Workshop on Mesoscopic and Nanoscopic Materials
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Summary and Recommendations

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A workshop on "Mesoscopic and Nanoscopic Materials" was held from August 29 – September 1, 2004, as part of a series of workshops on the "Future Scientific Directions for the Advanced Photon Source." The goal of the workshop was to identify future directions in scientific research in the field of mesoscopic and nanoscopic materials that could benefit from the Advanced Photon Source. The workshop brought together internationally renowned specialists in synthesis, characterization and applications of nanophase materials. The participants presented the frontier problems in their fields from experimental and theoretical perspectives.

Over the past decade, materials with nanoscopic to mesoscopic dimensions have been the subject of enormous interest because of the possibility of artificially creating materials not found in nature with completely new properties. These materials have the potential for wide-ranging industrial, biomedical, and electronic applications. Such materials can be metals, ceramics, polymeric materials, biomaterials or composite materials, and they are being assembled layer-by- layer or even atom-by-atom to generate new atomic arrangements with completely new properties. The interplay of confinement, proximity and organization of the atomic and molecular constituents is the key in realizing materials with novel and unpredicted behavior. Understanding, characterizing, controlling and tailoring materials with a view to harnessing materials properties on the nanometer to micrometer length scale and on femtosecond to second time scale is a key strategy for materials research. For instance, the surface chemistry of nanoparticles effects their reactivity behavior in catalysts or in wear and corrosion resistant materials. The self-organization of nanostructured biomaterials could lead to broad applications in drug encapsulation and delivery.

It is a well known paradigm for both biological and inorganic materials that structure determines function. There is also an emerging understanding that structure alone is not sufficient to determine function, but that dynamics play a critical role. Progress in the field of nanoscale materials is intimately related to the development of dedicated synthetic and analytical techniques that enable us to produce and examine the atomic and electronic structure of new nanoscale materials. These include optical methods, electron microscopy techniques, as well as x-ray microscopy, imaging and scattering techniques. It is well known that x-rays are unrivaled in their ability to determine structure in the nanoscale range, particularly in the bulk of the material, at buried interfaces, in-situ under a wide range of conditions, etc., and to study many properties not available to other probes such as global statistical properties. X-rays can also be used to monitor the dynamic response over a wide range of time scales including ultra-fast structural relaxation or dynamic and dissipative phenomena at surfaces and interfaces under extreme conditions. As the new hard x-ray tools deliver these types of capabilities, it is expected that the traditional boundaries between x-ray scattering, imaging, microscopy, interferometry and spectroscopy will disappear. This new paradigm will provide unprecedented opportunities for progress in nanoscience..

The focus of this workshop was to identify the frontier problems in understanding interfacial structures, nano-systems, confinement, and self-assembly of hard materials, soft materials, and biomaterials, as well as nanofluidic phenomena. There was also a major effort during the workshop to assess the applicability of a variety of hard x-ray tools available at the third generation synchrotron radiation sources, such as the Center for Nanoscale Material's hard x-ray Nanoprobe and other probes such as electron diffraction and microscopy which will become available at the new nanocenters at various DOE National Laboratories.

The workshop plenary sessions consisted of science overviews on materials, phenomena, characterization tools and techniques. Time was allotted in each session for discussions. Care was taken to ensure representation at the workshop by experts in the various fields of nanoscience and not solely synchrotron experts. It was clear from the excitement and enthusiastic participation in the discussions and recommendations that there is a great deal of enthusiasm for the potential inherent in synchrotron radiation for nanoscience.

The charge given to the workshop attendees was as follows:

1. Identify grand challenge mesoscopic and nanoscopic science that should be addressed during next 5-10 years using x-ray techniques at a third generation synchrotron radiation source.

2. Identify and justify the technical requirements to meet the grand challenge problems:
   - New instrumentation and techniques that need be developed on existing beamlines to perform new kind of science.
   - Need for new dedicated beamlines and instrumentations for this community

3. Identify both short- and long-term R&D needs in areas such as x-ray techniques, sample environment, optics, and data analysis that will prepare the community to address grand challenge problems

The workshop focused on three broad areas: controlled synthesis, directed assembly and the study of new or collective properties. The main challenges in nanoparticle synthesis consist of controlling the physical properties of the core; developing facile and effective coatings that allow introduction of one or more functions and determining the factors which determine the toxicicty of the nanoparticles (e.g. shape, size, chemical composition, coating).

There was a discussion of how to calculate (and therefore predict and even design) the various hierarchies of structures formed as molecules self-assemble, based on techniques such as steric and electrostatic models, Monte Carlo calculations, simulating the assembly using molecular dynamics or using other agent-based algorithms, etc. It was pointed out that it would be extremely useful to use, e.g. synchrotron-based methods for studying the details of the self-assembly of nanoparticle systems as a way of testing the validity of such calculations. There were presentations on methods and problems associated with nanoparticle synthesis, including the synthesis of functionalized nanoparticles with magnetic or other properties,such as iron oxides, the synthesis of inorganic-organic composite and inorganic-bio (e.g. DNA grafted onto inorganic nanoparticles).

There were discussions of assemblies of granular particles and their flow patterns and jamming transitions and how these could be studied by the complementary techniques of NMR, light scattering and X-ray microtomography; patterned assembly of nanoparticles on patterned substrates created by micro-phase separated block copolymers; assemblies of nanoparticles at air-liquid interfaces and the production of ultrathin membranes of controllable porosity, and wetting layers and nanodroplets at interfaces.

Along with these, participants heard about techniques for characterizing such systems ranging from coherent x-ray [‘lens-less’] imaging of single nanocrystals, to microdiffraction using microfocused synchrotron x-ray beams, x-ray diffraction of assemblies of nanoparticles, SAXS, GISAXS, X-ray reflectivity, X-ray standing wave induced fluorescence, X-ray photon correlation spectroscopy, and the complementary but non-synchrotron techniques of electron microscopy and atomic force microscopy.

Finally there were presentations which focused on the study of nanomaterials with new properties, such as molecular junctions used as transistors, composite magnetic films with exchange bias, spring magnets, magnetic/semiconductor composites for spin injection, quantum fluids and quantum well heterostructures, and nanobio systems for medical applications. Also presented as examples of self-assembled nanosystems of interest for study with synchrotron methods were purely biological systems such as the extracellular matrix and its response to external stimuli.

Findings and Recommendations:

The following findings and recommendations are seen as critical components for APS to maintain a leadership role in the rapidly growing field of mesoscopic and nanoscopic science.

Finding: It was recognized that the APS already supports and develops many tools important for characterization of materials at the nanoscale (microprobe, coherent diffraction (proof of principle, so far), GISAXS, SAXS). Many of these tools are available in a non-dedicated mode at various beamlines around the ring. In general, time for setup of these experiments is timelyIt is also recognized that the Hard X-ray Nanoprobe being built with the Center for Nanoscale Materials will be an important component to the APS nanoscience tool set, APS should continue to explore and support development of other new techniques as they become possible and to nurture the evolution of demonstration experiments to routine application, e.g., coherent 'lens-less' imaging.

> Recommendation: APS must make every effort to support users without synchrotron radiation experience by providing user friendly beamline and instrumentation support. The workshop participants expect a big demand for GISAXS, SAXS, and x-ray reflectivity measurements at the APS, and new and modern *dedicated* capabilities for these techniques should be developed to perform such studies in different sample environments. In the spirit of continued explosion of this field, APS staff should be provided adequate R&D support to jointly plan new and high-risk experiments with the new user groups and for developing new tools to perform such experiments.

Finding: It is clear that there is a critical need for a complete characterization of nanomaterials as they are synthesized at both the individual nanoparticle level and at the collective, ensemble level, both of which can be studied by complementary x-ray techniques. This requires in-situ and real-time experiments which in turn requires extended setup and characterization time, substantial support, and adequate hutch space.

Recommendations:

1) provide maximum beamtime for dedicated programs requiring *in-situ* studies,
2) optimize insertion devices, x-ray optics and end stations on *dedicated* nanoscience beamlines (including a new soft- x-ray beamline),
3) assure that the end-stations on these beamlines contain hardware that resides in-place for extended periods, and
4) support necessary R&D to develop advanced nanofocussing optics, scanning stages with sub-nanometric resolution, and development of image extraction software.

Finding: To optimize the benefit for Nanoscience from the advanced characterization tools available at the APS it will also be necessary to have a critical mass of world-class resident scientists, including experimentalists, technical innovators and theorists.

Recommendations: 1) The APS should provide funding on a long term basis with dedicated beamtime for experimental staff. In order to retain and attract the best talent, the APS should consider allowing its best and most productive scientists to dedicate some fraction of their time to their own research programs perhaps by raising their own research money's and effectively buying back their own time from User related activities that is the basis of their employment at the APS. 2) Implementation of a theoretical program, perhaps in collaboration with the Center to Nanoscale Materials virtual fab-lab, for theoretical modeling effort. Modeling tools developed in this program should be made available to the APS users.

These recommendations were designed to effectively utilize unique intrinsic capabilities of the APS and CNM for frontier mescopic and nanoscopic science; develop infrastructure/technology to make the tools for this field more broadly available; and expand the capacity of nanoscience experimentation at APS. Finally, the present and future scientific users in the nanoscience area who participated in the workshop were eager to be fully involved in the implementation and success of all of these recommendations.