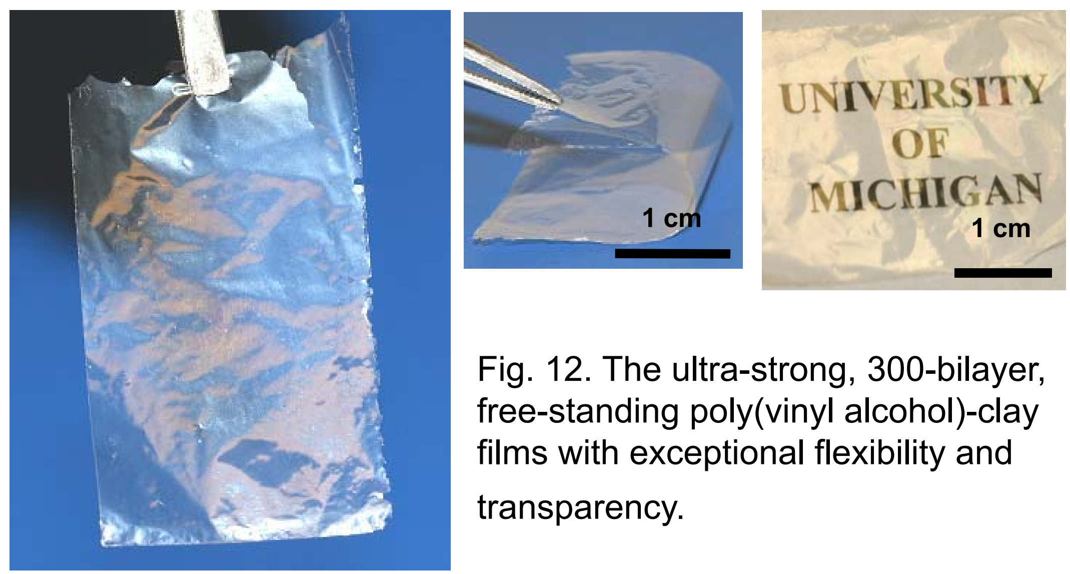

Fig. 12. The ultra-strong, 300-bilayer, free-standing poly(vinyl alcohol)-clay films with exceptional flexibility and transparency.

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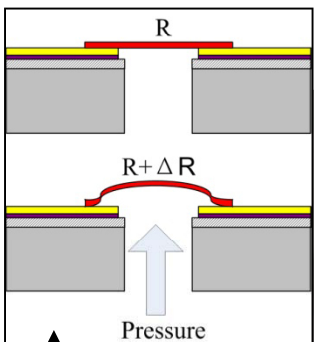
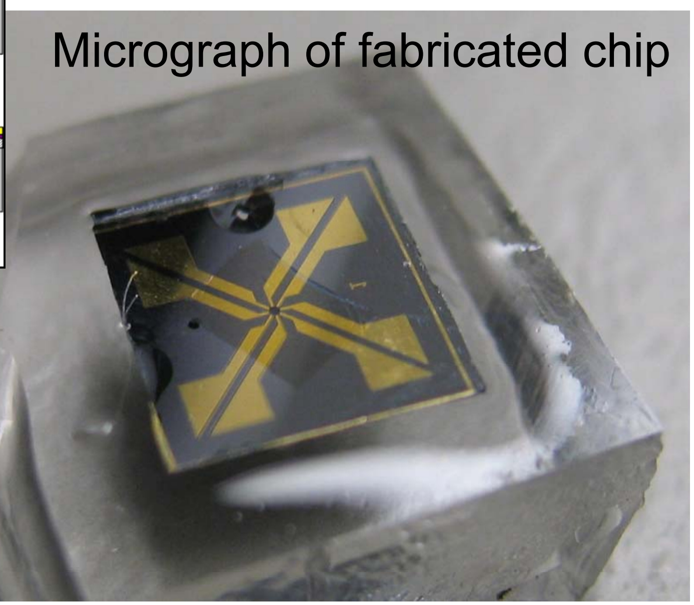
Major Research Accomplishments, 2006-2010

We are developing silicon chip for integrating the LbL films to realize highly sensitive mechanical sensor devices such as pressure sensor and force sensors.

A picture of the developed silicon chip embedded in a polydimethylsiloxane substrate is shown here.



Schematic diagram of pressure sensor



Micrograph of fabricated chip