WATER PURIFICATION

THE CENTER OF ADVANCED MATERIALS FOR THE PURIFICATION OF WATER WITH SYSTEMS WaterCAMPWS

FROM THE SEA TO SINK TO THE SEA AGAIN

When it comes to water, the statistics are staggering. Some 1.1 billion people worldwide lack access to safe drinking water, and 2.4 billion are without basic sanitation, according to estimates by the United Nations.

Here in the U.S., we are facing a critical shortage of potable water, says Mark A. Shannon, director of the *WaterCAMPWS,* headquartered at the University of Illinois at Urbana-Champaign (UIUC).

In addition to the problems of naturally occurring contaminants like arsenic, stresses such as human population growth and activities like agriculture, mining, and industrial operations are threatening our water supplies. Aquifers throughout the U.S. are suffering from declining water levels, saltwater intrusion, and inadequate recharging with fresh water. Major rivers and watersheds are being overdrawn.

Electric power plants are among the greatest users of water in the U.S., says Shannon, especially in certain parts of the Northeast, where 50 percent or more of the water withdrawals may go towards energy production.

To help ensure the continued supply of clean fresh water, researchers at the *WaterCAMPWS* are working to develop new materials and systems to safely and economically purify water for human use. At the same time, they are developing the diverse human resources needed to exploit the research advances and new knowledge base.

"It's a fundamental problem that resonates with people," says Shannon. "Water is connected to issues of the environment, energy, and human health."

The center serves as a hub for an 11-institution partnership. It is organized into interdisciplinary teams to address three major objectives for water purification: desalination/reuse, decontamination, and disinfection.

Co-leaders John Georgiadis and Menachem Elimelech are leading the effort to develop new materials, methods, and systems to improve the efficiency of desalination and reclamation processes. To remove contaminants from all types of water sources, co-leaders Yi Lu and Charlie Werth are leading the charge on methods for selective adsorption, catalytic reduction, and oxidation of pollutants that are conventionally difficult to treat. Items on their "hit list" include nitrate, perchlorate and arsenate, metal ions such as lead and mercury, and organic pollutants.

The center team on disinfection, led by Benito Marinas and Eric Mintz, is developing methods to economically destroy contaminants and pathogens without producing toxic substances. Projects in all of these areas were highlighted at the Spring 2007 national meeting of the American Chemical Society.

Work by several groups in the center on new photocatalysts is showing great promise as a means to treat wastewater without generating the toxic by products of chlorination. Work by Jian-Ku Shang and colleagues using nitrogen-doped titanium oxide, nicknamed TiON, as the photocatalyst has led both to a startup company and to an application project in conjunction with a metropolitan wastewater utility. Work on composites of TiON and alumina, a hydrated aluminum oxide, by Eric Mintz, a chemistry professor at Clark Atlanta University, is shedding light on the mechanism of the photoxidation process.

Another spinoff of center research has helped to spawn a major national effort on nanomanufacturing. Fundamental work by Paul Bohn, co-principal investigator of the *WaterCAMPWS,* and colleagues some years ago was focused on membranes that have many tiny cylindrical pores. This work in the area of "molecular gates" has led to new ways to move, manipulate, and chemically transform materials to effect exquisite 3-D control at the nanoscale. It has applications for chemical sensing as well as for the processing of materials, including water treatment.

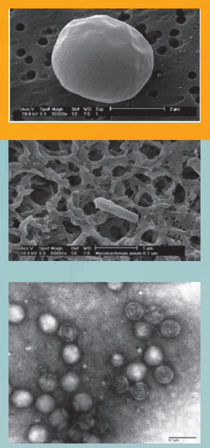
The work also led to the creation of a new $7.5-million NSF center for Nano-Chemical-Electrical-Mechanical Manufacturing Systems (Nano-CEMMS) headquartered at UIUC.

Bohn clarifies the relationship: "Part of the Nano-CEMMS was an outgrowth of part of the STC." A UIUC professor for some 23 years, Bohn recently moved to the University of Notre Dame as professor in the Departments of Chemical and Biomolecular Engineering and of Chemistry and Biochemistry.

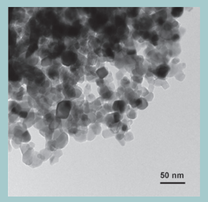
THREATS TO AMERICA'S WATER SUPPLY

More details can be found at http://www.watercampws.uiuc.edu and click on Water Crisis

- Increased demand by energy production
- Agricultural run-offs, such as:
  - Nitrates
  - Herbicides
  - Phosphates
  - Hormones
  - Pesticides
- Leaching of radioactive materials and heavy metals
- Depletion of aquifers
- Contamination of aquifers by:
  - Salt water
  - Pollution
  - Toxins



Disinfection Targets: Waterborne pathogens (top to bottom: protozoa, bacterial spores, viruses) are a major cause of disease/death in developing countries, and an emerging threat to public health in the U.S.



TiON nanoparticles. Nitrogen-doped titanium dioxide shows promise for photocatalytic water disinfection.
Image courtesy of Jian-Ku Shang, materials science and engineering, UIUC.

WaterCAMPWS director Mark Shannon, left, works with a student.

A CONVERSATION WITH THE DIRECTOR

Mark Shannon

WaterCAMPWS director Mark Shannon explains that the center is trying to address problems that are ten or more years down the line through what he calls a "mission approach."

The idea is to proactively bring researchers together to tackle mission-critical projects. In many cases, it is work that would not have happened otherwise, since these researchers likely would not have had any interaction with each other if it had not been for the center. Shannon recognizes it's not for everyone, noting some "attrition of those investigators that can't get into the mission approach." But he says, "We're finding that people are doing things they couldn't do before."

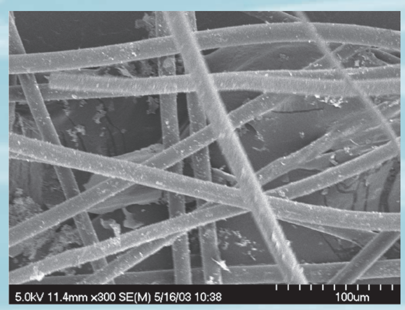
Case in point: the center was looking for investigators with strengths in polymer synthesis and in membrane technology to overcome the problem of membrane fouling in wastewater treatment processes for water reuse. Because wastewater has a high content of organic materials, microbes are used to break down these constituents. Membrane bioreactors—systems that combine conventional biological wastewater treatment with a membrane separation process—offer the promise of high water quality and small size. Although membrane bioreactors work well for digesting and converting organics, their use has been limited due to membrane fouling.

Shannon recruited to the project MIT professor Anne Mayes and Yale professor Menachem Elimelech with strengths in polymer synthesis and surface fouling, respectively. They started working with UIUC professor Eberhard Morgenroth, an expert in membrane bioreactors. "In an amazingly short time," says Shannon, "they started making membranes, testing them and characterizing them, doing postmortem analysis, and iterating on it until they hit on something that showed remarkable reduction in fouling potential." The work is published in the *Journal of Membrane Science* [285, 81-89, 2006].

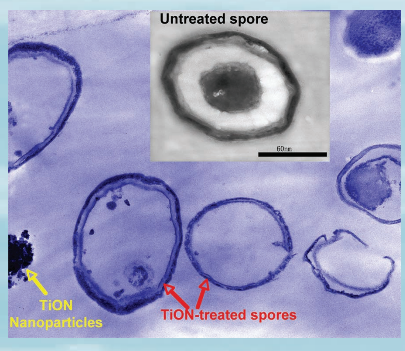
THE STORY OF TiON:

PHOTOCATALYTIC POWERHOUSE

Top Photo: Metropolitan Water Reclamation District of Greater Chicago



Left: TiON fibers. *Image courtesy of Jian-Ku Shang, materials science and engineering, UIUC.*



Bacillus Subtilis spores killed by TiON. *Image courtesy of Jian-Ku Shang, materials science and engineering, UIUC.*

Municipal wastewater is a soup of bacteria, viruses, and spores, inorganic compounds and metal ions, as well as organic compounds including pharmaceutical and personal care products.

After a biological treatment step, wastewater from the three largest plants at the Metropolitan Water Reclamation District of Greater Chicago (MWRD) is currently discharged into the river without disinfection because the waterway is currently designated for secondary contact. However, to be proactive, MWRD needs to understand the implications of disinfection if regulations were to change.

The price tag for a conventional method would be high—about $0.5 billion. The three large wastewater facilities typically process 0.75 million gallons of water per minute, so they need a disinfection method that is both inexpensive and rapid.

"We're looking for ways to improve current operations, to save energy, to improve process efficiency," says Catherine O'Connor, coordinator of technical services at the MWRD. "Costs have gone up 30 percent over the past year in energy costs alone. We're considering energy every step of the way—and that's why we're so enthused about the technology that Jian-Ku Shang and his group at the *WaterCAMPWS* have developed."

She's talking about the development of a photocatalyst called TiON—a nickname for titanium oxide to which nitrogen has been added. Historically, titanium dioxide has been extensively studied as a photocatalyst, capable of carrying out photoxidation of organic substances in water. Center researchers have enhanced its performance in two fundamental ways.

First, by adding nitrogen and co-dopants, they shifted the energy of the process from the ultraviolet range into the more practical range of visible light. Secondly, by altering the physical form of the material to have an ultrahigh surface area by means of processing it into powders, films, or fibers, they have increased the disinfection rate by more than six orders of magnitude compared to conventional titanium dioxide, that is, by a factor of more than 1,000,000.

Furthermore, early attempts to improve on titanium dioxide using TiON powders couldn't kill spores such as those from anthrax. Second generation materials using a co-dopant were able to readily kill sizable concentrations of bacteria such as E. coli and Staphylococcus aureus ("staph") within about 30 minutes, and killed spores in a matter of hours. Generation four of the material can remove 100,000 E. coli per milliliter in less than 20 seconds—"the fastest anybody has every achieved," says Jian-Ku Shang, professor of materials science and engineering at UIUC.

Various versions of the material are the subject of U.S. patent applications, notes Shang, and the technology is the focus of a spin-off company called E&S Fibers, Inc., Champaign, Ill. The early-stage venture, now in the process of fund-raising, is developing systems using TiON and activated carbon to remove contaminants in water.

Generation four TiON is being tested at the Chicago MWRD using real wastewater in the laboratory setting. "The preliminary results showing E. coli inactivation with very rapid, flow-through treatment using TiON and visible light were quite encouraging," says O'Connor. "I think it's very much a breakthrough."

The researchers envision a modular photocatalytic system that could be installed at the end of the treatment process. "When you think of the construction of a wastewater utility, every one of them has, at the end of the process, a water clarifier in the open air," explains Richard Sustich, Industrial and Govermental Development Manager for the *WaterCAMPWS* and former assistant director of research and development at the MWRD.

"During daylight hours, you have a pretty good source of light" says Sustich, and because the center technology uses light in the visible range, it may be possible to use conventional lighting sources, like street lights. "Every plant has essentially the same physical spot at the end of the treatment process where you could apply the catalytic disinfection. So the process would be scalable for any size wastewater plant. We're thinking of this as a generic application for any wastewater plant anywhere."

The partnership provides a way for center researchers to test their technologies in the real world. "Prior to dealing with us, they've shown very encouraging results but it's all been with lab grade water," says O'Connor. "While our plant effluent is very clean, and we outperform what our national pollution discharge elimination permits require, the big issue is that there are still 1 to 2 mg/liter of suspended solids." These make treatment much more difficult compared to spiking lab grade water with microbes and disinfecting that water.

O'Connor estimates that the technology is more than three years a way from the marketplace, and that the potential is "huge."

"There's a one billion dollar industry in U.S. for reuse of photofinishing wastewater alone," says O'Connor, "and that's just one of many markets—disinfection in wastewater and water treatment, pump-and-treat contaminated groundwater. The opportunities are enormous."

DNA SENSOR TECHNOLOGY FROM *WaterCAMPWS* IS FOCUS OF ILLINOIS STARTUP COMPANY

A catalytic DNA sensor developed by Yi Lu of the *WaterCAMPWS* and colleagues may lend itself to development as a simple, inexpensive field test kit.

The sensor uses DNAzymes—segments of DNA with enzymatic activities—that can bind analytes of interest. By coupling the DNAzymes with dyes or gold nanoparticles, the researchers can make sensitive and selective colorimetric sensors for a variety of contaminants in water.

For example, a fluorescent sensor made in this way can detect lead ion down to a level of 0.2 parts per billion (ppb)—significantly below the 15-ppb level for drinking water set by the U.S. Environmental Protection Agency (U.S. EPA), say the researchers. The work was selected as one of the top five presentations at the Materials Research Society Spring Meeting in San Francisco in April 2006.

This technology has become the focus of a start-up company, Dzyme Tech, funded by the U.S. EPA, the National Institutes of Health, and an Illinois venture-capital firm.

Sensor researcher Yi Lu of the WaterCAMPWS works with students.

CENTER COSPONSORS SYMPOSIA ON "CHEMISTRY FOR A SUSTAINABLE WATER SUPPLY" AT THE SPRING 2007 NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY

Sustainability was highlighted at a recent national meeting of the American Chemical Society, and thanks to the efforts of the *WaterCAMPWS*, new technologies for sustainable water supply featured prominently.

The looming shortage of potable water in the U.S. is a serious problem that many people underestimate, notes Eric Mintz, a center investigator and professor of chemistry at Clark Atlanta University. "We're running out of cheap water," he stresses. "We shouldn't take water for granted."

The center helped to sponsor eight symposia, bringing more than 100 presentations to conference-goers in Chicago around the central theme of water:

- Advanced Membrane Technology for Water Reuse
- Advances in Adsorption Processes for Drinking Water Treatment
- Advances in Desalination of Sea and Brackish Water
- Advances in Drinking Water Disinfection Processes
- Advances in Oxidation Processes for Water Treatment
- Catalytic Control of Emerging Micropollutants
- How Pure Is Our Drinking Water: Advances in Detection and Quantification of Water Contaminants
- Occurrence, Formation, Health Effects and Control of Disinfection By-Products in Drinking Water

Eric Mintz, a professor of chemistry at Clark Atlanta University and researcher in the *WaterCAMPWS.*