

Nanoscale Science & Engineering Center for Integrated Nanopatterning and Detection Technologies

NSF NSEC Grant Number ECC-0118025

PI: Chad Mirkin

Northwestern University

The NU-NSEC brings together recognized leaders with diverse expertise from Northwestern University (NU), University of Chicago (UC), University of Illinois/Urbana-Champaign (UIUC), Argonne National Laboratories (ANL), as well as educational partners from the Museum of Science and Industry, Chicago, and Harold Washington College. Housed in NU's \$34 million Center for Nanofabrication and Molecular Self-Assembly (Figure 1), one of the first joint federally and privately funded facilities of its kind in the country, NU-NSEC members represent a broad spectrum of disciplines (medicine, biomedical engineering, chemistry, mechanical engineering, materials science, chemical engineering, and electrical and computer engineering), and address opportunities that are too complex and multifaceted for individuals or small groups of researchers to attempt on their own. By facilitating synergistic science and engineering research in the emerging areas of nanopatterning and nanoscale detection technologies, the NU-NSEC is making contributions to cross-disciplinary research and advancing pre-college education, workforce training, and public understanding of nanoscale science and engineering.

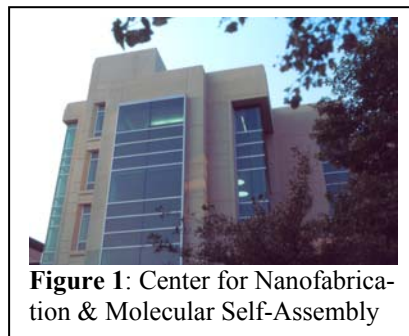


Figure 1: Center for Nanofabrication & Molecular Self-Assembly

Center research is focused on the development of state-of-the-art nanopatterning technologies that are compatible with soft materials and can be used for the development of powerful new detection systems. Research is organized into the following three synergistic research groups (SRGs): (1) Nanopatterning SRG - developing state-of-the-art sub-100 nm patterning capabilities for a large variety of molecules, substrates, and environments; and developing the molecular surface chemistry that controls the assembly of target molecules and nanostructure signaling systems on integrated devices; (2) Optical Nanoarray Sensor SRG - focusing on nanoparticle-based optical technology as a route to ultra-sensitive and selective nanoscale molecular detection; (3) E-chip SRG - focuses on developing chip-based sensor technology that uses electrical or electrochemical methods to signal target-driven nanostructure assembly; developing rugged sample processing systems. The Center also supports seed projects in new and emerging areas.

Significant Accomplishments

Some of the significant accomplishments realized at the Center over the past year are listed below.

(1) The site- and shape-specificity of the dip-pen nanolithography (DPN) approach and the versatility of sol-based precursor inks were combined to fabricate arrays of nanodisk inorganic sensors.¹ Nanodisks are directly deposited in-between prefabricated electrodes, facilitating the direct measurement of a sensor response in real-time and provide an aid to on-site detection (Figure 2). The nanodisk sensors show rapid response and ultra-fast recovery for oxidative (e.g., nitrogen dioxide) and reducing (e.g., acetic acid) species, and model simulants for sarin and related species. Based on the principle of pattern recognition of the olfactory system, an electronic nose that can "smell" different species has been demonstrated. The gas recognition ability, instant response and rapid recovery, compact size and integration with the established microelectronics platform make the nanodisk arrays a significant development for on-site and real-time detection of life-threatening gases.

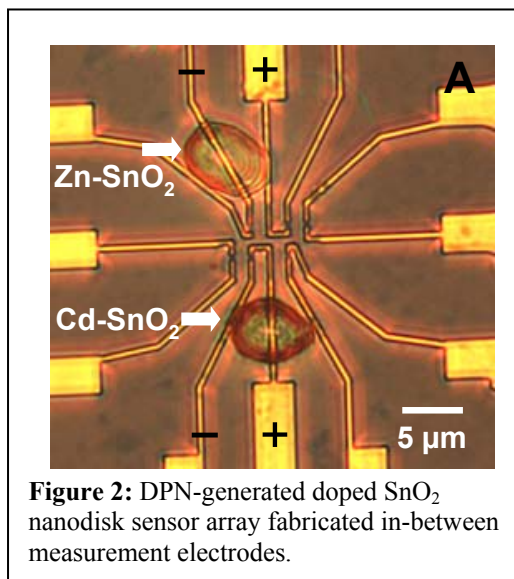


Figure 2: DPN-generated doped SnO₂ nanodisk sensor array fabricated in-between measurement electrodes.

(2) Direct-write DPN was used to deposit proteins on modified silicon oxide surfaces, offering patterning capabilities over the 50-550 nm length scale.² Proteins were successfully transferred from a hydrophilic poly(ethyleneglycol) (PEG) modified AFM tip and immobilized on two different types of modified surfaces (negatively charged and aldehyde-derivatized surfaces) through either electrostatic or covalent interactions. The protein nanostructures (rabbit IgG and human IgG, fluorophore labeled anti-rabbit IgG and anti-human IgG) including multiple proteins in a single pattern generated in direct-write fashion by DPN have been characterized by AFM (Figure 3) and fluorescence microscopy.

(3) Scanning probe microscope (SPM) based nanopatterning techniques all suffer from limited throughput due to their inherently serial nature. Consequently, significant effort within the NU-NSEC has been directed towards parallelizing SPM nanolithography using micromachining technology. In particular, one dimensional arrays of individually addressable and thermally actuated cantilever arrays were fabricated and interfaced (Figure 4).³ The optimal conditions for generating nanolithography patterns in parallel fashions were determined, thus allowing for successful use of cantilever arrays for DPN. To extend cantilever arrays to two dimensions, a new and efficient microfabrication process for realizing SPM probes was developed. This process, which can be widely applied to polymer and metal materials, has allowed large two-dimensional arrays (100×100) of cantilevers to be fabricated with high yield. This development implies a four order of magnitude improvement in throughput for SPM based nanopatterning techniques.

(4) The NU-NSEC team collaborated with Dr. M. Käll in Sweden to use E-Beam lithography to make planar arrays of silver disks and triangles. Extinction spectra were determined for the resulting arrays as a function of particle density.⁴ Figure 5 presents TEM images for several representative arrays. It was discovered that the planar arrays of silver or gold nanoparticles exhibit a collective plasmon extinction spectrum with a characteristic response that both narrows and blue shifts with increasing particle density greater than about 100 nm, but red shifts and broadens as particle separation decreases for smaller separations. This unexpected result establishes a basis for plasmon resonance mediated sensing with array structures that significantly improve on the current generation of isolated nanoparticle sensors. Detailed theoretical studies of the optical properties of the particle arrays were performed, which provide insight as to the conditions leading to blue shifts and to red shifts.

(5) A new type of DNA/protein sensor was developed.⁵ In the case of sensing DNA the sensor uses nanoparticle-tagged DNA capture strands in solution and additional complementary strands on a micropatterned metal surface (Figure 6). The approach already yields sub-picomolar detection limits for DNA target strands

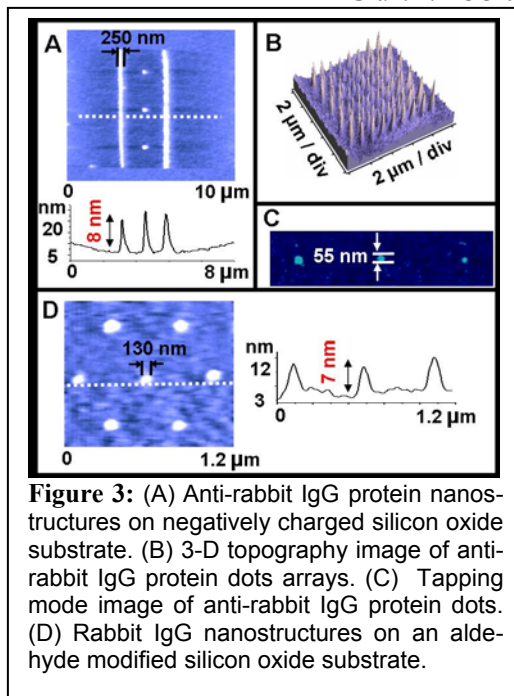


Figure 3: (A) Anti-rabbit IgG protein nanostructures on negatively charged silicon oxide substrate. (B) 3-D topography image of anti-rabbit IgG protein dots arrays. (C) Tapping mode image of anti-rabbit IgG protein dots. (D) Rabbit IgG nanostructures on an aldehyde modified silicon oxide substrate.

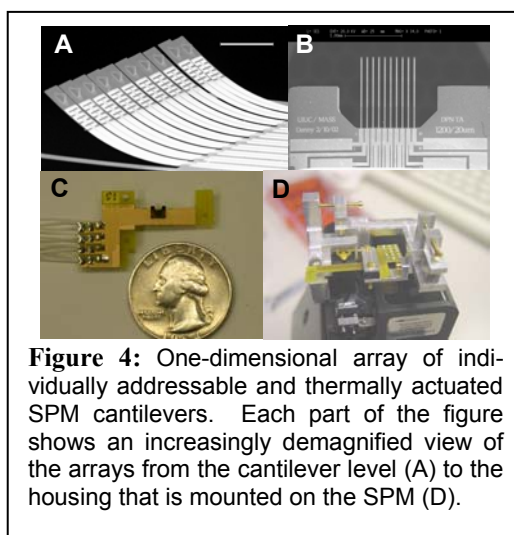


Figure 4: One-dimensional array of individually addressable and thermally actuated SPM cantilevers. Each part of the figure shows an increasingly demagnified view of the arrays from the cantilever level (A) to the housing that is mounted on the SPM (D).

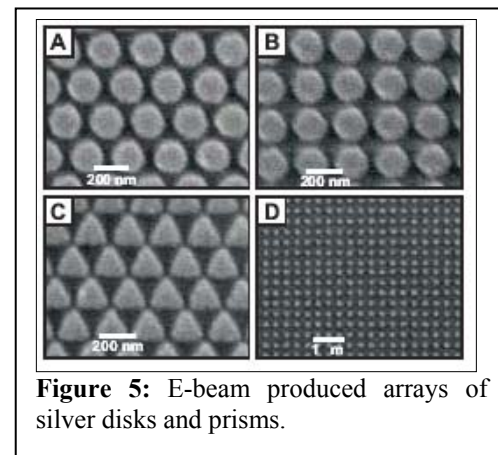


Figure 5: E-beam produced arrays of silver disks and prisms.

and is expected to improve with optimization. An advantage of this approach is that it provides real-time information on DNA hybridization kinetics. Importantly, it is observed, that depending on the probe color used, large negative responses in the diffraction intensity, large positive responses, or essentially nulled sensor responses can be engendered. This implies signal tunability based on nanoparticles, electronic spectral properties, and opportunities for multiplexed assays. The observed wavelength effects, resonance amplification effects, and bound analyte concentration (DNA target strand + tagged complementary strand) were modeled and demonstrated that the observed signals are dominated by modulation of the imaginary components of the nanoparticles' and platform's electronic absorption spectra, and provides a basis for predicting responses under other conditions and with other tags and platforms.

In addition to innovative research, the NU-NSEC seeks to restructure teaching and learning at all levels to include nanoscale science concepts and to nurture the scientists, technicians, and teachers of tomorrow. Since its inception in September 2001, the NU-NSEC has initiated the following educational outreach programs:

(1) Two summer research programs for undergraduates - the Research Experience for Undergraduates (REU) and the Minority Internships in Nanotechnology (MIN) programs provide meaningful research experiences for students from around the country (Figure 7). (2) An innovative Research Experience for Teachers (RET) program provides participants with hands-on nanoscale research during the first summer, and guidance and support to develop teaching units introducing nanotechnology in high school classrooms during the second summer. (3) A "Nanostuctures Module" is under development by NU-NSEC researchers, high school teachers, and administrators to supplement curriculum in pre-college classrooms. (4) The Center is collaborating with the Museum of Science and Industry, to develop a conceptual design plan for a nanotechnology exhibit, which ultimately will introduce millions of museum visitors each year to nanotechnology. (5) The Small Business Evaluation and Entrepreneurs (SBEE) Program was initiated in partnership with Northwestern's Kellogg Graduate School of Management to create a streamlined way to initiate start-up companies based upon NSEC developments. (6) A nanotechnology website for children and nanotechnology presentations are under development.

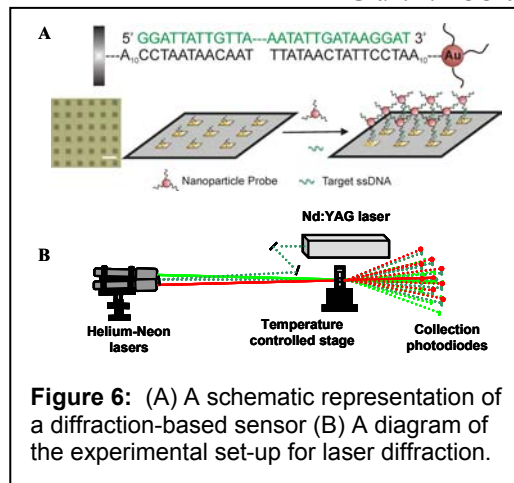


Figure 6: (A) A schematic representation of a diffraction-based sensor (B) A diagram of the experimental set-up for laser diffraction.

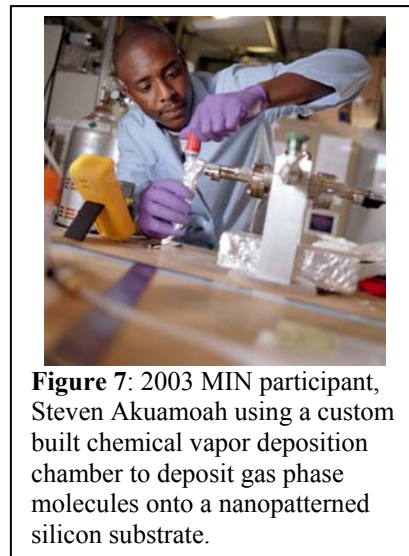


Figure 7: 2003 MIN participant, Steven Akuamoah using a custom built chemical vapor deposition chamber to deposit gas phase molecules onto a nanopatterned silicon substrate.

¹ Su, M.; Li, S.; Dravid, V.P.; Submitted to *Science*, Feb. 6, **2003**. Patent Disclosure, "Miniaturized Semiconductor Sensors Fabricated by DPN Using Sol-Inks" NU-22101, V.P. Dravid, M. Su.

² Lim, J.-H.; Ginger, D.S.; Lee, K.-B.; Heo, J.; Nam, J.-M.; Mirkin, C.A.; *Angew. Chem. Int. Ed.* **2003**, 42, 2309-2312.

³ Bullen, D.; Wang, X.; Zou, J.; Hong, S.; Chung, S.; Ryu, K.; Fan, Z.; Mirkin, C.; Liu, C.; *Proceedings of 16th IEEE International Micro Electro Mechanical Systems Conference, MEMS 2003*, Kyoto, Japan, 19-23 Jan 2003.

⁴ Haynes, C.L.; McFarland, A.D.; Zhao, L.; Van Duyne, R.P.; Schatz, G.C.; Gunnarsson, L.; Kasemo, B.; Kall, M.; *J. Phys. Chem. B.*; **2003**; 107(30); 7337-7342.

⁵ Bailey, R.C.; Nam, J.-M.; Mirkin, C.A.; Hupp, J.T.; *J. Am. Chem. Soc.*; **2003**; 125(44); 13541-13547.