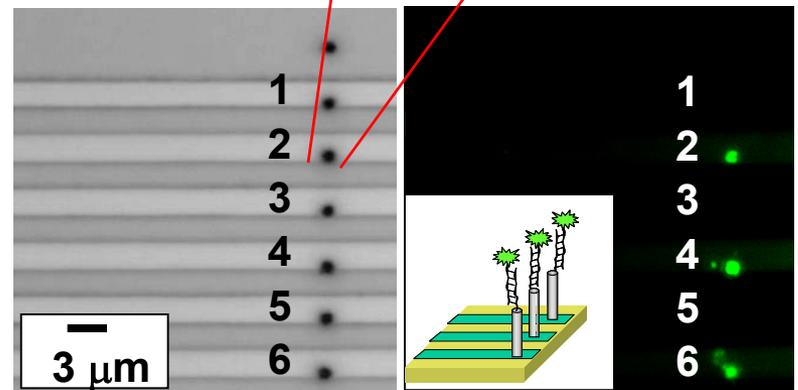
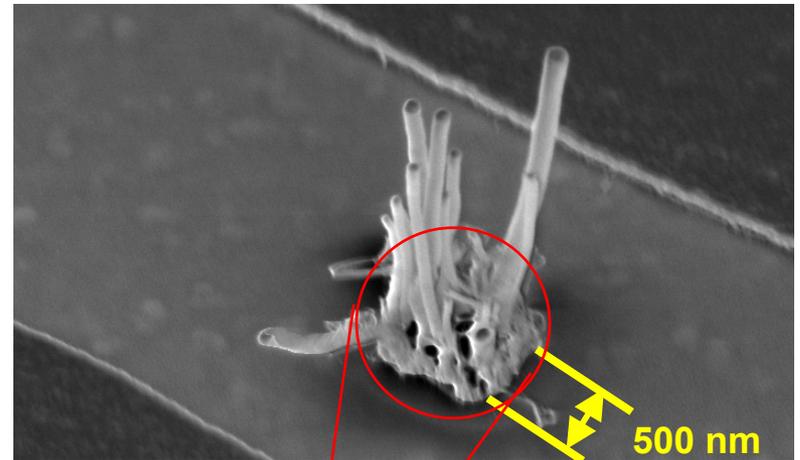
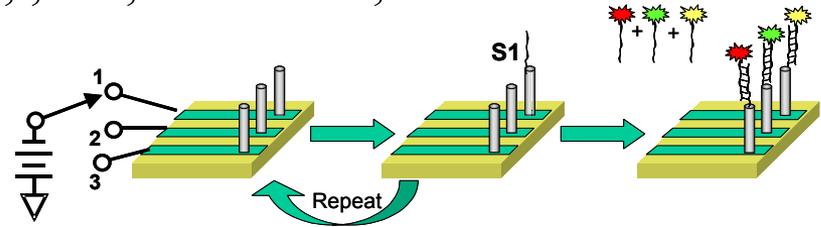


# Electrically addressable biomolecular functionalization of carbon nanotubes and carbon nanofibers

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We have developed a way to easily create “addressable” arrays of biologically-modified nanotubes and nanofibers on a chip. By using an electrochemical surface reaction to control one critical step in the modification process, we can use a small electrical control voltage to select specific nanotubes/nanofibers for chemical/biological modification without any specialized fluid handling. We have used this to fabricate small arrays of DNA-modified nanofibers and even individual carbon nanotubes, and we have shown that these have excellent biomolecular recognition properties. This new method opens the door for automated fabrication of ultradense arrays of nanoscale biological recognition sites for applications such as electronic biosensing, homeland security, and environmental monitoring.



DNA-modified nanofiber bundles hybridized with fluorescent DNA

While there has been a great deal of interest in the potential uses of nanoscale materials such as nanotubes and nanowires for chemical and/or biological sensing, one of the persistent challenges has been the issue of how to functionalize these materials with delicate biomolecules in a practical way that can be easily scaled up to thousands or millions of chemical/biological sensing elements in a cost- and time-effective manner. We have developed a simple procedure that uses small electrical potentials ( $\sim 1.8$  V) to selectively modify specific nanotubes/nanofibers on electrodes, thereby achieving electrically-addressable chemical/biological modification. This procedure completely eliminates any need for microfluidics, and because it is based on an electrochemical surface reaction, should be able to achieve spatial resolution as small as one nanometer. In this procedure, carbon nanotubes and/or carbon nanofibers are grown on conductive electrodes and the nanotubes/nanowires are reacted with a diazonium molecule containing a nitro group. This step takes place over the entire chip (consisting of thousands or millions of array elements). To address specific nanotubes/nanofibers for subsequent modification, a small ( $-1.8$  V) potential is applied to the electrode of interest; this reduces the nitro groups on this specific nanotube/nanowire electrode to primary amine, and makes the nanotubes/nanofibers reactive. The free amine groups on the nanotube/nanowire of interest can then be used to link biomolecules such as DNA to the array elements. By repeating this process it is possible to build up a high-density array of biologically-modified nanotube/nanowire elements, whose properties can be measured via fluorescence or by electrical means.

The SEM image above shows one molybdenum electrode with a small 500 nm bundle of  $<100$  nm-diameter carbon nanofibers. The image at lower left shows a white-light image; here, the the nanofibers appear as fuzzy diffraction-limited spot, one bundle per electrode (electrode are labeled 1-6) The nanofibers on electrodes 2,4, and 6 were selective reduced, linked to DNA, and then hybridized with complementary DNA bearing a fluorescent label. The image at lower right shows the resulting fluorescence image – high intensity is observed from the nanofibers that were “addressed” for functionalization. The high intensity at these locations demonstrates that the selective chemistry was successful and that the DNA-

modified nanofibers retained their biomolecular recognition capability, while the dark background demonstrates that there is little or no reaction outside of the “addressed” nanofibers. In more recent and ongoing work, we have extended this to successfully modify individual single-wall carbon nanotubes, and we demonstrated the ability to fabricate small arrays functionalized four four different sequences of DNA, with excellent recognition properties.

The importance of this work is that there has been a major, unmet need for the ability to chemically/biologically modify nanoscale elements such as nanotubes and nanofibers with distinct, specific biomolecules of interest. While there has been great interest in using nanotubes and nanowires to create ultra-dense arrays of biomolecular recognition elements, most people have taken the approach of trying to use nanofluidics to control the delivery of reagents to specific locations. The approach we have developed avoids microfluidics completely, and is simple and easily scalable to very large numbers of electrodes. Since electron transfer reactions typically take place only within  $\sim 1$  nanometer of an interface, we expect this method to be capable of specific chemical/biological functionalization all the way down to  $\sim 1$  nm. So, this electrochemical method opens the door to simple fabrication of ultrahigh-density arrays of chemically- or biologicaly-modified nanotubes/nanofibers for a wide range of applications, especially real-time biosensing.

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## **Education:**

- **Five graduate students (Sarah Baker, Kevin Metz, Arianne Baker, Matt Marcus, Lu Shang, and John Peck), one postdoc (Chang-Soo Lee), two high school students (Paresh Agarwal and Jesse Benck), and two eighth-grade students (Justin Bilantekin and Richard Pang), contributed to this work. Agarwal was a National Merit Finalist and now attends MIT. Peck completed his Ph.D. and is working at Stanford Research Systems.**

- **Hamers developed and conducted a workshop for science and engineering graduate students on leadership skill development and time-management skills through the UW Center for Engineering Education.**

- **Graduate student Kevin Metz co-organized a student-lead symposium, “Creating Complete Scientists: Graduate Student Visions of Doctoral Reform” at the American Chemical Society National Meeting in Philadelphia.**

## **Outreach:**

**With graduate students Kevin Metz and Beth Nichols, the PI mentored two eighth grade students, (Justin Bilantekin and Paresh Agarwal) and two high school students (Paresh Agarwal and Jesse Benck). Agarwal and Benck did full-time summer research projects in nanotechnology. Graduate student Kevin Metz has been working with science teachers and students at Jefferson Middle School as part of the K-through-infinity program.**



*10<sup>th</sup>-grade student Jesse Benck in  
UW-Madison Labs*

The investigators and their students have been actively involved in education and outreach activities. Graduate students are extensively involved in all aspects of the research, and have been actively engaged as mentors to undergraduates, high school students, and 8<sup>th</sup>-grade students.

Graduate student Kevin Metz was one of two principal organizers (with another student, Andrew Mangham) of an student-lead symposium at the American Chemical Society National Meeting in Philadelphia focusing on the topic of “Creating Complete Scientists: Graduate Visions of Doctoral Reform”. The seeds of this symposium were planted by R.J. Hamers and by Dr. Cathy Middlecamp, both of whom strongly supported the students in this exciting opportunity. This 2-day symposium was well attended and received a great deal of attention.

Hamers has been working with students in chemistry and in engineering on development of leadership skills and time management skills; this involved developing and presenting a formal workshop on “Learning and Leading: Maximizing your Effectiveness In and Out of the Classroom”. Student evaluations were very high, and Hamers has been invited to continue this workshop and to take a leadership role in development of future Engineering Education work activities.

Outreach activities have involved students and teachers at a variety of levels.

Particularly notable is our continued involvement with high school students and 8<sup>th</sup> grade students. High school students have been placed in our laboratories for the last two summers, where they work full-time for the entire summer on a research project of interest. Paresh Agarwal graduate from high school this year, work in our labs for a second straight summer, and is now at MIT majoring in physical science.

Eighth-grade students have been doing research in our labs through the EAGLE School Science Mentor program. These students work at the university on a research project for approximately 6 weeks duration, then do a paper and presentation on their work.