Developing Green Nanotechnology: Challenges and Opportunities Through Innovation

B.L.S. Maddux[*,**], R.D. Rung[**] and J.E. Hutchison[*,***]

[*]Materials Science Institute, University of Oregon, 1252 University of Oregon, Eugene, OR 97403, bettye@greennano.org
[**]Oregon Nanoscience and Microtechnologies Institute, Corvallis, OR, skip@onami.us
[**]Department of Chemistry, University of Oregon, Eugene, OR 97403, hutch@uoregon.edu

ABSTRACT

Nanotechnology is an emerging field that holds enormous societal benefits. As with any new technology, the risks need to be delineated along with benefits. The Safer Nanomaterials and Nanomanufacturing Initiative (SNNI) is one of the Oregon Nanoscience and Microtechnolgies Institute's (ONAMI) major research thrusts. We are developing inherently safer nanomaterials by merging green chemistry and nanoscience. In this article, we outline our relationship with ONAMI and our proactive design strategies that are critical for developing nascent, inherently safer nanomaterials.

Keywords: green nanoscience, nanotechnology, proactive design strategies, nanoparticles, toxicity

1 OREGON NANOSCIENCE AND MICROTECHNOLOGIES INSTITUTE

ONAMI (Oregon Nanoscience and Microtechnologies Institute) is Oregon's first "signature research center" for the purpose of growing research and commercializing technology. Although not widely known outside the Pacific Northwest region until fairly recently, Oregon has long been home to many of the world's leading "small tech" industrial R&D and advanced manufacturing sites (Intel, HP, FEI, many more). But it has not been commensurately successful at in-state entrepreneurship and technology transfer. To powerfully address this issue, the decision was made to establish and fund initiatives from which nationally recognized science leadership and consequent economic development benefits would emerge.

The process and criteria for signature research theme selection were settled in late 2002, in order to maximize the intersection of:

- Competitive institutional research (universities, national laboratory)
- Future market opportunities (sources of job growth)
- "Line of sight" to existing industry (talent pool, supplier infrastructure, etc.)

It was further recognized that Oregon's research universities (18,000-20,000 students at each institution) had outstanding talent, but were relatively small, and that success would most likely require an unprecedented level of collaboration in order to assemble the most competitive research teams and infrastructure. Finally, to better serve industrial partners and investors, a common, fully accessible set of user facilities and intern/student placement programs should be assembled. The implementation framework thus became:

- A collaborative research engine (with 3 or 4 areas of focus) designed to tap the collective research strengths within the regional universities
- A remotely accessible network of complementary user facilities open to all researchers on equal terms, and available for industry/startup collaborations
- A supply of "gap" (translational research) and early stage equity funding for technologies ready for commercialization

The ONAMI effort, which has received $28M in state funds so far, is managed by a 501c3 non-profit corporation (ONAMI, Inc), with a majority of industry members (representing Intel, HP, FEI, Invitrogen, Tektronix, and Battelle) on its board of directors. It is also assisted by a Commercialization Advisory Council (for the gap fund) comprising many of the leading venture capital partners active in the state.

The results and benefits so far are rapid growth (60%/year since FY04) in research grants and contracts, two gap fund awards (after the first 4 months of fund operation) to cases where the commercialization partners are under serious consideration for multi-$M A-rounds, a growing set of networked equipment and facilities used by hundreds of researchers and over 30 companies, and rapidly growing placements (over **30** per year) of graduate student interns in Oregon high-tech companies. Based on good initial results and confidence in the operating models so far developed, Oregon's governor has included $10M for ONAMI operating funds in his 2008-2009 budget.

The ***Safer Nanomaterials and Nanomanufacturing Initiative (SNNI)*** is one of four thrust areas, and has proven to be a great collaborative success (25 investigators in three multidisciplinary task teams from UO, OSU, PNNL, PSU) in an area correctly predicted to be of high national interest at about this time. Sub-investigations in SNNI that would not have been possible without intensive networking among campuses (and provision of funds for competitive internal solicitations) are now yielding results from multi-PI teams bringing skills as diverse as quantitative molecular toxicology experimental models, green chemistry synthesis strategies, advanced imaging and analytical techniques and novel manufacturing approaches to multi-step reactions and material purification.

As major capital projects are completed over the next 6-18 months and research investigations deliver results, ONAMI will place increasing emphasis (with its own funds) on gap fund projects and assistance to efforts to raise (in 2007) a $20-$25M accelerator-style early stage equity fund.

2 SAFER NANOMATERIALS AND NANOMANUFACTURING INITIATIVE (SNNI)

Nanotechnology is an emerging field that has great potential for use in many applications from alternate energy sources to stain-resistant clothing. Current estimates suggest that this new technology will exceed the impact of the industrial revolution and become a 1 trillion dollar industry within the next decade. Nanomaterials and the manufacturing methods used to create them, however, may pose adverse environmental, health and safety effects. The putative risks associated with manufacture and use of these new nanomaterials has been the subject of much debate. One of the challenges, then, is designing nanomaterials and subsequent nanomanufacturing methods that provide maximum efficiency while minimizing these risks. Merging green chemistry and nanoscience into "green nanoscience" will provide opportunities to meet these challenges and to develop sustainable technologies and materials [1]. Proof of concept of 'safer nanomaterials' must be ascertained through toxicological testing of nascent nanomaterials. Biological and environmental testing should be done in concert with design such that toxicological testing is incorporated into the design scheme. This proactive paradigm is an iterative process that simultaneously includes synthesis, toxicological testing, and redesign until inherently safer nanomaterials and nanomanufacturing methods are established (Figure 1). Through this holistic approach, we can develop new nanomaterials and nanomanufacturing approaches that are ultimately more cost effective and offer a high level of performance, yet pose minimal harm to human health or the environment.

The SNNI[1] is a unique program established to meet this objective. Our goals are to implement the principles of green nanoscience to: (1) design environmentally benign nanoparticles for use in a variety of applications, such as electronic and optical applications; (2) develop greener methods for large-scale nanoparticle production, (3) and develop more efficient approaches for interfacing nanoparticles with each other or with other components in functional devices. Each of these objectives is critical to the development of safe, yet high performance applications of nanoscience and nanotechnology.

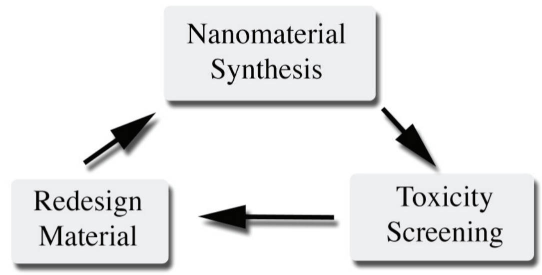

Figure 1: Proactive Design Paradigm. Synthesis reactions are designed for engineered nanoparticles, tested in biological/environmental systems, and redesigned until safer nanomaterials are produced. This approach is carried out in tandem with optimization of the desired physical properties.

2.1 Designing Safer Nanomaterials

We are developing methods to prepare libraries of functionalized metal nanoparticles in which the size, shape and functionality can be widely varied. Production of gold nanoparticles is one example of how we use green chemistry to produce safer nanoparticles. The traditional approach to creating gold nanoparticles uses the highly toxic and flammable diborane gas and the potent carcinogen, benzene [2]. This method is not only hazardous, but time consuming, and labor intensive. Furthermore, purification requires large volumes of solvents, produces relatively low yields and is expensive. Hutchison's laboratory developed a greener method that uses sodium borohydride and toluene/water in small quantities (Figure 2) [3, 4]. The method is safer, faster, easier, and can produce gram quantities of gold nanoparticles. The projected cost is ~$500/g for the greener method, whereas material produced by the traditional method has been priced at ~ $300,000/gram.

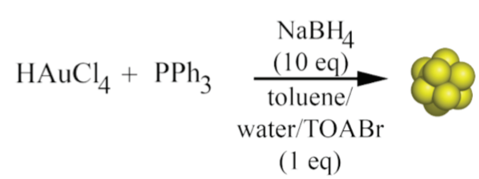

Figure 2: Greener synthesis of gold nanoparticles. Sodium borohydride and toluene/water replace more caustic agents to produce nanoparticles in higher quantities and greater purity.

We can functionalize the surface of these nanoparticles to yield nanoparticles with tunable properties, for example

1 http://greennano.org/

directing self-assembly, or tuning electronic or optical coupling. Figure 3 shows just a few examples of functionalized nanoparticles within our library.

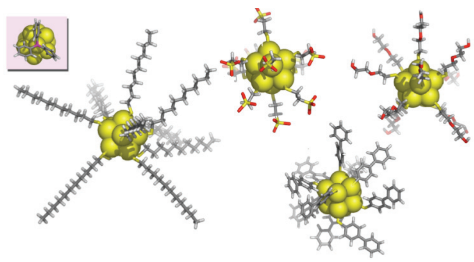

Figure 3. Examples of functionalized nanoparticles. Inset (upper left) represents the core nanoparticle.

By controlling the functionalization, we can further enhance the biological safety of these nanoparticles. To ascertain the biological impacts of our functionalized nanoparticles, we use a tiered approach.

Tier 1: *Nanoparticle testing in cells, tissues, and whole organisms.* We begin with screening level evaluations by testing the materials in cell cultures, tissue and whole organisms with a goal of defining the structural properties of nanomaterials that elicit defined biological responses.

Tier 2: *Cellular targets and bioaccumulation studies (in vivo).* The nanoparticle uptake and distribution is tracked within organisms and the cellular targets are identified for the nanomaterials that elicit a response.

Tier 3: *Molecular expression-gene response profiles.* Global level expression profiles in responses to nanomaterial exposures are compared using microarrays.

The data is then compiled, placed in a database and analyzed according to structure, function and biological response. This information is fed back into the synthesis designs to further guide the development of inherently safer nanoparticles using an iterative approach.

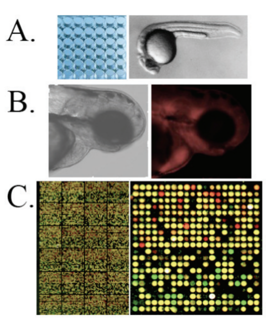

Figure 4. Tiered approach to biological testing. Testing regime: [A]. analyze in cells, tissues and whole organisms; [B.] measure the bioaccumulation in whole organisms; and [C] analyze the global molecular expression profiles in response to change. [S. Harper, R. Tanguay, E. Johnson unpublished]

Figure 4 represents our tiered approach for measuring biological toxicity. In this example, we use zebrafish as a model analysis. Like other fish models, the zebrafish shows very high sequence and developmental homology to humans and thus represents an excellent in vivo model organism for predictive toxicology [5].

2.2 Greener Nanomanufacturing of Engineered Nanoparticles

Microreactors hold significant promise for greener syntheses of nanoparticles because their dimensions promote rapid mixing and enhanced process control. Using the methods developed for nanoparticle synthesis, we are identifying nanoparticle formation reactions that can be carried out in a single solvent phase. In-line monitoring will allow us to control nanoparticle core size, dispersity and functionality. From these studies, we will develop an integrated microreactor platform for deploying the chemistries described above to produce larger quantities of nanoparticles. As shown in Figure 5, the integrated platform will include inline mixers, valves for reagent introduction, reaction domains with thin film heaters for reaction control, integrated waveguides for monitoring and feedback control, and sorting operation for assessing purity. Production level quantities will be obtained by incorporating parallel microchannels within the reactors.

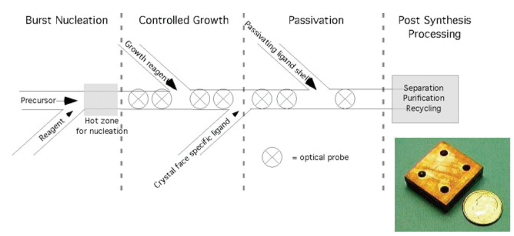

Figure 5. Microchannel nanofactory design. Key features include rapid mixing, temporal separation of reaction steps, enhanced process control, onboard post synthesis processing, and rapid, consistent scale-up. [J.E. Hutchison, B. Paul, C-H. Chang, and V. Remcho, unpublished]

We are also exploring gas-phase production of ceramic nanoparticles in microreactors to produce materials that should expand our capabilities to produce novel devices for transportation, energy, sensors and medicine. Microchannel reactors for these syntheses has many advantages, including high heat transfer rates, high temperature gradient for quenching the reactions, short, controllable residence times, and ability to control diffusion length and reagent mixing. We will be able to scale up to production quantities using parallel arrays.

We will use reactive gas streams in parallel arrays of microchannel reactors for the greener synthesis and processing of silicon nitride nanoparticles. For example, the corrosive reagents such as silicon tetrachloride and silicon tetrafluoride and its associated by-products (e.g. hydrogen

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fluoride) can be replaced with silicon powder, which can be obtained from scrap silicon to produce ceramic nanoparticles (Figure 5).

$$NH_3 + SiO \rightarrow Si_3N_4$$

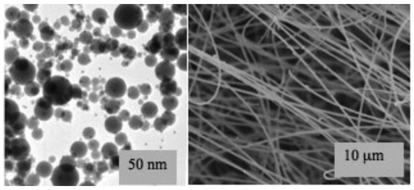

Figure 5. Production of silicon nitride in the presence of Ar and heat. [S. Atre, unpublished]

2.3 Interfacing Nanoparticles to Nano-and MacroStructures for Device Applications

Nanomaterials are driving innovation in optical and electronic devices, however, realizing the full potential of nanoscale matter in device technologies requires the integration of the nanoscale building blocks with other components of the device. Nanostructures can also be important precursors in the low-cost and greener manufacture of more traditional microscale devices and to exotic new materials. Thus, developing environmentally-benign assembly methods and identifying approaches to interface nanomaterials with macroscopic structures are being explored to produce greener, high-performance devices and nanostructured materials.

For example, we are developing bottom-up, self-assembly based approaches for production of 1D and 2D nanoparticle arrays using molecular combing techniques. A “bottom-up” approach is more efficient and less wasteful than traditional ‘top-down” or traditional patterning methods. By using specifically tailored nanoparticles as building block, we are able to precisely control such features as interparticle spacing, which further allows us to develop micro- or macro- structures for device applications.

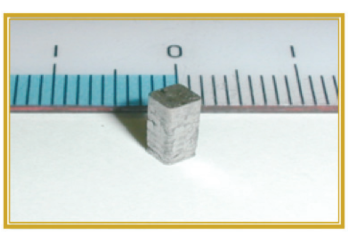

Figure 6. Example of nanostructured material based on low-temperature and solution-based processing of nanostructured inorganic materials.

Additionally, we are developing benign approaches for integrating nanostructures into thin films for applications in electronic materials and thermoelectrics using solution-based and vapor deposition techniques to create nanolaminated oxide thin films. These films are applicable in thermoelectric systems, electronic devices (e.g semiconductors), or dielectric materials (Figure 6).

3 SUMMARY

Our objectives are to develop new nanomaterials and nanomanufacturing approaches that offer a high level of performance, yet pose minimal harm to human health or the environment. Our research merges the principles of green chemistry and nanoscience to produce safer nanomaterials and more efficient nanomanufacturing processes in the context of producing nanoparticles and nanostructured materials for applications in fields such as photovoltaics, nanoelectronics and sensing. SNNI brings together chemists, biologists, materials scientist and engineers from ONAMI to pioneer new approaches to the design, production and use of nanomaterials.

SNNI’s efforts in green nanoscience address (1) the design of inherently safer nanoparticles for use in electronic and optical applications, such as sensing, optics, and photovoltaics; (2) the development of greener methods for large-scale nanoparticle production; and (3) the discovery of efficient approaches for interfacing nanoparticles with each other or with other components in functional devices. Each of these objectives is critical to the development of safe, yet high performance applications of nanoscience and nanotechnology.

4 ACKNOWLEDGEMENT

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