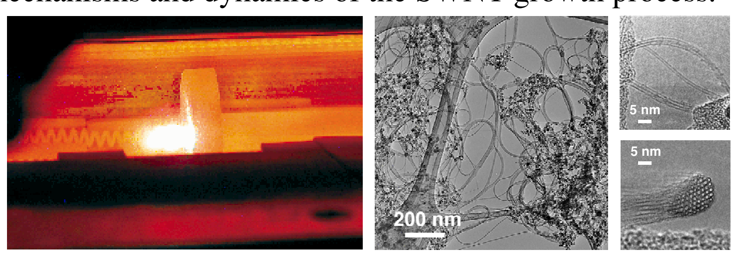
Nanomaterials Science at Oak Ridge National Laboratory

Oak Ridge National Laboratory (ORNL) *http://www.ornl.gov* is a multidisciplinary laboratory managed for the Department of Energy by UT-Battelle, LLC a consortium between the University of Tennessee and Battelle. ORNL employs approximately 1500 scientists and engineers, 2500 other employees, and serves the collaborative research needs of approximately 3000 visitors who spend more than 2 weeks per year. With the many postdoctoral appointments administered by the Oak Ridge Institute of Science and Education (ORISE) *http://www.orau.gov/orise.htm* and graduate students from the nearby University of Tennessee in Knoxville *http://www.utk.edu* , the ORNL campus is a lively, collaborative research environment with state-of-the-art research facilities. A continuing goal at ORNL is to foster further research collaborations with universities.

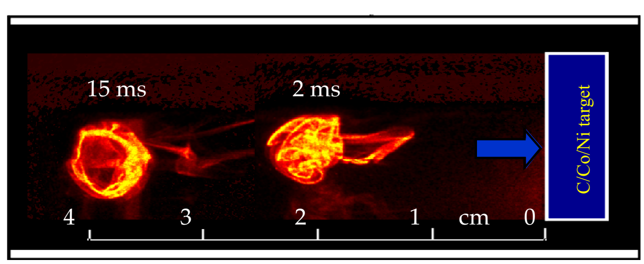
Nanoscale Science, Engineering and Technology (NSET) is a research area already pursued by many researchers at ORNL *http://www.ornl.gov/ORNLReview/rev32_3/brave.htm* . It overlaps several of the laboratory's core competencies, which include: (1) a strong core materials science and engineering program, (2) a variety of capabilities and expertise to synthesize new materials and process them into nanoscale configurations molecule by molecule, (3) world-class characterization facilities that can "see" new materials configurations at the atomic level and determine their properties, and (4) high-performance computer modeling and simulation capabilities to understand materials properties and predict new configurations. ORNL selected NSET as a major focus area to receive targeted internal funding from our Laboratory Directed Research and Development Program through FY2003, with 16 projects ongoing currently

ORNL has a strong record of research in condensed matter synthesis, characterization, theory and modeling. *Understanding and controlling* synthesis at the atomic level is a key goal of nanomaterials science at ORNL. For example, the laser vaporization (LV) method is an unexpectedly efficient way to grow high-quality single-wall carbon nanotubes (SWNT). However the mechanism and dynamics of growth by this method are still the subject of much speculation, principally due to the lack of *in situ* measurements of the synthesis conditions. At ORNL, *in situ* time-resolved spectroscopy and imaging are being applied to understand the mechanisms and dynamics of the SWNT growth process.

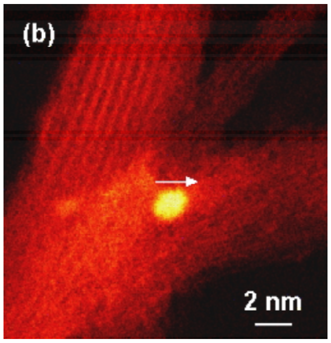
High yields of SWNT (microns long) can be grown in the plume of ablated material generated by single laser shots onto a composite target containing C (98%), Ni(1%) and Co(1%). Through *in situ* time-resolved laser-induced luminescence imaging and spectroscopy at different times (t) after ablation, the ORNL results showed that much of the growth appears to occur during extended annealing times while the plume is suspended in 500 Torr of slowly-flowing Ar at ~1000°. TEM analyses of collected deposits showed that SWNT grow at average rates ~ 1 µm/s, and that the majority of SWNT growth occurs at t > 100 ms in the ablation plume from a feedstock of aggregated clusters and nanoparticles. These aggregates form within a few milliseconds after



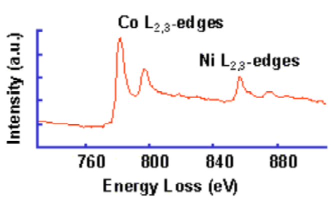
Single-wall carbon nanotubes (above right) grow from material vaporized from a carbon/metal target inside a tube furnace. The naked eye can see only the bright laser plasma (above left) which lasts for ~ 200 µsec, however time-delayed lasers can visualize the plume and help measure its constituents for several seconds longer (as shown in the Rayleigh scattering images below). Using this technique, TEM analyses of materials grown for different times and conditions are revealing the timescales, rates, and feedstock for SWNT growth, essential steps for controlled synthesis. (Puretzky,Geohegan, Fan, et al. ORNL http://www.ornl.gov/~odg)

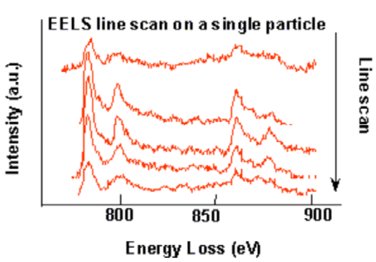


ablation, and normally anneal for several seconds more as they traverse the oven while suspended in the gas flow. These results imply that SWNT synthesis during LV-production occurs by the *condensed phase conversion* (CPC) of carbon clusters or nanoparticles by metal catalyst nanoparticles (diameters < 20 nm)during extended annealing periods, a conclusion which is supported by recent *ex situ* annealing experiments.

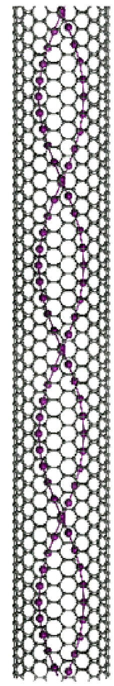


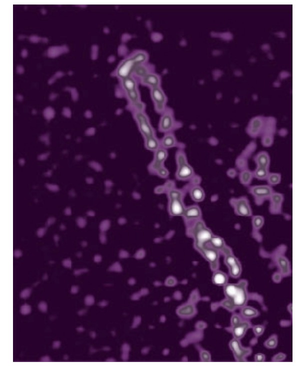
Z-contrast scanning transmission electron microscope image(above) of individual iodine atoms a Ni-Co metal catalyst nanoparticle lodged in a bundle of single-wall carbon nanotubes. EELS linescans of the 2 nm particle revealed Ni and Co present in nearly equal concentrations, with no variation across the particle (below).



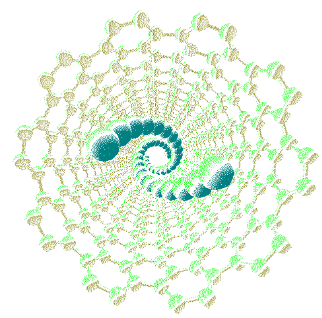


In order to understand nanomaterial synthesis and function, *atomic scale* characterizational tools are required. High-resolution Z-contrast STEM imaging and simultaneous EELS (electron energy loss spectroscopy) are two techniques developed at ORNL and applied to nanomaterial science. Recently, Z-STEM was used to observe *individual* dopant *atoms* inside single-wall carbon nanotubes in order to understand the sites they occupy. In addition, the stoichiometry and spatial uniformity of individual nanoparticles (e.g. metal catalyst nanoparticles used for SWNT synthesis) have been measured with EELS linescan determination of the energy-loss near edge structure. These techniques are just two examples of the many novel atomic-scale characterizational techniques under development at ORNL.





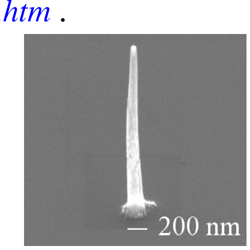
Z-contrast scanning transmission electron microscope image(left) of individual iodine atoms inside a single-wall carbon nanotube (as visualized at left and below)

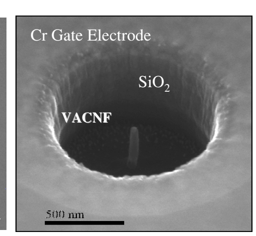


STEM/EELS by X. Fan and S. J. Pennycook ORNL

Two aberration-corrected electron microscopes (STEM/TEM) will soon deliver sub-Å resolution at ORNL. The current record (1.2 Å) for resolution by a STEM was demonstrated at ORNL, and new aberration-correction technology will attempt to more than double this resolution (~ 0.5 Å). These improvements will provide much sharper, higher-intensity images of nanomaterials. One of these instruments will be totally automated and located at the HTML (High Temperature Materials Laboratory), a DOE user facility which concentrates on materials characterization. *http://www.ms.ornl.gov/htmlhome/default.htm* .

ORNL is also strongly involved in the functional properties of nanomaterials, exploring new applications in the physical, chemical, and biological sciences as well as electronics. For example, understanding the fundamental aspects of growth and alignment of carbon nanofibers made by plasma-enhanced CVD has permitted an deterministic placement of individual VACNF's (see right) for careful measurements of their field emission characteristics. These studies enabled the development of a new class of vacuum microelectronic devices made by growth inside

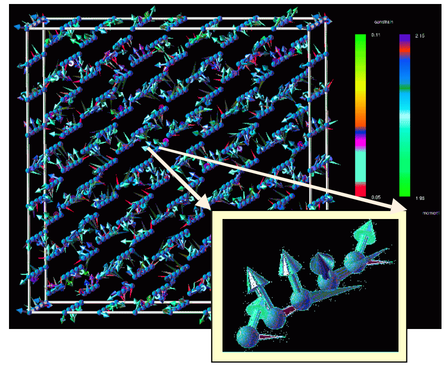




Vertically-aligned carbon nanofiber (VACNF, left) and as-grown vacuum-microelectronic field emitter device incorporating a single VACNF. Merkulov, et al. ORNL - JVST B (in press, 2001).

nanolithographically-patterned microstructures (see http://www.ornl.gov/ment/) .

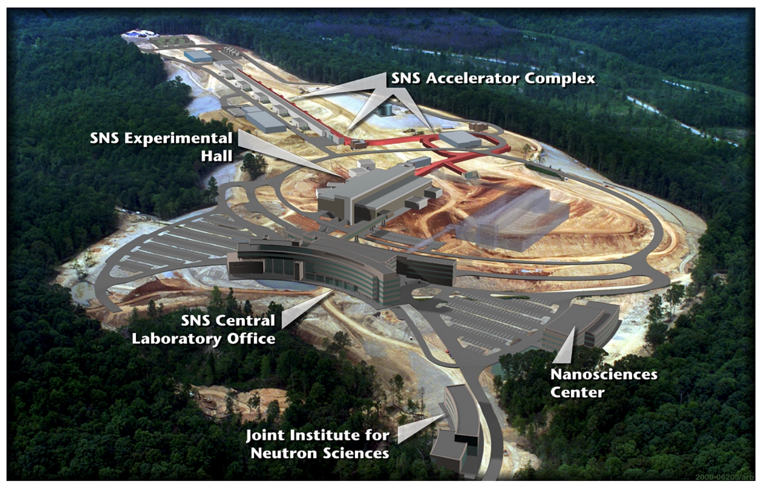
Theoretical understanding of nanoscale interactions and their collective phenomena requires the simulation and calculation capabilities such as those from the massively parallel supercomputers. The first 1-teraflop computer code was developed at ORNL to relate magnetic moment formation and forces driving their motion to the underlying electronic structure of a magnetic material *(right)* http://theory.ms.ornl.gov/~gms/M4home.html. Other uses for supercomputers involve the first calculation of the normal modes of a single-wall carbon nanotube containing over 3000 atoms *(Yang et al. ORNL http://www.ornl.gov/ORNLReview/v33_2_00/breaking.htm).*



The magnetic properties of materials (e.g. Fe) are determined by the dynamics of local moments. Simulated with a constrained local moment (CLM) model (G.M. Stocks, et al. ORNL).

These few examples only indicate a small fraction of the research in nanoscale science, engineering and technology underway at ORNL. Much more is planned for the future, with the development of the **Spallation Neutron Source (SNS)** and a **Center for Nanophase Materials Sciences (CNMS).**

The Spallation Neutron Source (SNS) is a 1.4 billion dollar accelerator-based science facility which will provide neutron beams that are 12 times more intense than any other such source in the world. SNS will provide opportunities for up to 2000 researchers each year from universities, national labs and industry for basic and applied research and technology development in the fields of materials science, magnetic materials, polymers and complex fluids,chemistry and biology. Construction of the SNS began in December 1999 and completion is expected in 2006.



Conceptual plan for the Spallation Neutron Source and the associated Center for Nanophase Materials Sciences at ORNL.

ORNL, together with partner universities, have proposed a Center for Nanophase Materials Sciences (CNMS) which is in the planning stage. The CNMS will be located on the SNS site and will provide a unique resource for nanoscale science research, permitting the assembly of teams to address problems with the scope, disciplinary breadth, and complexity which cannot be done by small-group efforts . The CNMS will integrate nanoscale research with neutron science, synthesis science, and theory/modeling/simulation to confront the *controlled synthesis* of nanophase materials. Well over half of the use of the center will be by researchers from academia, industry, and other national laboratories.

It is expected that the CNMS's major scientific thrusts will be in nano-dimensioned soft materials, complex nanophase materials systems, and the crosscutting areas of reduced dimensionality that become scientifically critical on the nanoscale. An interdisciplinary *Nanomaterials Theory Institute* within the CNMS will provide a needed focus and stimulate U.S. leadership in the use of theory/modeling/simulation to both design new materials and investigate pathways to their synthesis.

It is the hope and goal that these user facilities, along with those existing already at ORNL and personal collaborations, will be useful mechanisms by which university personnel can team with those at ORNL to pursue studies in nanomaterials science, engineering, and technology.

D. B. Geohegan, ORNL for NSF "Partnership in Nanotechnology Workshop" (see http://www-unix.oit.umass.edu/~nano/)