



THE Ames Laboratory  
Creating Materials & Energy Solutions

# FY2014 LDRD Annual Report

*Innovations and Progress*

Laboratory Directed  
Research and Development  
Program Activities

Office of the Director  
December 2014



U.S. DEPARTMENT OF  
**ENERGY**

Ames Laboratory is a U.S. Department of Energy  
Laboratory managed by Iowa State University

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## **ABOUT AMES LABORATORY**

Ames is a U.S. Department of Energy Laboratory managed by Iowa State University under contract DE-AC02-07CH11358.

The Laboratory's main administration facilities are at 311 TASF on the campus of Iowa State University.

For more information about Ames Lab and its pioneering science and technology programs, see [www.ameslab.gov](http://www.ameslab.gov).

## **DISCLAIMER**

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I am pleased to submit the Ames Laboratory's Annual Report on its Laboratory Directed Research and Development (LDRD) activities for fiscal year 2014 (FY2014). Our LDRD Program was inaugurated midyear in FY2013. The LDRD funds enable creative and innovative R&D projects at Ames Laboratory (AMES) that directly support our mission and initiatives. Selection of projects is the responsibility of the Laboratory Director, with each project identified as strategic in nature and reflects scientific quality, innovativeness, and value to mission-related initiatives.

LDRD is an invaluable resource that permits us to anticipate, and prepare to contribute to, the future science and technology needs of the Department of Energy (DOE) and the nation. The LDRD program objectives are to stimulate innovation and creativity, and to enhance the research activities to keep the Ames Laboratory at the forefront of science and technology. LDRD funding will continuously refresh the Laboratory's scientific and technological vitality, and enable AMES to respond to emerging R&D opportunities of clear potential benefit to DOE's mission. The program enhances AMES' ability to attract and retain the high-caliber scientists and engineers essential to pursue the mission of DOE and the needs of the nation. The LDRD program helps insure that AMES will continue providing scientific and technical leadership in its mission areas.

I can attest that in managing the AMES' LDRD Program, we have adhered without exception to the requirements of DOE Order 413.2b and associated guidelines. Our program management continually strives to be more efficient. In addition to meeting all reporting requirements, our LDRD Program Office continues to implement improvements that better serve all LDRD stakeholders, from our researchers, managers, budget office, to our DOE Site Office colleagues.

The individual project reports that follow demonstrate the AMES' researchers have pursued projects at the forefront of their respective fields and have contributed significantly to the advancement of our major initiatives. Evidence of the strength of the program is found from the contributions to significant aspects of the laboratory's Strategic Plan, with future evidence anticipated through follow-on sponsorship and technology transfer.

Adam Schwartz  
Director, Ames Laboratory

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## Acknowledgements

AMES' LDRD Program Office comprises the Chief Research Officer, Dr. Duane D. Johnson, Associate Laboratory Director for Sponsored Research, Deb Covey, and LDRD Program Administrative Specialist, Tessa Lemons. The program reports to the Laboratory Director, Dr. Adam Schwartz, through the Chief Research Officer. The LDRD program's management is grateful for the critical support received throughout the year – from the division's business offices and lab budget office. Special appreciation is due to the many experts who proposed and perform the research and provide the project reports; to the technical and administrative management of AMES' programs and divisions in which the R&D is pursued; to those experts throughout the DOE complex who provide anonymous peer review for LDRD proposals; and to the leaders in the laboratory's strategic initiative areas, whose vision and understanding of the nation's technological needs guide and refine the content of AMES' LDRD portfolio.

## Research Reports – by Component

Within a given LDRD Components (Lab Strategic Initiatives, Novel Projects, or Exceptional Opportunities), the projects are list by [LDRD Number], (Strategic/Mission Area) and TITLE.

### Novel Projects

[2013-GOR-1218] (*Cyber Security / Applied Math*) Dynamic Whitelist Generation for Automated Intrusion Prevention (6/10/13 to 9/30/2015) ..... 10

### Strategic Initiatives

#### – Materials Discovery and Design (MADD) Science

[2013-WAN-0113] (*Basic Science and Energy Security*) Femtosecond-resolved Polarimetry Probes of Electronic Nematicity in Iron-pnictide Magnetic Superconductors (6/10/13 to 9/30/2014) ..... 11

[2013-JON-0114] (*Basic Science and Energy Security*) Rapid, Small-scale, High-purity Rare-earth Metal Preparation (6/10/13 to 9/30/2014) ..... 12

[2013-MAKI-0513] (*Basic Science and Energy Security*) Demistifying the Hydration Layer on Nano-Oxide Suspension by Liquid-Cell Transmission Electron Microscopy (6/10/13 to 9/30/2014) ..... 13

[2014-LOG-1212] (*Basic Science and Energy Security*) Self-Healing Adaptive Structural Coatings (6/10/13 to 9/30/2014) ..... 14

#### – Greener Advances in Catalysis for Energy (GrACE)

[2013-HUA-0413] (*Basic Science and Energy Security*) Atomic and Electronic Level Control of Nanocluster Catalysts Encapsulated in Metal-Oxide Frameworks (MOFs) (6/10/13 to 9/30/2014) ..... 15

[2014-SLO-0802] (*Basic Science and Energy Security*) Customized Assembly of Catalytic Systems by 3D Printing Technology (6/10/13 to 9/30/2014) ..... 16

[2014-LWA-0413] (*Basic Science and Energy Security*) Adsorption-induced Shape-changing in Nanoalloys: Extended Alloy Wulff Construction with First-principles Calculations (12/15/13 to 9/30/2015) ..... 17

#### – Solid-State NMR Sciences (PRIMROSE)

[2014-SAD-0709] (*Basic Science and Energy Security*) Sensitizers for Dynamic Nuclear Polarization NMR Spectroscopy (6/10/13 to 9/30/2014) ..... 18

### Exceptional Opportunities

n/a in 2014

## LDRD Objectives

The objectives of AMES' LDRD portfolio are to enhance the Laboratory's ability to achieve its mission by enabling selected critical projects for which no other source of funds is available. LDRD funds will be used: (1) to foster innovation and creativity from the scientific and technical staff by supporting their pursuit of novel, forefront science and technology research ideas, new concepts, and high-risk/high-reward research and development projects; (2) to develop, recruit, and retain the researchers needed to maintain and enhance the scientific, engineering, and technical vitality and capabilities of the Laboratory; (3) to exploit the technical potential of the Laboratory for the benefit of the nation; and (4) to enable the Laboratory's R&D planning by supporting its mission and strategic plans, as described in its Strategic and Lab Plans.

## LDRD Components

The program provides support for *Initiatives, Novel Projects, and Exceptional Opportunities*.

*Strategic Initiatives* are employee-initiated proposals that address at least one of the strategic goals or an area of potential growth within AMES' Strategic Initiatives.

The **Strategic Initiatives** are as follows:

- Materials Discovery and Design (MaDD) Science
- Greener Advances in Catalysis and Energy (GrACE)
- Primary Research Initiative on Magnetic Resonance of Solid-state for Energy (PRIMROSE)

**Novel Projects** are a balance of basic, applied, single-investigator, and multidisciplinary projects in new areas or directions, not necessarily in direct support of our initiatives.

**Exceptional Opportunities** is an integral part of the pursuit of capabilities in a strategic area that enhances human and physical resources to support that area. This component consists of projects that do not fit neatly into the other two or that can arise outside the normal fiscal-year schedule, e.g., strategic hires, collaborations with external institutions where a superior expertise resides, or projects offering exceptional R&D opportunities for AMES. The laboratory director retains the option to identify and support these exceptional types of LDRD projects.

LDRD projects are pursued in forefront areas of basic and applied science and technology that support the DOE mission, enrich Laboratory capabilities, generally advance the knowledge and technology base, and have the potential to generate follow-on funding from DOE offices and programs. Individual LDRD projects will be relatively small and generally fall into one or more of the following categories.

1. Advanced study of hypotheses, concepts, or innovative approaches to scientific, technical, or computational problems.
2. Experiments, theoretical studies, simulations, and analyses directed toward "proof of principle" or early determination of the utility of new scientific ideas, technical concepts and devices, or research tools.
3. Concept creation and preliminary technical analyses of advanced, novel experimental facilities/devices or of facilities for computational science.

## LDRD Updates

DOE approved the Ames Laboratory's FY2014 LDRD Plan and expenditures, **not to exceed \$1.2M**. A list of projects begun thus far in FY2014, by project number and title is provided below.

Approved LDRD Plan components:

**1. Novel Projects**

**2. Strategic Initiatives**

- *Materials Discovery and Design (MADD) Science*
- *Greener Advances in Catalysis for Energy (GrACE)*
- *Solid-State NMR Sciences (PRIMROSE)*

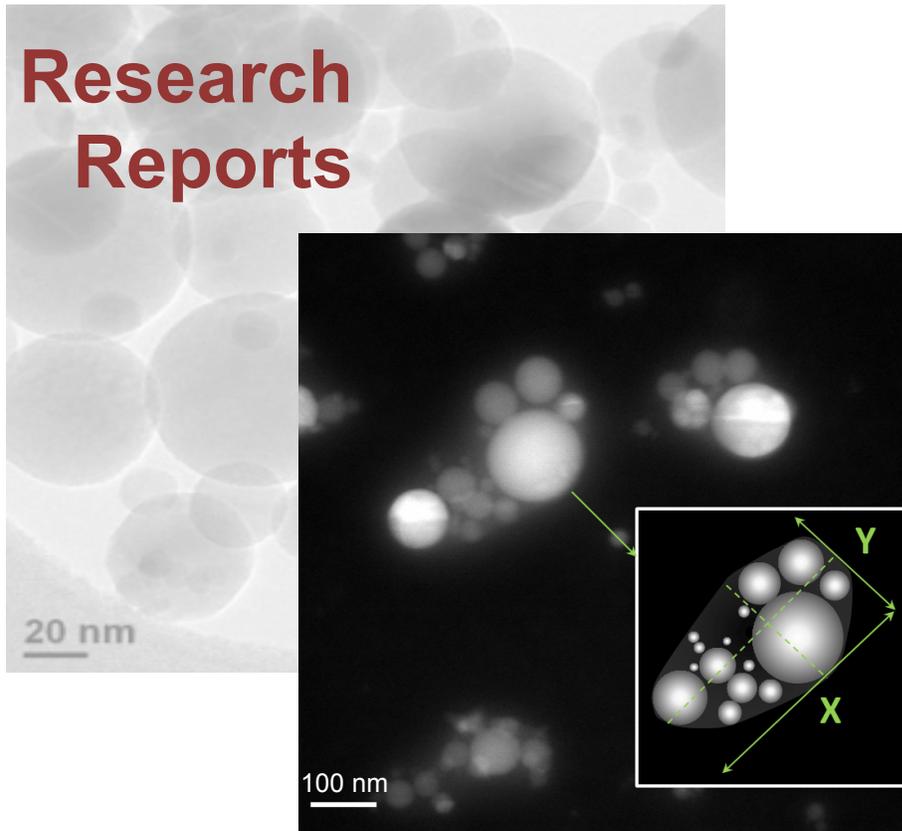
**3. Exceptional Opportunities**

## Funding Summary (\$ in thousands) for Projects Active in FY2014

DOE approved the Ames Laboratory's FY2014 LDRD Plan and expenditures, not to exceed \$1.2M. A list of projects begun in FY2014 (in \$K), by project number and title is provided below.

Proposal No.	2012	2013	2014	2015	2016	Total
<b>Novel Projects</b>						
2013-GOR-1218	0	\$89	\$232	\$169	--	\$490
<b>Strategic Initiatives</b>						
2013-WAN-0113	0	\$49	\$41	--		\$90
2013-JON-0114	0	\$63	\$45	--		\$107
2013-AKI-0310	0	\$68	\$135	--		\$203
2013-FAN-0313	0	\$102	--	--		\$102
2013-HUA-0413	0	\$102	\$150	--		\$252
2014-LOG-1212	0	0	\$70	\$72		\$142
2014-SLO-0604	0	0	\$144	\$118	--	\$262
2014-LWA-0413	0	0	\$55	\$57	--	\$112
2014-SAD-0709	0	0	\$172	\$175	\$180	\$527
<b>Exceptional Opportunities</b>						
	0	0	0			0
	0	0	0			0

# Research Reports



## Dynamic Whitelist Generation for Automated Intrusion Response [2013-GOR-1218]

### Novel Project: CyberSecurity

PI: Chris Strasburg and Mark Gordon

#### Project Description

As automation, sophistication, and potential damage of cyber attacks grow the Department of Energy and other organizations are under increasing pressure to automate cyber-defenses, e.g. blocking malicious websites. However, the risk of self-inflicted damage due to such automation is often significant. While *whitelists*, i.e., catalogs of resources that should not be disrupted, are one approach to mitigate this risk, manual construction of such lists is inherently error-prone and incomplete. Our goal is to develop an automated, learning-based approach to identify significant organizational relationships from network flow data, and then also examine its utility. These relationships can then be protected from disruption or identified for additional monitoring by automated cyber defense mechanisms.

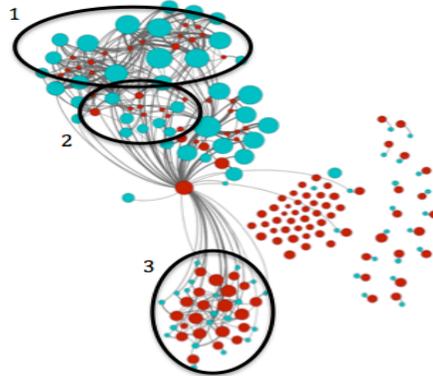
#### Mission Relevance

For cyber-security mission, this project expects to directly demonstrate the utility of a *dynamic whitelist generation for automated intrusion response*. We will produce a packaged implementation suitable for sharing with other DOE sites – and the general public (an open-source utility). Automated identification of critical relationships between organizations will improve data confidentiality, integrity, and availability by enabling safe and effective use of automated cyber-defense, and focusing analysts' attention on those cyber events that have the highest expected mission impact.

#### Results and Accomplishments

Data tests and analysis were performed on Ames Laboratory cyber data. We showed that precision and recall of a dynamic whitelisting was improved between 20 to 35% by incorporating semantic and statistical flow features. We clearly demonstrated that incorporating features that inform both the **nature of relationships** and their **strength** is crucial to achieve sufficiently accurate results for automated decision making.

Figure 1. Graph of clustered communication patterns from Ames Laboratory. Lab IP (external) clusters are red (blue) nodes. Three regions indicated are collections of 1) external clusters communicating with our servers (e.g., web, email); 2) external systems communicating with remote access services (e.g. VPN, SSH); and, 3) external systems communicating with IP addresses that are not 'live' (performing recon).



We also uncovered some key challenges to be addressed before this approach can be applied broadly throughout DOE. The current approach relies heavily on expensive lexical analysis of relatively scarce public web pages related to IP addresses. This will not scale to large sites, much less multiple sites. Another challenge is the need to labeled training data. Because models are specific to individual organizations, manually generating sufficient labels is not feasible.

#### Additional Work Product

- Results were presented at FloCON 2014, a network-flow based analysis conference.
- Network Security Monitors presentation was given in May 2014.
- Published open-source version of the initial code: <https://github.com/Ames-Laboratory-Cyber-Group/Cydime>
- Established collaboration with PNNL to distribute our model across the DOE complex using data from the Cooperative Protection Program (CPP).

#### FY2015 Proposed Work

We will address scalability and labeling challenges to warrant direct support by DOE. We will support an integrated component to DOE Cyber Fed Model project and work with PNNL to leverage collected flow data across the DOE complex. This will enable deployment for complex-wide data.

## Femtosecond-Resolved Polarimetry Probes of Electronic Nematicity in Iron Pnictides [FY2013-WAN-0113]

Strategic Initiative: MADD Science

PI: Jigang Wang

### Project Description

Understanding electronic nematicity has emerged as a cross-cutting theme critical for both the high-temperature superconductivity and quantum magnetism. Such underpinning has been essentially impossible using conventional static optical/electrical transport methods since they probe the time-averaged properties where the critical divergence of nematic fluctuations associated with the buildup of the new order are hidden inside. We propose to solve this problem via probing photoexcited femtosecond dynamics of the nematic order parameter using ultrafast polarimetry. This will reveal dynamic fluctuations and disentangle various correlation mechanisms in the time domain. We will focus on superconducting model systems  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ , and aim to establish this approach as a benchmark to other anisotropic interacting quantum fluids.

### Mission Relevance

We directly target - “superconductivity”, “ultrafast science” and “characterization of complex systems/emergent behavior”, which are specifically identified from the DOE Basic Energy Science (BES) Grand Challenges Report and are recurring instrumentation needs described in the Basic Energy Need (BRN) series. Our results thus far has provided some very compelling cases to advance one of the most poorly-addressed territories in condensed matter physics/materials science/device physics today – non-equilibrium mesoscopic quantum dynamics that aligns very well to the DOE new focus into the mesoscopic realm.

### Results and Accomplishments

Our LDRD work showed that the ultrafast spectroscopy distinguished macroscopic critical fluctuations associated with the Ising-nematic symmetry breaking in the normal state of iron-pnictide superconductors. Our time-resolved ellipsometry simultaneously characterizes ultrafast dynamics of magnetic and nematic order parameters.

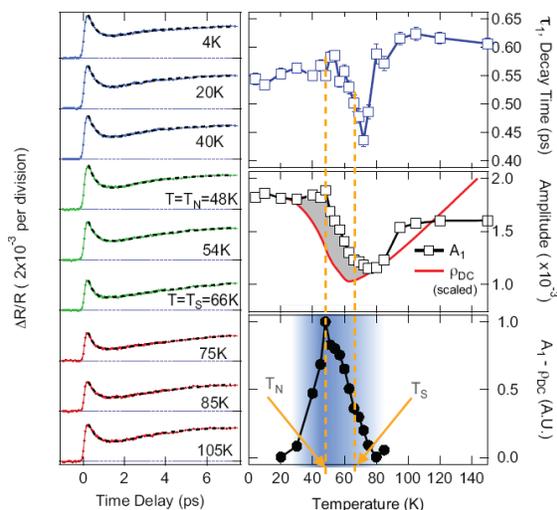


Figure 1. Femtosecond-resolved differential reflectivity traces,  $\Delta R/R$ , for the  $x=0.047$  Cobalt-doped  $\text{BeFe}_2\text{As}_2$  at multiple temperatures, shown together with the fitting of decay profiles. The extracted  $t_1$  (blue squares) with error bars (standard-deviation), exhibit critical behaviors at  $T_S=66$  K (yellow dashed line), the structural transition temperature. The signal amplitude (black square) is constant up to the magnetic ordering temperature  $T_N = 48$  K, but then the amplitude decreases, which reveal the critical spin fluctuations near  $T_N$  (black circles)

Our results indicate existence of an underlying independent nematic phase different from magnetic and structural orders – resolving a heated debate in the community.

### Additional Work Product

Two High-Impact Publications:

A. Patz, T. Li, S. Ran, R. M. Fernandes, J. Schmalian, S. L. Bud'ko, P. C. Canfield, I. E. Perakis and J. Wang, "Ultrafast Observation of Critical Nematic Fluctuations and Giant Magnetoelastic Coupling in Iron Pnictides" *Nature Communications* **5**, 3229 (2014).

Aaron Patz, Tianqi Li, Sheng Ran, Rafael M. Fernandes, Joerg Schmalian, Sergey L. Bud'ko, Paul C. Canfield and Jigang Wang, "Evidence of Critical Spin Fluctuations Driving Electronic Nematicity in Iron Pnictides," *Phys. Rev. Lett* (2014), [submitted](#).

**Rapid, small-scale, high-purity rare-earth metal preparation [2013-JON-0114]**  
**Strategic Initiative: MADD Science**

PI: *Larry Jones and Trevor Riedemann*

**Project Description**

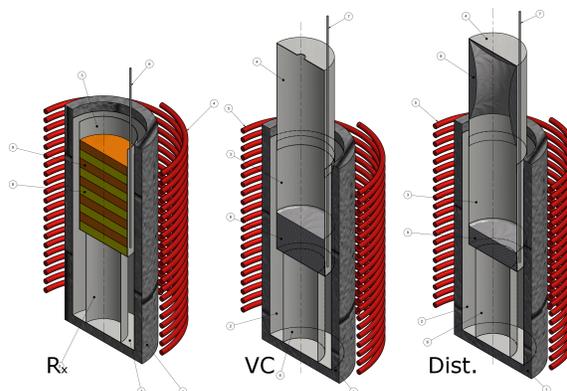
The project developed a new methodology for small batch (≤500 gram) preparations of rare-earth metal (REM) having the required high purity for use in fundamental materials research and discovery. In addition, sources for *off-the-shelf* supplies will be identified (ex. crucibles) with the intent to eliminate any need for custom fabrication and reduce labor. This development will shorten the processing arc while maintaining the high-purity standard for which Ames Laboratory REM is internationally recognized.

**Mission Relevance**

Development of small-scale REM production and process efficiencies directly supports research into functional materials for energy security, and enhances our expertise in materials synthesis and processing. This process can be leveraged by rare-earth sciences across the DOE complex, e.g., *Critical Materials Institute, an energy innovation hub*, and may evolve technology transfer. Ames Laboratory technical staff and, by extension, REM community, will be trained in the new capabilities. Our work *enhances* our process capabilities and *perpetuates* our position as *the* pre-eminent producer of the world’s purest REMs for materials research.

**Results and Accomplishments**

Vacuum casting and distillation was complete for first preparation initiated in FY13. Two more small-batch runs were completed, with the third process successfully producing high-purity REM comparable to Ames Laboratory historical quality. An outside assay found our third batch (HOM-LDRD-3) to be 99.99% for Li-U, and 99.999% with respect to REM plus Y and Sc. Interstitial content for O, N, and C were found by weight to be 115 ppm, 227 ppm, and 26 ppm, respectively. Nitrogen content is higher than desired (i.e., 100 ppm), but weighed against the remainder of the assay it is acceptable. The



*Figure 1. Rx shows a loaded reduction crucible, VC is the setup for vacuum casting, and Dist. shows the setup for distillation with some metal collected in the condenser head. Drawings by Alon Klekner, ESG/AL.*

labor and lead times estimated before project start were slightly lower than realized, but within 5-8%.

As can be seen in the table below, there are trade-offs to be made. Total overall production costs are lower – there is less labor and lead time is reduced, but the price-per-gram for final material is higher due to reduced yield (only 22% of a “full” batch). Use of the small batch methodology will have to be carefully considered based on the immediate need, rate of use, and budget of producer and consumer.

Process procedures were recorded and will serve as the model process, or “recipe”, for future small-batch production at Ames Laboratory’s Materials Preparation Center (MPC). This methodology is immediately applicable to the entire suite of REM’s prepared by the MPC.

This project closed March 2014.

**Additional Work Product**

Procedures based on successful completion were written and transferred to the Metals Processing Center (MPC) for future use in REM production requests, and potential technology transfer.

	Full	Small	Estimates SB	Small/Full	Expect/Est.
Lead time (days)	27	23	21.3	85%	108%
Labor (hours)	147	86.5	82	59%	105%
Produced Mass (g)	2400	538	500	22%	108%
Cost per gram (\$)	\$24.23	\$46.79	\$49.14	193%	95%
Total Cost (\$)	58125	25173	24570		

## Demystifying Hydration Layer on Nano Oxide in Suspensions by Liquid Cell Transmission Electron Microscopy

[2013-MAKI-0513]

Strategic Initiative: MADD Science

PI: Tanya Prozorov and Mufit Akinc

### Project Description

Using a novel *Continuous Fluid Flow Liquid Cell Platform* within a transmission electron microscope (TEM), we studied hydrated oxide nanoparticles in a liquid. This project used the *in-situ* liquid cell characterization of aqueous alumina *nano*-powder dispersions to demonstrate this unique and powerful technique to ceramic nanoparticle suspensions, probe the hydration layer around the nanoparticles, and monitor its thickness. We were able to relate the observations to the viscosity measurements on the same system.

### Mission Relevance

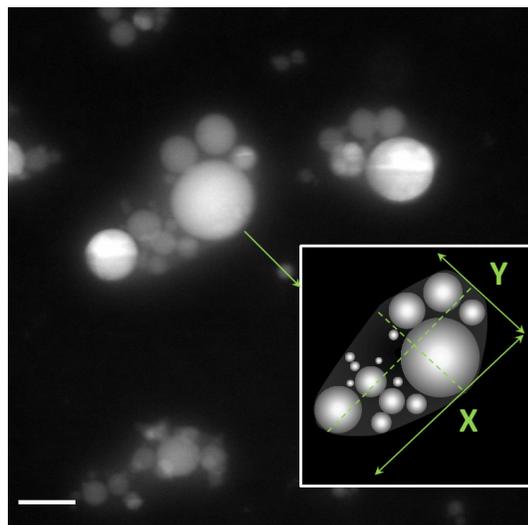
Rheological behavior of nanoparticle suspensions is of high importance in many existing sectors of industry, and any improvements to the inherent flow characteristics translates to large cumulative energy savings – part of our energy security mission. However, the control over these systems relies on a fundamental understanding of the underlying processes, including the hydration of suspended nanoparticles, as well as their stability, flocculation, and flow dynamics.

### Results and Accomplishments

We have described a new approach to visualization of oxide surfaces in aqueous systems, thus providing critical information for many technologically significant studies. We have observed formation of the hydration layer over the particle aggregates and showed that these hydrated aggregates constitute new particle assemblies, see **Figure 1**, that in turn alter the flow behavior of the suspensions. These nanoclusters alter the effective solids content and the viscosity of nanostructured suspensions. Our findings are of direct relevance to many branches of industries dealing with colloidal nanometer-scale slurries.

We have determined that in aqueous solutions alumina nanoparticles aggregate to form hydrated clusters of significantly larger sizes with various aspect ratios, compared to the primary alumina particles (**Figure 1**). Formation of such hydrated

clusters increases the effective solids content and decreases available free liquid carrier of the suspensions, resulting in high viscosities.



**Figure 1.** *In situ* fluid cell HAADF STEM image of diluted aqueous alumina slurry (scale bar: 100 nm). The hydration layer is manifested as a cloud enveloping aggregated nanospheres. Inset shows schematics of the formed aggregate with the size and aspect ratio different from that of initial spherical particles.

Our findings explain the discrepancy between the theoretical viscosities calculated for systems comprised of monodisperse nanoparticles and the viscosity values determined experimentally in colloidal suspensions, where the nanoparticles exist in form of hydrated aggregates. We incorporated results of the *in situ* analysis of alumina nanoparticles in liquid to resolve the apparent disparity between the experimentally measured and predicted viscosities of alumina nanoparticulate suspensions.

Our results prompt the revision of the parameters employed by the industry in forecasting of viscosity of colloidal solutions and necessitate the establishment of new realistic models based on the observed hydration behavior of alumina nanoparticles.

### Additional Work Product

Demystifying the Hydration Layer on Alumina Nanoparticles with the Fluid Cell STEM *in situ*,” *Nature Materials* (2014), [submitted](#).

## Self-Healing, Adaptive Structural Coatings [2014-LOG-1212]

Strategic Initiative: MaDD Science

PI: Barbara Lograsso

### Project Description

A prototype adaptive material is being developed that regulates mechanical properties under service conditions via an artificial structural array of magnetoelastic (ME) phases in a composite to mimic biological mechanoreceptors. ME materials are ferromagnetic materials that change elasticity based on the strength of impinging magnetic fields. Under applied magnetic field and stress, ME phases will resonate at specific property-dependent frequencies. The material is an array of tiny adaptive structures formed by ME and permanent magnet (PM) separated by a flexible substrate. The three-layer structural zones are embedded inside a matrix, and elasticity of the ME materials is altered subject to the PM field strength.

### Mission Relevance

Mastering capabilities of living systems to discover, design and synthesize new materials is identified as a BES *Grand Challenge*. We focus on self-adaptive materials that automatically regulate mechanical properties under service conditions, which involve both sensing structure and function, as inspired by organisms that synthesize elaborate structures for multiple functions.

### Results and Accomplishments

In response to an applied field impulse, a ME material emits a magnetic flux with a characteristic resonant frequency. Resonant waves are produced, modulated, and detected depending on elasticity, permeability, and magneto-mechanical coupling. The frequency depends upon the magnitude of *dc*-biasing field and mass loading (*pressure or stress*) on the surface. Thus, we measured amplitudes of the longitudinal ME resonant waves versus stress at given magnetic field, and biasing PM phase.

For combinations of ME/Flex/PM trilayers, we created a fixture for measuring higher-order harmonic fields in response to the applied magnetic field impulse and stress. A 2960 turn coil connected to a signal analyzer was used to detect changes in the amplitude of the higher-order harmonic response of ME waves excited by two 500 turn Helmholtz coils (dia. 25 cm) that provide the AC and

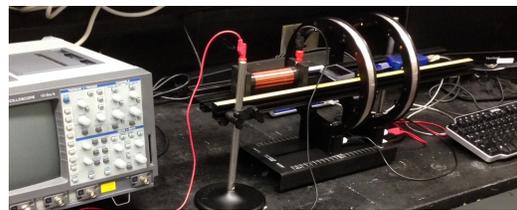


Figure 1. Apparatus for measuring the harmonic response.

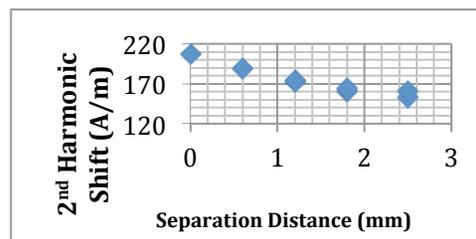


Figure 2. Preliminary resonant harmonic response of the layered materials vs. increasing separation between cast PM material and Metglas 2826.

DC excitation fields (Figure 1). To simulate local change, we tested for scale of microstructure by a minimum distance between ME and PM materials needed for detecting levels of harmonic resonant frequency (Figure 2).

The macroscale layer combinations are being evaluated to establish candidates for microscale fabrication. ME materials under investigation are:

1.  $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$  [Metglas brand 2826MB]
2.  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$  [TerfenolD].

PM materials studied show a range of induction and orders of magnitude of coercivity:

1. Strontium ferrite and iron oxide [presintered]
2. Cast alloy of Fe-Al-Ni-Co-Cu-Ti
3. Rare-earth Nd-Fe-B magnet.

Matrix material selections represent several orders of magnitude for elastic modulus [polycarbonate, 2.6 GPa, and iron-based materials, 200 GPa] to explore range of applicability for these materials.

### FY2015 Proposed Work

Fabricate microstructures and examine other candidate materials and their range of properties. Microstructures will be built layer-by-layer with macroscale materials to demonstrate the stress-pressure capability of the structure. Test flexible substrates with varied elasticity to see if useful pressure range can be altered (more rigid substrates increase pressure). Relate stress and changes to 2<sup>nd</sup>-order harmonic shift to constitutive equations of elasticity and magnetism for layer combinations, permitting design of self-healing, adaptive structural coatings.

## Atomic and Electronic Level Control of Nanocluster Catalysts Encapsulated in Metal-Organic Frameworks

[FY2013-HUA-0413]

Strategic Initiative: GrACE

PI: Wenyu Huang and Linlin Wang

### Project Description

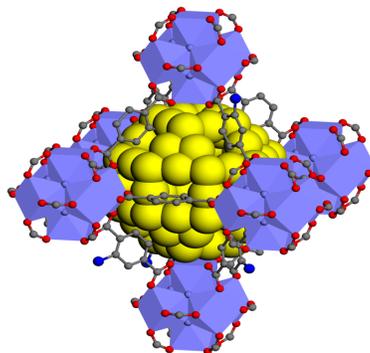
The proposed new initiative aims to control heterogeneous catalytic properties of nanoclusters (NCs), and to relate those properties to the atomic and electronic features around the NCs. To control heterogeneous catalysis at the atomic and electronic level represents one of the most challenging research areas. Using metal-organic frameworks (MOFs) as hosts of metal NCs, we could reach an atomic- and electronic-level control of heterogeneous catalysts due to the well-defined structure of MOFs. Zr-based MOFs (UiO-66 Series), renowned for unprecedented thermal and chemical stability, have recently spurred tremendous interest and served as our discovery platform.

### Mission Relevance

Two DOE-BES reports, "Catalysis for Energy" and "Directing Matter and Energy: Five Challenges for Science and the Imagination", identified that catalytic technology is essential for sustained economic development, energy security, and environmental preservation for our society. To synthesis high-performance catalysts, and ultimately to design materials with desired catalytic properties, we need to improve our understanding on the structure-catalytic property relationship at the atomic and electronic level, which is exactly the research objective of this LDRD proposal.

### Results and Accomplishments

Using Zr-MOF as support, we utilized Dynamic Nuclear Polarization Enhanced Solid-State NMR Spectroscopy to explore the selective host-guest interaction between metal ions and MOFs. Combined with X-ray absorption spectroscopy and density functional calculations, we determined that each Pt(II) ion coordinates with two amino groups from the Zr-MOF and two Cl<sup>-</sup> ions from the metal precursor. DFT calculations provided a detailed atomic picture for the binding of Pt(II) inside the Zr-MOF, with Pt-N and Pt-Cl bond lengths agreeing well with our measured values.



**Figure 1.** Schematic of a nanocluster encapsulated in amino functionalized Zr-MOF. Carbon (black), oxygen (red), nitrogen (blue), metal atoms (yellow) and Zr cluster (purple polyhedra) are indicated.

We studied the kinetic interaction between Pt(II) ions and MOFs using *in situ* X-ray Absorption Spectroscopy. All Zr-MOFs included in this work were able to coordinate with K<sub>2</sub>PtCl<sub>4</sub> in aqueous solution. The coordination of K<sub>2</sub>PtCl<sub>4</sub> with Zr-MOFs was first order with respect to the concentration of K<sub>2</sub>PtCl<sub>4</sub>, while amino functionalized Zr-MOF has the highest coordination rate constant.

With the detailed atomic-scale understanding of bonding configurations between metal ions and MOFs, we demonstrated the potential of Zr-based MOF catalysts in chemoselective hydrogenation and tandem reactions. Pt nanoclusters encapsulated in Zr-MOFs show excellent catalytic activity and chemoselectivity in cinnamaldehyde hydrogenation to cinnamyl alcohol. Bifunctional Pd@Zr-MOF catalysts were utilized in the one-pot tandem reaction of benzyl alcohol oxidation and acetalization reactions.

### Additional Work Product

- Z. Guo *et al.*, "Pt Nanoclusters Confined in MOF Cavities for Chemoselective Cinnamaldehyde Hydrogenation", *ACS Catalysis* **2014**, 4, 1340-1348. DOI: [10.1021/cs400982n](https://doi.org/10.1021/cs400982n)
- C. Xiao *et al.*, "*In situ* X-ray Absorption Spectroscopy Studies of Kinetic Interaction Between Platinum(II) Ions and UiO-66 Series Metal-Organic-Frameworks", *J. Phys. Chem. B* **2014**. DOI: [10.1021/jp5066456](https://doi.org/10.1021/jp5066456)
- Z. Guo *et al.*, "Selective Host-Guest Interaction between Metal Ions and MOFs using Dynamic Nuclear Polarization Enhanced Solid-State NMR Spectroscopy", *Chem. Eur. J.* **2014**. DOI: [10.1002/chem.201403884](https://doi.org/10.1002/chem.201403884)
- X. Li *et al.*, "Tandem Catalysis by Palladium Nanoclusters Encapsulated in Metal-Organic Frameworks", *ACS Catalysis* **2014**, 3490-3497. DOI: [10.1021/cs5006635](https://doi.org/10.1021/cs5006635).

## Customized Assembly of Catalytic Systems by 3D Printing Technology

[2014-SLO-0802]

Strategic Initiative: GrACE

PI: Igor Slowing and Aaron Sadow

### Project Description

This initiative aims to integrate the bottom-up self-assembly of nanostructured materials into mesoscopic arrays with the top-down manufacture of macroscale reactors, to bridge the gap between molecular and macroscopic control of matter. Functionalized catalyst nanoparticle inks will be developed and printed into 3D structures using additive manufacturing technologies. This will enable simple and efficient customization of catalytic setups in the laboratory, and facilitate the translation of fundamental catalyst discovery into process chemistry for industrially relevant conversions. The work aligns with the Ames Laboratory's Strategic Initiative of Greener Advances for Catalysis for Energy (GrACE).

### Mission Relevance

DOE-BESAC identified a set of opportunities in mesoscale sciences for clean energy technologies. One of the priority directions is "Directing the assembly of hierarchical functional materials". Combination of this mission with the Grand Challenge in DOE-BESAC's report on Catalysis for Energy: "Design and controlled synthesis of catalytic structures", can be addressed by the merger of novel top-down additive manufacturing technologies with the bottom-up mesoscale self-assembly of nanostructured catalytic materials, which is the target of this project.

### Results and Accomplishments

Four 3D-printing technologies were identified for assembling catalytic systems: filament extrusion, extrusion under inert atmosphere, liquid/paste injection, and photochemical conversion.

Inks have been formulated using polymer scaffolds to bind metal ions via pending carboxylates, and by dispersing metal or mesoporous nanoparticles in ABS filaments. These formulations are designed for printing via filament extrusion/fused deposition.

Inks are being developed by functionalizing nanoparticles with acrylates, and via synthesis of metal acrylates, these precursors are mixed with

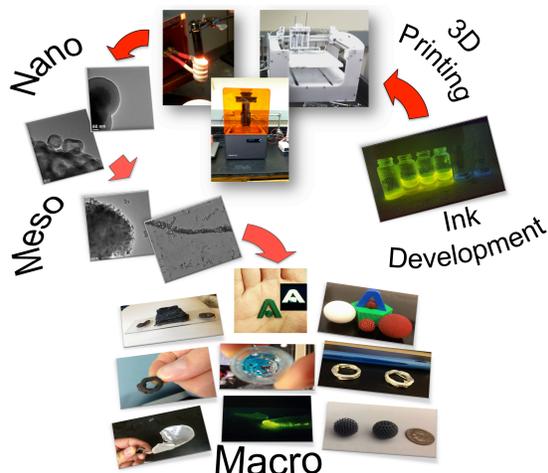


Figure 1. Process for additive manufacturing of novel catalytic structures – ink development to 3D printing of nanostructured particles that assemble in mesoscale structure, giving macroscopic solids with controlled shapes and properties.

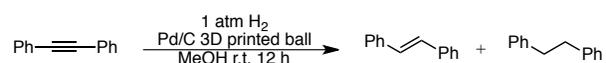
acrylate oligomers and are ready for 3D printing via photopolymerization.

Inks are being developed by crosslinking monomer-functionalized nanoparticles with oligomers to give suspensions that become solids upon hot injection. These inks are ready for 3D printing via syringe.

Melting of metals with localized heating has been accomplished but control of deposition is limited by lack of compatibility of printer setup. This burden could be overcome by acquisition of a moving stage, but funds are insufficient to pursue this promising new direction.

### Additional Work Product

- **Invention disclosure** for patent application is in preparation.
- Hydrogenation reactions achieved with a photochemically printed nanoparticle catalyst.



### FY2015 Proposed Work

Optimize dispersion, crosslinking, and load of nanoparticles is in progress. Full characterize the prints, complete catalytic activity screening, and assembly of multicatalyst systems.

## Adsorption-induced Shape-changing in Nanoalloys: Extended Alloy Wulff Construction with First-principles Calculations [FY2014-LWA-0413]

Strategic Initiative: GRACE and MaDD Science

PI: Linlin Wang

### Project Description

We propose to extend alloy Wulff construction (continuous modeling) to include the effect of molecule chemisorption via first-principles calculations (atomistic modeling) to predict the equilibrium shape-changes of nanoalloys (i.e., alloyed nanoparticles, NPs) in chemically reactive environment. The goal is to establish a quantitative relation between nanoalloy's shape (with specific surface composition) and the coverage of molecule adsorbates for nanoalloys of different sizes and initial bulk compositions. Such details permit design of heterogeneous (electro)catalysts. This combined continuous and atomistic modeling approach is developed within the Thermodynamic Tool Kit (TTK) software providing unique capabilities for nanoalloy design to Ames Lab.

### Mission Relevance

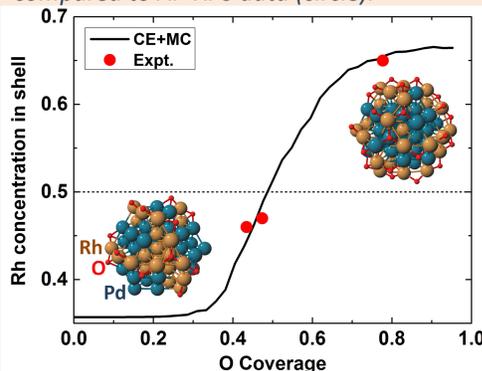
New findings from *in situ* experimental techniques of nanoalloys at atomic resolution under working conditions demand new computer simulation methods that incorporate the operating environment to explain observations, provide high-throughput predictive capabilities, and design nanoalloys from bottom up. The proposed research will help solve one of the DOE grand challenges to design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties, and help achieve Ames Laboratory's mission.

### Results and Accomplishments

A non-exchangeable coupled lattice cluster expansion (CE) method has been successfully extended and implemented in TTK to describe configurational thermodynamics of nanoalloys and alloy surfaces under working conditions with adsorbates. For the CE in a heterogeneous system, we also developed a new strategy to establish the effective cluster interactions via a two-step approach that accounts for the relative strength of interactions to yield small prediction error and fast convergence.

Exemplified with PdRh nanoparticles having O-coverage up to a monolayer, we find that PdRh core-shell NPs only around 50%Rh experience a core-shell reversal induced by O-coverage, agreeing

Figure 1. Rh shell-concentration vs. O-coverage for Pd<sub>0.5</sub>Rh<sub>0.5</sub> nanoparticle. New theory (line) compared to AP-XPS data (circle).



with observations. Rh shell concentrations of Rh vs. effective O-coverages for a 50% Rh alloyed nanoparticle (Figure 1) agree with those extracted from the *in situ* experimental data, reflecting the same origin for core-shell reversal, i.e., the relative strength of metal-O, metal-metal and O-O interactions.

For adsorbate-induced structural changes, we have studied how a large molecule adsorbate, such as C<sub>60</sub>, can induce vacancies on noble metal surfaces. The energetics of C<sub>60</sub> on the reconstructed Ag and Au(111) surfaces with different orientations have been calculated for comparison to successfully explain the 30 degree difference observed in STM experiments.

### Additional Work Product

- L.-L. Wang, T. L. Tan and D. D. Johnson "Configurational thermodynamics of alloyed nanoparticles with adsorbates", *Nano Letters* **14**, 7077-7084 (2014). <http://dx.doi.org/10.1021/nl503519m>
- H. Shin, et al., "Structure and dynamics of C60 molecules on Au(111)," *Phys. Rev. B* **89**, 245428 (2014). <http://dx.doi.org/10.1103/PhysRevB.89.245428>
- **Invited Talk:** *Computational Modeling of Transition-Metal Alloyed Nanoparticles in Working Condition, XXVI IUPAP Conference on Computational Physics, CCP2014, Boston, 8 August 2014.*

### FY2015 Proposed Work

With this new capability, rational design of nanoalloys for hydrogen-oxidation and oxygen-reduction reactions will be carried out to include the effects of changing alloy configurations and adsorbate-adsorbate interactions under working conditions. Extension of the cluster expansion method to describe shape-changes in nanoparticles and include alloy Wulff construction based on the surface free energy of nanoalloys with adsorbates under working condition will be explored.

## Sensitizers for Dynamic Nuclear Polarization NMR Spectroscopy [2014-SAD-0709]

PI: Aaron D. Sadow, Marek Pruski, Igor I. Slowing, William S. Jenks

### Project Description

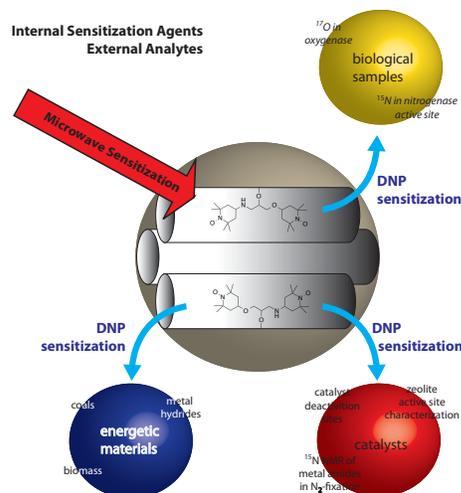
This project aims to prepare polarization agents (PAs) for Dynamic Nuclear Polarization (DNP) enhanced solid-state Nuclear Magnetic Resonance (SSNMR) spectroscopy. DNP is an emerging technology in NMR that can provide significantly enhanced signals for analytes to give insight into composition, structure, chemical environment, and bonding in materials. The polarization agents will be shown to be effective for NMR signal enhancement of energy-related materials, such as catalysts, to provide unique insight into their structures and methods of operation. The current polarization agents reported in the literature are biradicals derived from the nitroxyl functionality  $R_2NO\cdot$  such as TOTAPOL and bTbK, but the application of these agents to a range of important materials has not yet been developed. Thus, we are studying known PAs on energy-relevant materials, developing new radicals to enhance sensitization. From this work, DNP SSNMR spectroscopy will allow Ames Lab researchers to address important and strategic scientific and technological challenges.

### Mission Relevance

The DOE-BESAC report "Directing Matter and Energy: Five Challenges for Science and the Imagination" identifies Grand Challenges for controlling matter and processes at the level of electrons and atoms. NMR spectroscopy, is a critical tool for characterization of catalysts and materials and will provide a component of the analytical methods needed to control matter and processes for efficient synthesis and energy generation, transportation, and use. The methods and PAs developed in this project directly facilitate characterization of materials at the atomic level.

### FY2014 Results and Accomplishments

The emerging nature of DNP SSNMR spectroscopy has led to its successful application in inorganic and organic-inorganic materials characterization. We developed a standardized method of evaluating the enhancement factors of new and known PAs using well-defined hexyl and phenyl-ureido-propyl (PUP) functional mesoporous



**Figure 1** Sensitization of inorganic materials with immobilized PA based on TOTAPOL.

silica nanospheres (MSN) as hydrophobic and hydrophilic standards for testing radicals. We developed expertise using Electron Spin Resonance (ESR) spectra to understand radical abundance (spin counting) and coupling of spins within poly-radicals.

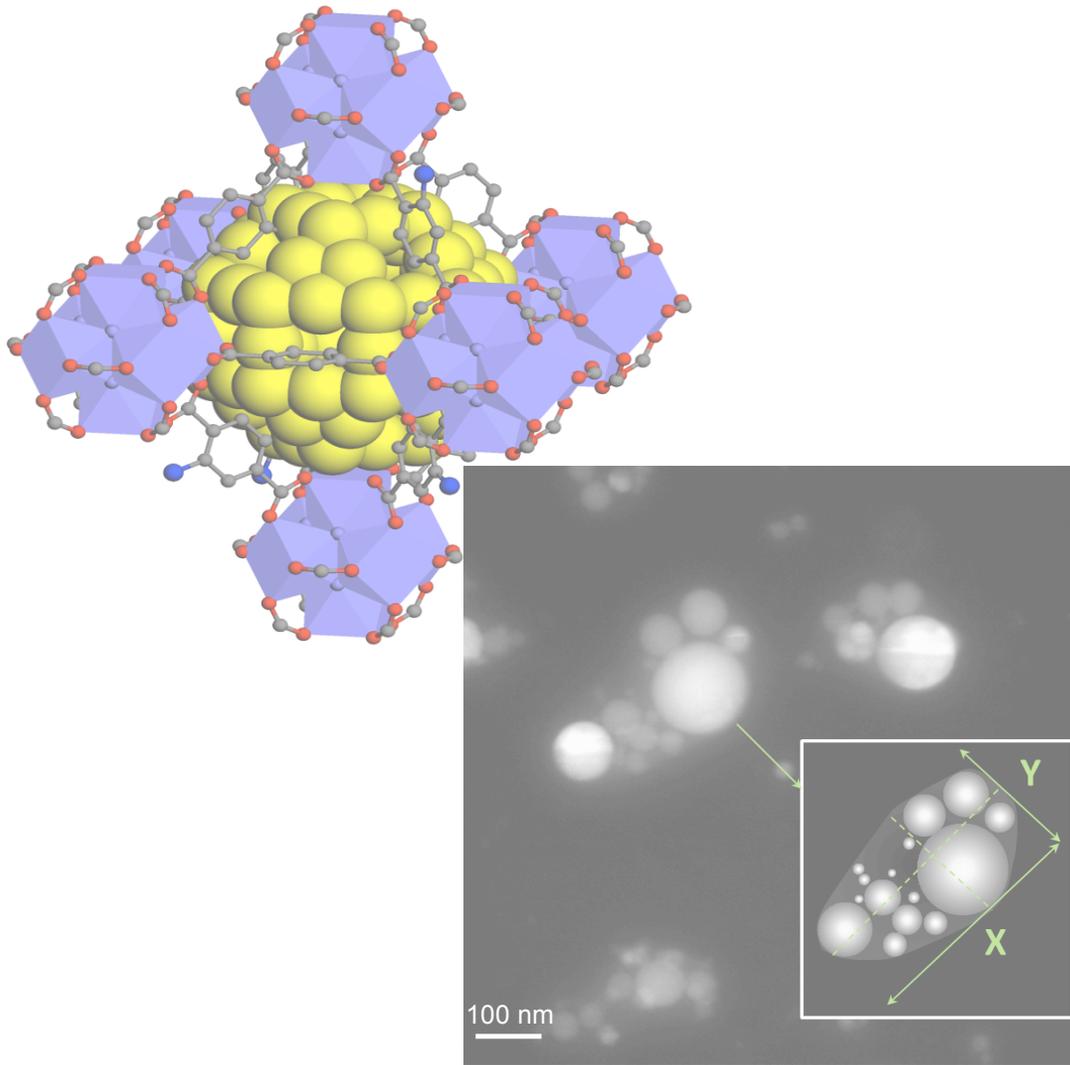
We prepared a series of new and known biradical, triradical, and tetraradical molecules based on the nitroxyl unit using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals and organic synthetic methods for coupling involving organic and inorganic (phosphorus, silane) linking groups. We also prepared MSN materials derivatized with mono-, bi-, and triradicals. These compounds and materials have been characterized by ESR spectroscopy and mass spectrometry, when appropriate, and are currently being tested on the newly installed DNP spectrometer.

### FY2014 Work Product

No publications have yet been submitted from this LDRD support. Patent disclosures on new materials and PAs are currently in preparation.

### FY2015 Proposed Work

We have also discovered new challenges that need to be overcome. Namely, the PA of hydrogen-poor materials presents a direct challenge to DNP applications (e.g., in metal oxides and semiconductor materials). Our efforts in synthesis of PAs therefore are directed based on solvent-PA and solvent-material interactions.



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