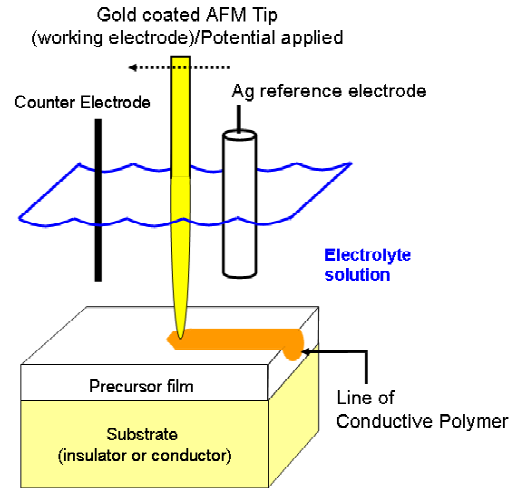
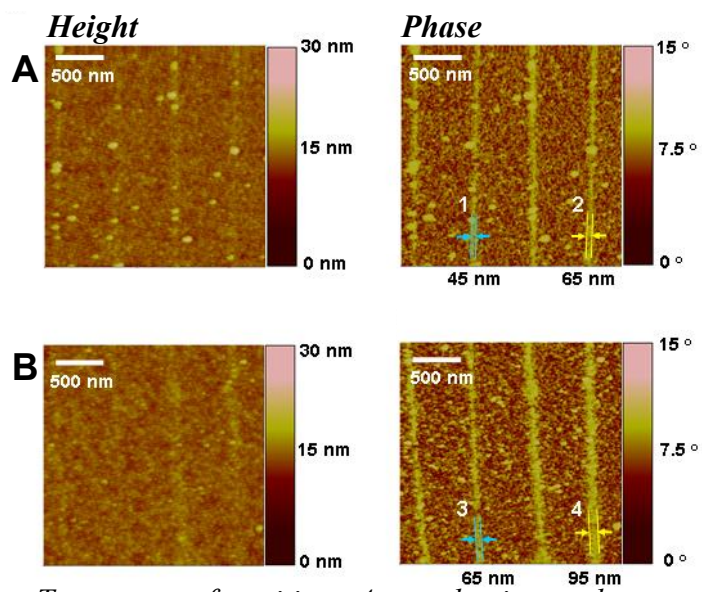
Novel Conjugated Macromolecules from Fused Heterocyclics and from Oxidative Solid-state Crosslinking

Gregory A. Sotzing, NSF-CAREER (CHE-0349121)

There is an increasing need to process conductive polymers onto flexible plastic in addition to finding new procedures to rapidly pattern and reduce feature size into the nano-regime. We have developed a process that we have termed solid-state oxidative crosslinking (SOC) by which a processable insulating precursor polymer is converted, oxidatively, to a crosslinked conductive polymer (orange) in the solid-swollen state. This technique has been applied to the direct-writing of nanometer width lines of conductive polymer via electrochemical atomic force microscopy (top right). Presently, our direct-write speeds are as high as 60 μm/s making our writing 6,000 to 60,000 times faster than the only other reported method for direct nanowriting of conductive polymers, electrochemical dip pen nanolithography (E-DPN). With our direct-write process, there is no material transfer from the tip, writing can be performed on any substrate type, and line widths can be varied by tip diameter, write speed, write mode (tapping vs. contact), and applied potential. Another potential benefit is that the conductive polymer nanolines are imbedded in a continuous insulating polymer film (bottom right, A & B). In a separate component of the CAREER, we have sulfonated polythienothiophene resulting in self-doped water processible polythiophenes having band gaps as low as 1 eV. Ultra thin films (16 nm, 0.8 nm/bilayer) are prepared via the layer-by-layer technique. Optical tuning is accomplished via degree of sulfonation and via counterion effects upon deprotonation.





Two sets of writing 4 conductive polymer nanolines in tapping mode at 15 (1), 10 (2), 10 (3), and 5 μm/s (4). Films on glass substrate.

Jang, S.; Marquez, M.; Sotzing, G. A. *Macromolecules* **2004**, 37, 4351-4359.
Jang, S.; Marquez, M.; Sotzing, G. A. *ACS Symp. Series* **2004**, *874*, 44-53.
Jang, S.; Marquez, M.; Sotzing, G. A. *J. Am. Chem. Soc.* **2004**, *91*, 9476-9477.

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Outreach:

Being only the 5th month of the program, the PI has not had the opportunity for significant outreach. The PI has been planning a device workshop for inner city CT high school/s which will take place over the next academic year. The workshop will either be held at UConn, or at the H.S. if it is more convenient for the students and teachers. The workshop will be oriented around the use of polymers in electrochromics and gas sensors (electronic nose). Students will assemble and operate the devices. The goal of this is to educate the next generation on the impact that polymer chemistry has on modern society and to hopefully entice them into the fields of chemistry and polymer science through playing with gidgets.

Education:

A senior level graduate student, Sung-Yeon Jang partially funded through this grant is set to earn his Ph.D. in late August and has accepted a post-doc at UC-Berkeley. A second graduate student, Eric Catuccio (2nd yr) is learning electrochemical atomic force microscopy. Arvind Kumar (2nd yr graduate student) is working on synthetic aspects of the work in the synthesis of thieno[3,4-b]furan. Byoungchul Lee (3rd yr grad. Student) is working on the sulfonation of polythienothiophenes. Presently, there are two summer undergraduates, Warren Mino (Intern, U. Conn.) and Heather Palko (REU, U. Hartford) carrying out research in nanodevice fabrication and heterocyclic synthesis. Warren will continue his research over the next academic year and plans to write a senior research thesis on his work. Group meetings are held once/week wherein the students present their research findings and are educated in conductive polymers, nanotechnology, and heterocyclic synthesis.

From Left to Right: Warren Mino (undergrad), Greg Sotzing, Eric Catuccio (grad)