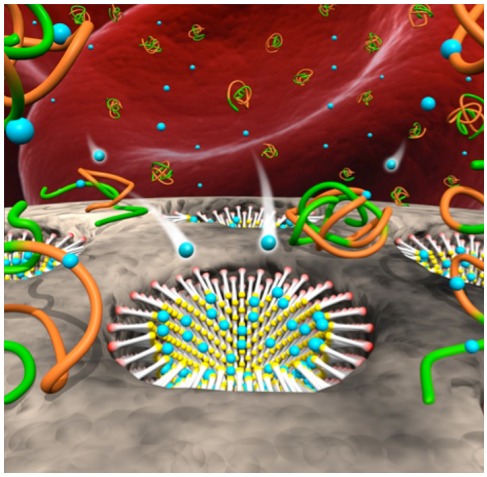
Pacific Northwest NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

Application of Nanomaterials to National Security

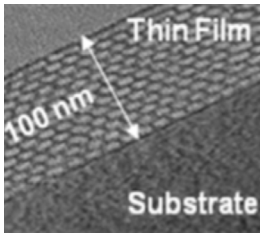
PNNL is developing and demonstrating a range of nanomaterials with application to national security needs. We design and create nanomaterials for specific applications by controlled integration of specific surface chemistries with nanostructures that provide unique capabilities. Materials are systematically constructed to provide specific solutions using sequential chemical synthesis processes supported by careful material characterization. The nanostructures provide novel and valuable features such as high surface areas to enable better chemical collection, high optical output for better signaling or high magnetism to provide dynamic material control for separations. Installation of a surface chemistry on the nanomaterial can impart high affinity and selectivity for the targeted species (e.g. heavy metals, toxic chemical, radionuclides, and protein toxins to name only a few). With this approach we can design and produce materials with unmatched affinity and specificity for the capture of trace level analytes that span chemical, biological, and radiological areas with applications ranging from forensic signature collection to protective barriers. Hierarchically ordered materials, produced with multiscale synthesis, will provide solutions for some of the most difficult and enduring problems in the national security arena.



Surface-functionalized nanoporous silica (brownish-gray) is shown capturing analtyes of interest (blue) from a complex matrix—a biological fluid in this case. The surface chemistry can be tuned to selectively capture specific classes of analytes. The nanomaterials structures can be created to enhance collection and assay for a wide range of sensitive applications.

EXPLOSIVES

The detection of ultratrace levels of explosives is critical to applications ranging from airport security to IED detection. Improved sampling and concentration of explosive compounds provides improved sensitivity, selectivity, speed and reduced false alarm rates. PNNL has been developing novel materials that provide enhanced and selective collection (and release) of explosive materials, both in vapor and particle form. The nanostructures provide higher sensitivity and easy integration with existing explosive detection systems. Tailored surface chemistry provides improved affinity and selectivity in collection and release. Competitive testing and evaluation of the new materials for explosive screening and detection is underway and preliminary results show over a 10X increase in performance over currently deployed systems.



A nanoporous thin film can increase surface area by 10-1000X, and can be utilized to improve detection sensitivity. The film can be chemical modified to improved selectivity.

NUCLEAR

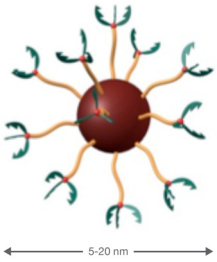
The collection of radionuclides is critical to many national security areas including; monitoring and detection of undeclared nuclear activity, determination of treaty compliance, response and triage after a nuclear event, nuclear medicine, and environmental characterization and remediation.

U.S. DEPARTMENT OF ENERGY

In many cases sorptive materials provide an effective means for the rapid collection (and subsequent assay) of radionuclides. PNNL has designed and synthesized a range of nanostructured sorbents that have demonstrated superior performance for the capture of many radioisotopes. Selected examples that have been developed inlcude magnetic nanoparticles for dynamic collections, nanoporous thin films for rapid assay and mesoporous materials for larger volume applications.

CHEMICAL WEAPONS

Effective personal protection and counter terrorist forensic analyses require efficient capture of chemical weapons materials and the exclusion of interferents. Surface functionalized nanostructured sorbent materials developed at PNNL provide higher selectivity and capacity for chemical weapons compounds than current sorbents. These enhancements enable novel forensic applications and can improve detection of hazardous chemicals. Personnel and facility protection applications benefit from the improved filtration capacity provided by the high surface area of nanostructured sorbents.



Superparamagnetic nanoparticle with high affinity surface chemistry to capture signatures of interest.

BIOLOGICAL MATERIALS

Rapid separation and detection of biological weapons signatures is the pivot point for responding to terrorist activities and minimizing event impact. PNNL has conducted research into the use of novel engineered nanomaterials to improve the speed, accuracy, and sensitivity of assays designed to detect protein toxins from complex samples. Specifically, we have investigated the use of novel luminescent quantum dots to drive the sensitivity of assays for botulinum toxin in complex samples to extremely low levels with a very short analysis time. The quantum dot materials were coupled to antibodies that have some of the highest reported affinities toward the botulinum toxin allowing us to bind the toxin tightly and selectively out of very complex samples and then detect its presence using simple fluorescence measurements.

ABOUT PNNL

Pacific Northwest National Laboratory, a U.S. Department of Energy Office of Science laboratory, solves complex problems in energy, the environment, and national security by advancing the understanding of science. PNNLemploys more than 4,900 staff, has a business volume exceeding $1.1 billion, and has been managed by Ohio-based Battelle since the Lab's inception in 1965.

R&D 100

Federal Laboratory Consortium FLC for Technology Transfer

SELECTED PUBLICATIONS

"Collection of fission and activation product elements from fresh and ocean waters: A comparison of traditional and novel sorbents." Bryce E. Johnson, Peter H. Santschi, Raymond Shane Addleman, Matt Douglas, Joseph D. Davidson, Glen E. Fryxell, Jon M. Schwantes. *Applied Radiation and Isotopes*, 2011, **69**, 205–216.

"In Vitro and In Vivo Evaluation of a Novel Ferrocyanide Functionalized Nanoporous Silica Decorporation Agent for Cesium (Cs) in Rats." Charles Timchalk*, Jeffrey A Creim, Vichaya Sukwarotwat, Robert Wiacek, R Shane Addleman, Glen E Fryxell and Wassana Yantasee. *Health Physics*, 2010, **99**(3), 420-429.

"Functional Sorbents for Selective Decorporation of Plutonium, Americium, Uranium, and Thorium in Blood." Wassana Yantasee*, Thanapon Sangvanich, Jeffery A Creim, Kanda Pattamakomsan, Robert A Wiacek, Glen E Fryxell, R Shane Addleman, Charles Timchalk, Jide Xu, and Kenneth N. Raymond. *Health Physics*, 2010, **99**(3), 413-419.

"Functionalized Nanoporous Silica for the Removal of Heavy Metals from Biological Systems: Adsorption and Application." Wassana Yantasee, Ryan D. Rutledge, Vichaya Sukwarotwat, Wilaiwan, Chouyyok, Galya Orr, Cynthia L. Warner, Marvin G. Warner, Glen E. Fryxell, Robert J. Wiacek, Charles Timchalk, R. Shane Addleman*. *ACS Applied Materials and Interfaces*, 2010, **2**(10), 2687-2964.

"Thiol-Ene Induced Diphosphonic Acid Functionalization of Superparamagnetic Iron Oxide Nanoparticle." Ryan D. Rutledge, Cynthia L. Warner, Jonathan W. Pittman, R. Shane Addleman, Mark Engelhard, Wilaiwan Chouyyok, and Marvin G. Warner*. *Langmuir*, 2010, **26**, 12285.

"High-performance, superparamagnetic, nanoparticle-based heavy metal sorbents for removal of contaminants from natural waters." Warner, Cynthia L; Addleman, R Shane; Cinson, Anthony D; Droubay, Timothy C; Engelhard, Mark H; Nash, Michael A; Yantasee, Wassana; Warner, Marvin G*. *ChemSusChem*, **Vol. 3**, 749-57, 2010.

"Quantum dot immunoassays in renewable surface column and 96-well plate formats for the fluorescence detection of botulinum neurotoxin using high-affinity antibodies." Marvin G. Warner, Jay W. Grate, Abby Tyler, Richard M. Ozanich, Keith D. Miller, Jianlong Loub, James D. Marks, Cynthia J. Bruckner-Lea. *Biosensors and Bioelectronics*, 2009, **25**, 179–184.

"Design and Synthesis of Self-Assembled Monolayers on Mesoporous Supports (SAMMS): The Importance of Ligand Posture in Functional Nanomaterials." Fryxell GE, SV Mattigod, Y Lin, H Wu, SK Fiskum, KE Parker, F Zheng, W Yantasee, TS Zemanian, RS Addleman, J Liu, J Xu, KM Kemner, S Kelly, and X Feng. *Journal of Materials Chemistry*, 2007, **17**:2863-2874.

"Removal of Heavy Metals from Aqueous Systems with Thiol Functionalized Superparamagnetic Nanoparticles." Yantasee, W.; Warner, C.L.; Sangvanich, T.; Addleman, R.S.; Carter, T.G.; Wiacek, R.J.; Fryxell, G.E.; Timchalk, C.; Warner, M.G. *Environ. Sci. Tech.* 2007, **41**(14), 5114-5119.

RESEARCH PROGRAMS SUPPORTED BY:

National Institute of Allergy and Infections Diseases

Homeland Security

U.S. DEPARTMENT OF ENERGY

For more information, please contact:

Shane Addleman, Ph.D.
Pacific Northwest National Laboratory
P.O. Box 999, MSIN P7-50
Richland, WA 99352
(509) 375-6824
raymond.addleman@pnl.gov

Marvin Warner, Ph.D.
Pacific Northwest National Laboratory
P.O. Box 999, MSIN P7-50
Richland, WA 99352
(509) 371-6480
marvin.warner@pnl.gov

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

www.pnl.gov

December 2010

PNNL-SA-76614