CHAPTER 11

APPLICATIONS: HIGH-PERFORMANCE MATERIALS
AND EMERGING AREAS

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11.1 VISION FOR THE NEXT DECADE

Changes in the Vision over the Last Ten Years

The field encompassed by the term “nanomaterials” has changed dramatically over the past ten years. While it was useful in 2000 to describe nanomaterials on the sole basis of our ability to understand and control matter at the nanoscale where material properties possess a distinct size-dependence, the field has now grown well beyond that earlier definition. For example, it is evident in 2010 that additional factors beyond constituent nanoparticles (e.g., high surface/interface area, proximity, and novel chemical, physical, and/or biological moieties) are also playing major roles. New work envisioned at the turn of the 21st century (Siegel et al. 1999; Roco et al. 2000) on organic-inorganic composite materials, multifunctional materials, self-healing materials, and nanoscale sensors has become a reality in the past ten years, while exploratory ideas about bio-abiotic heterogeneous systems, information-nano-bio integration, electronic-neural interfaces, and nano-information-biological-cognitive systems (Roco and Bainbridge 2001) have received increased recognition in the scientific community and funding programs.

The past decade has seen an evolution in scientific understanding and capabilities, from working with isolated nanoparticles, nanotubes, and nanowires to working with hybrid nanocomposites whose properties are controlled not only by the constituent nanomaterials but also by their morphology, spatial anisotropy, and relative proximity with respect to one other and the host matrix. The worldwide scientific focus on nanostructured hybrid material systems based upon synthetic or natural polymers combined with metal, ceramic, carbon, or natural (e.g., clay) nanostructures represents a truly revolutionary change in our thinking and in our ability to create nanostructured materials and coatings to solve real problems to benefit society. Specific examples include:

- Biopolymer/inorganic-nanoparticle hybrid assemblies for targeted drug delivery or precise environmental sensors
- Synthetic polymer coatings containing dispersed enzymes
- Ceramic or metal nanoparticles for antiseptic or antifouling surfaces

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- Diverse synthetic polymer/clay or nanoparticle dispersions for various industrial applications

**Vision for the Next Ten Years**

Over the next ten years, R&D programs will focus on a range of issues that will improve the performance, multifunctionality, integration, and sustainability of nanomaterials in a range of emerging and converging technologies. In particular, methods are required for nanomaterials and nanosystems by design; scaling up high-quality and monodisperse nanomaterial production; for rapidly measuring and characterizing quality and reproducibility of manufacturing processes incorporating nanomaterials; and for manufacturing nanostructures into bulk materials, coatings, and devices while retaining enhanced nanoscale properties. Through controlled assembly of nanoconstituents that have distinct properties, the next generation nanocomposite material is expected to have the unique and powerful attribute of independent tunability of previously coupled properties. For example, bulk materials with high electrical conductivity typically possess high thermal conductivity, whereas these properties have the potential of being decoupled in next-generation nanocomposites. This specific example has broad implications for thermoelectric devices that convert waste heat into useful electricity. Similarly, the decoupling of electrical conductivity and optical reflectivity would enable a new class of transparent conductors that could serve as the basis of improved photovoltaic and display technologies. Ultimately, the rational assembly of nanomaterials into nanocomposites will yield high-performance materials with new combinations of properties, thus underpinning the development of previously unrealizable applications.

11.2 ADVANCES IN THE LAST TEN YEARS AND CURRENT STATUS

The main advances in nanostructured materials and coatings in the past ten years have centered on hierarchical hybrid nanostructured material systems consisting of a potentially wide range of biological and non-biological building blocks; nanostructure-matrix interfaces in such nanocomposites; and the rapidly developing ability to create engineered interfaces with novel chemical, physical, and/or biological moieties for a variety of systems. While these high-performance nanomaterials have arguably touched and impacted nearly all fields of science and engineering, this section will provide a few specific examples for illustrative purposes.

**Nanofibrous Media**

During the past decade, nanotechnology has enabled significant expansion of consumer and industrial products by the use of nanofibrous media. Nanofibrous media are fabricated by techniques such as electrospinning and “islands-in-the sea” fiber spinning. While nanofibers have been known for some time, the concepts around the use of nanofibers have finally come into their own with nanotechnology allowing an understanding of their usage (Grafe et al. 2001). Specifically, companies such as Donaldson, E-Spin, United Air Specialists, and Argonide have built multimillion-dollar businesses using nanofibrous membranes. Initially, these membranes were developed for simple air filtration due to the achievement of high filtration efficiency at low operating pressure. More recently, these membranes have been incorporated into more sophisticated filtration systems with other functional effects such as bacteria removal using titanium dioxide fibrous webs, as depicted in Figure 11.1 (Yuranova et al. 2006). Recently, the National Aeronautics and Space Administration (NASA) recognized Argonide Corporation for its NanoCeram® water filter, which is capable of filtering >99.99%
of hazardous particles from water (National Aeronautics and Space Administration (NASA) 2009).

While specific data regarding the growth of nanofiber-web-based materials are confidential to specific company product lines, it is estimated that nanofiber-web-based filtration media have grown by approximately $500 million in the previous decade from a base of about $200 million. Early nanofiber-web-based filtration media were used almost exclusively in military applications; these media are now found in automotive and other applications. This expansion has been driven by improved understanding of nanofiber phenomena such as the origin of observed low pressure drops and particle interactions.

![Titanium dioxide fibrous web decorated with TiO$_2$ that is used for bacteria removal in advanced filtration systems (Yuranova et al. 2006; false color SEM image courtesy of David Knox, MeadWestvaco Corporation).](image)

Beyond air filtration, the high degree of hydrophobicity in nanofibrous materials yields "instant clean" effects on everything from shirts to tablecloths to surgical and medical devices. For example, Nano-Tex has developed technology and products that incorporate nanowhiskers to allow for virtually stain-free surfaces. This application alone has blossomed into an estimated $200 million per year market.

**Nanocrystalline Metals**

Ten years ago, it was known that nanostructured metals were strong, but it was believed that they were brittle in nature, which would limit their applications as structural materials. In the past decade, extensive progress has been made in the area of processing defect-free nanocrystalline metals using electrodeposition and plastic deformation techniques (Karimpoor et al. 2003; Li and Ebrahimi 2004; Lowe and Valiev 2004). Consequently, it has been proven that nanocrystalline metals are not inherently brittle and that their tensile ductility befits their high strength (Li and Ebrahimi 2006; Koch et al. 2005). Figure 11.2 compares the tensile stress-strain curve of a nanocrystalline Ni-Fe alloy with a medium carbon quenched and tempered steel demonstrating the high strength (over 2 GPa) of the single-phase nanocrystalline metal and its reasonable ductility in comparison to a high-performance steel. The fact that nanocrystalline metals and alloys have reasonable ductility makes them candidates for multifunctional structural applications, where other properties such as corrosion resistance, magnetic properties, and optical properties are important in addition to high strength. Through the past decade, it has been demonstrated experimentally and by computational techniques that constraints imposed by the small grain size of nanocrystalline materials makes mechanisms that are relatively inconsequential in conventional polycrystalline metals to become dominant at the nanoscale. Examples include:
• Observation of mechanical twinning in face-centered cubic (fcc) metals with relatively high stacking-fault energy, such as aluminum and copper (Chen et al. 2003; Wu et al. 2006)
• Motion of unpaired partial dislocations in fcc metals (Wolf et al. 2003)
• Grain boundary-mediated deformation and grain rotation (Van Swygenhoven et al. 2006; Van Swygenhoven and Derlet 2001; Shan et al. 2004)
• Grain growth and coupled grain boundary migration (Haslam et al. 2003; Jin et al. 2004; Zhang et al. 2005; Cahn et al. 2006; Mompiou et al. 2009)

![Figure 11.2](image_url)

Figure 11.2. A comparison of the tensile stress-strain curve of a nanocrystalline Ni-Fe alloy (average grain size of 9 nm) with a structural hardened steel (courtesy of Fereshteh Ebrahimi, University of Florida).

Because of the dominance of the grain-boundary-mediated deformation in nanocrystalline materials, the structure of the boundaries plays a significant role in the plastic deformation of these materials. For instance, low-temperature annealing can relax the grain boundaries of as-processed materials considerably and makes the processes of dislocation nucleation from grain boundaries and grain boundary sliding more difficult (Hasnaoui et al. 2002). To illustrate this point, Figure 11.3 demonstrates that low-temperature annealing can result in an increase in strength and significant loss of ductility (Ebrahimi and Li 2007).

Simulation studies have elucidated that as the grain size is reduced below a critical level (10–20 nm, depending on the metal), the dominant deformation mechanisms change from dislocation activities within the crystals to grain-boundary-mediated deformation (Wolf et al. 2003). This transition causes a loss of strength, resulting in the so-called “inverse Hall-Petch” phenomenon. Detailed investigations using scattering techniques have revealed that because of the mechanistic differences in the plastic deformation, the overall deformation behavior of nanocrystalline metals is also different in comparison to conventional metals (Li et al. 2008).
The experimental and simulation data suggest that during the plastic deformation of nanocrystalline materials, only a fraction of grains deform plastically (Ebrahimi et al. 2001; Bitzek et al. 2008; Raeisinia et al. 2008). Therefore, these materials can be envisioned as composite materials consisting of both elastic (smaller grains) and plastic (larger grains) components. More specifically, the large grains contribute to plastic deformation and the smaller elastic grains contribute to strain hardening. Consequently, strength and ductility of nanocrystalline metals depend strongly on the grain size distribution. Based on this idea, it has been demonstrated that metals with duplex grain size distributions can exhibit an optimum combination of strength and ductility (Zhao et al. 2006). Emerging results on the fracture of nanocrystalline metals suggest that in contrast to conventional fcc metals, whose fracture mode occurs by the plasticity-induced microvoid coalescence mechanism, nanostructured fcc metals appear to fracture by cleavage (i.e., by breaking atomic bonds) (Li and Ebrahimi 2005; Ebrahimi 2006).

It has been known for nearly 50 years that reducing the specimen size results in different stress-strain behavior (Honeycombe 1984), and thin samples such as whiskers exhibit strength levels close to the ideal strength (Kelly and MacMillan 1986). In the past ten years, more experimental results have confirmed that smaller samples are indeed stronger (Nix 2009). This increase in strength has been attributed to the lack of dislocation sources. One of the concerns regarding the application of nanocrystalline materials has been their stability or lack thereof. In the last decade, it has been established that alloying can significantly stabilize the grain boundaries through the solute drag mechanism (Ebrahimi and Li 2006; Koch et al. 2008). For example, Figure 11.4 shows that the grain growth in Ni can be retarded significantly by the addition of Fe (Ebrahimi and Li 2006).
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Figure 11.4. Grain size evolution as a function of annealing temperature for pure Ni and Ni-Fe alloys (courtesy of Fereshteh Ebrahimi, University of Florida).

Cellulose-Based Nanomaterials

Over the past decade, the forest products industry has identified nanotechnology as a means to tap the enormous undeveloped potential of trees as photochemical “factories” that produce abundant sources of raw materials using sunlight and water. Forest biomass resources provide a key platform for sustainable production of renewable, recyclable, and environmentally preferable materials to meet the needs of society in the twenty-first century. Wood-based lignocellulosic materials (i.e., forest biomass) provide a vast material resource and are geographically dispersed.

The forest products industry nanotechnology roadmap (American Forest and Paper Association [AF&PA] and Energetics, Inc. 2005) identifies the industry vision as “sustainably meeting the needs of present and future generations for wood-based materials and products by applying nanotechnology science and engineering to efficiently and effectively capture the entire range of values that wood-based lignocellulosic materials are capable of providing.” In addition, the forest products industry sees its inherent strengths as including stewardship of an abundant, renewable, and sustainable raw material base; supporting a manufacturing infrastructure that can process wood resources into a wide variety of consumer products; and being uniquely positioned to move into new, growth markets centered on bio-based environmentally preferable products.

At the nanoscale, wood is composed of elementary nanofibrils (whiskers) that have cross-sectional dimensions of about 3–5 nm and are composed of cellulose polymer chains arranged in ordered (crystalline) and less-ordered (amorphous) regions (Tamerler and Sarikaya 2008; Postek et al. 2008; American Forest and Paper Association [AF&PA] and Energetics, Inc. 2005; Jones and Wegner 2009). Wood is approximately 30-40% cellulose by weight, with about half of the cellulose in nanocrystalline form and half in amorphous form (Figure 11.5). Nanocrystalline cellulose is relatively uniform in diameter and length; these dimensions vary with plant species. Cellulose is the most common organic polymer in the world, representing about 1.5 x 10^{12} tons of the total annual biomass production. Cellulose is expressed from enzyme rosettes as 3–5 nm–diameter fibrils that aggregate into larger fibrils up to 20 nm in diameter. These fibrils self-assemble in a manner similar to liquid crystals, leading to nanodimensional and larger structures seen in typical plant cell walls. The
theoretical modulus of a cellulose molecule is around 250 GPa, but measurements for the stiffness of cellulose in the cell wall are around 130 GPa. These measurements imply that cellulose is a high-performance material comparable with the best fibers technology can produce.

Because of the hundreds of millions of tons of wood available for processing, commercial production is both sustainable and renewable and represents an industrially significant supply. High-value, renewable nano-enabled composites can be produced by identifying commercially attractive methods to liberate both nanofibrils and nanocrystalline cellulose and by establishing methods for characterization, stabilization, and blending of these wood-based nanomaterials with a variety of other nanomaterials.

11.3 GOALS, BARRIERS, AND SOLUTIONS FOR THE NEXT 5–10 YEARS

Over the next ten years, nanoscience researchers will focus on a range of issues to improve the performance, multifunctionality, integration, and sustainability of nanomaterials in a variety of emerging and converging technologies. Specific goals are described in the subsections below.

Separation, Fractionation, and Purification

The defining feature of a nanomaterial is that its properties depend not only on composition but also size and shape. Any polydispersity in size or shape leads to inhomogeneous properties that are generally undesirable in commercial technologies. Consequently, researchers will seek scalable and economical strategies for separating, fractionating, and purifying nanomaterials as a function of size and shape, thus yielding monodisperse
nanoscale building blocks. The resulting uniform properties will enable reliable and reproducible performance in devices, technologies, and composite materials based on nanomaterial constituents. Furthermore, with monodisperse nanoscale building blocks in hand, controlled polydispersity can also be achieved and may be desirable where a controlled range of properties are required (e.g., photovoltaic technology requires conductive films with a range of optical transparencies matching the broadband solar spectrum).

Hierarchical Metamaterials

With monodisperse nanomaterials, it will become possible to assemble them into ordered crystalline structures where the constituent nanoparticles play the role of artificial atoms (Figure 11.6). While some progress has been made along these lines in the field of quantum dots in the past decade, over the next decade additional levels of control will be sought. Through controlled self-assembly and directed assembly of nanoconstituents of distinct properties, the next-generation nanocomposite material will have the unique and powerful attribute of independent tunability of previously coupled properties. For example, bulk materials with high electrical conductivity typically also possess high thermal conductivity; however, these properties have the potential of being decoupled in next-generation nanocomposites. This specific example has broad implications for thermoelectric devices that convert waste heat into useful electricity. Similarly, the decoupling of electrical conductivity and optical reflectivity would enable a new class of transparent conductors, which serve as the basis of photovoltaic and display technologies. Ultimately, the goal will be to rewrite the solid state physics textbooks regarding relationships between charge, energy, spin, phonon, exciton, and mass transport.

Nanomanufacturing

To bring nanomaterials to the mainstream marketplace, significant improvements in nanomanufacturing will be required. Problems surrounding scale-up, cost, sustainability, energy efficiency, process control, and quality control need to be overcome in order to realize mass production of microscale and macroscale nanocomposite materials that reliably retain the attributes of the nanoscale constituents. Fabrication of bulk products with retained nanoscale features will likely require scalable self-assembly techniques, durable surface-modification methods, and hierarchical processing and assembly. Ideally, this nanomanufacturing optimization will be informed by advanced computational capabilities that will allow improved design principles to be incorporated into the nanocomposite fabrication process.

Inspiration from Biology

Materials in biological systems possess a number of features that are not currently realized in engineered nanomaterials, including hierarchical, non-equilibrium, self-healing, reconfigurable, and defect-tolerant structures. Biological systems also possess optimized interactions between organic and inorganic media. Research in the next decade will seek to emulate this powerful combination of features in nanocomposite materials. To achieve these goals, improved control, characterization, and understanding of internal interfaces will be required. It will be highly desirable to monitor dynamic processes and directly observe the evolution of internal interfaces under the application of external stimuli.
Figure 11.6. Fullerenes, atomic clusters, and larger inorganic nanocrystals can be used as assembly elements for creating materials with tailored properties. Applications include photovoltaics (top), optical biosensors (middle), and electronics (bottom) (Claridge et al. 2009; courtesy of Paul Weiss, UCLA).

Combinatorial and Computational Approaches

Nanocomposite materials represent an immense phase space that includes the size, shape, and composition of the nanoconstituents, surface functionalization, and matrix. This phase space cannot be efficiently explored via serial, empirical study. Consequently, alternative strategies, including massively parallel combinatorial approaches and multiscale modeling, will be pursued in the next decade. The former will require innovative experimental design and parallel characterization capabilities, while the latter will benefit from expected improvements in computational power and algorithm optimization. Efforts to improve the performance and durability of nanoparticle surface functionalization can likely be guided by previous and ongoing research in surface science. These hierarchical hybrid nanostructured material systems with appropriate functionalities will enable application to a much wider range of important societal problems in the areas of energy, environment, and health care. Towards these ends, researchers must not only continue to create the fundamental understanding and necessary tools to assemble and fully characterize these nanomaterials and systems, but also develop reliable design capabilities to move from an era of "best-guess" nanomaterials to truly engineered systems.

Emerging and Converging Technologies

Realization of the aforementioned goals will create a suite of new nanocomposite materials with unprecedented properties and unique combinations of properties. In particular, the unique combinations of properties will allow previously disparate technologies to converge into single, multifunctional platforms. Specific examples include thermoelectrics, transparent conductors, combined supercapacitor and battery structures, integrated diagnostic and therapeutic devices, sensors/actuators, optoelectronics, and communication/computational systems.

11.4 SCIENTIFIC AND TECHNOLOGICAL INFRASTRUCTURE NEEDS

To realize the goals that were delineated in the previous section, significant improvements in scientific and technological infrastructure will be required. For example, new instrumentation is needed to investigate the localized nature of interfaces in nanostructured material systems and to probe the fundamental properties of nanomaterials (e.g., mechanical,
electric, thermal, chemical, biological, optical, and magnetic). Reliable multiscale design techniques for hierarchical nanocomposites are also critical. Only with the widespread availability of these tools, both experimental and theoretical, will the field reach its future potential.

Beyond these infrastructure needs, it is imperative to have a highly trained, multidisciplinary workforce. Highly skilled scientists and engineers should be continually encouraged and greatly facilitated on a global scale. Within the United States, the educational system from K–12 through postgraduate has to be significantly improved, and greater encouragement must be given to all students, particularly those in under-represented groups (e.g., women and minorities) to develop their interests and capabilities in the Science, Technology, Engineering, and Mathematics (STEM) fields. A creative new system of national scholarships for students following STEM career paths might incentivize such an effort. Furthermore, improved educational materials are needed—ranging from conventional textbooks to online curricular materials—to promote better teaching and learning in the emerging field of nanomaterials.

Ongoing guidance to realize these scientific and technological infrastructure needs should be provided by a panel of experts. This panel should be heavily populated with people who have already achieved success and have proven leadership and vision (e.g., Nobel laureates, National Academy members, business leaders).

11.5 R&D INVESTMENT AND IMPLEMENTATION STRATEGIES

While the investment of taxpayer funds in the U.S. National Nanotechnology Initiative and similar government initiatives globally has been considerable, the return on investment has been even greater. Consequently, continued investment at even higher levels is needed to secure the gains already made in this rapidly advancing, but still developing field. For example, the U.S. National Science Foundation Nanoscale Science and Engineering Centers have been a resounding success. However, some of these centers are nearing their ten-year funding limit. A mechanism should be instituted for national investment in these centers to be sustained and even increased in order to secure their research successes and develop them into intellectual property that can directly benefit society. In addition, individual and small group grants warrant continued support to seed efforts that can eventually blossom into the basis of additional center-level initiatives. Toward that end, it would be desirable to incentivize the teaming of smaller nanoscience research efforts into networks in an effort to minimize redundant work. Interdisciplinary and international collaborative efforts are also likely to yield important advances in this field. As the nanomaterials field matures, future science and technology policy should not only identify areas of research and development that deserve support but also identify specific directions where support should be reduced or eliminated (i.e., winners and losers should be identified).

Investments by the Federal Government should be matched by state and local governments, as well as by the private sector (i.e., industry) in public-private partnerships. A global industry consortium would be particularly useful for funding efforts with commercial potential. Nanotechnology is rapidly progressing to the point where all potential funding bodies will reap the benefits of these investments in better national and local security, improved economies and quality of life, and significant job (and hence tax) creation. Such leveraged investments should become the norm for fields such as nanotechnology that have broad positive impact on society.
11.6 CONCLUSIONS AND PRIORITIES
The past decade has seen an evolution from nanomaterials that are isolated nanoparticles, nanotubes, and nanowires to nanomaterials that are hybrid nanocomposites where the properties are controlled not only by the constituent nanomaterials but also by their morphology, spatial anisotropy, and relative proximity with respect to each other and the host matrix. The worldwide focus on nanostructured hybrid material systems represents a true paradigm shift in our thinking and in our ability to create nanostructured materials and coatings to solve real problems that benefit society. The next ten years will see a research focus on a range of issues that will improve the performance, multifunctionality, integration, and sustainability of nanomaterials in a range of emerging and converging technologies. Specific priorities include:

- Separation, fractionation, and purification in an effort to realize nanomaterials with monodispersity in composition, size, and shape
- Realization of hierarchical metamaterials with independent tunability of previously coupled properties
- Improvements in nanomanufacturing capabilities, including solving problems related to scale-up, cost, sustainability, energy efficiency, process control, and quality control
- Realization of nanomaterials with biologically inspired attributes, including non-equilibrium, self-healing, reconfigurable, and defect-tolerant structures in hybrid organic/inorganic media
- Combinatorial and computational approaches that enable efficient exploration of the vast phase space for nanocomposites, including the size, shape, and composition of the nanoconstituents, surface functionalization, and matrix
- Utilization of new nanocomposite materials with unprecedented properties and unique combinations of properties in emerging and converging technologies

11.7 BROADER IMPLICATIONS FOR SOCIETY
Throughout history, advances in materials have fueled advances in technology. Undoubtedly, nanomaterials and nanocomposites are already having and will continue to have profound positive benefits for society. In particular, through controlled assembly of nanoconstituents of distinct properties, the next generation nanocomposite material will have concurrent and independent tunability of distinct properties (e.g., mechanical, electrical, thermal, chemical, biological, optical, and magnetic). In this manner, next generation nanocomposites are expected to decouple properties that are intimately intertwined in bulk materials. For example, the decoupling of electrical and thermal conductivity will have broad implications for thermoelectric devices that convert waste heat into useful electricity. Similarly, the decoupling of electrical conductivity and optical reflectivity will enable improved transparent conductors, thus leading to improved photovoltaic and display technologies. Ultimately, the rational assembly of nanomaterials into nanocomposites will yield high-performance materials with new combinations of properties, thus driving the development of previously unrealizable applications as schematically depicted in Figure 11.7.
Figure 11.7. Real-world examples of applications of benefit to society that are based on nanostructured hybrid materials (courtesy of Richard Siegel, Rensselaer Polytechnic Institute).

11.8 EXAMPLES OF ACHIEVEMENTS AND PARADIGM SHIFTS

11.8.1 Monodisperse Single-Walled Carbon Nanotubes

Contact person: Mark Hersam, Northwestern University

Single-walled carbon nanotubes (SWNTs) are high-aspect-ratio cylinders of carbon ~1 nm in diameter whose walls are one atomic layer thick with an atomic arrangement analogous to graphite. The atomic structure of a SWNT is uniquely defined by a two-dimensional chiral vector whose components are typically specified by a pair of positive integers: \((n,m)\). This so-called chirality of the SWNT dictates its resulting properties. Unfortunately, current synthetic methods for producing SWNTs lack control over the chirality, thus leading to significant polydispersity in the resulting properties of as-synthesized SWNTs. Consequently, while many applications have been proposed for SWNTs, their widespread use in high-performance technology such as electronics, photonics, and sensors has been limited to date by their inhomogeneity.

In an effort to realize the technological promise of SWNTs, many techniques have been developed to sort SWNTs by their physical and electronic structures. Leading examples are dielectrophoresis (Krupke et al. 2003), chemical functionalization (Strano et al. 2003), selective etching (Zhang et al. 2006), controlled electrical breakdown (Collins et al. 2001), anion exchange chromatography (Zheng et al. 2003), and size-exclusion chromatography (Zheng and Semke 2007). While each of these approaches has its own attributes and has been implemented for small-scale use in research laboratories, none of them have yet been adopted for industrial-scale separation of SWNTs.

In 2005, an alternative strategy was developed for sorting SWNTs, called density gradient ultracentrifugation (DGU), which combines several desirable attributes for large-scale production, including scalability, compatibility with a diverse range of raw materials, non-covalent and reversible functionalization chemistry, and iterative repeatability (Arnold et al. 2005; Arnold et al. 2006). Historically, DGU has been widely utilized in biochemistry and the pharmaceutical industry for separating subcellular components such as proteins and nucleic acids (Graham 2001). DGU works by exploiting subtle differences in buoyant density; in
particular, the species of interest are loaded into an aqueous solution that possesses a known density gradient. Under the influence of a centripetal force introduced by an ultracentrifuge, the species will sediment toward their respective isopycnic points (i.e., the position where their density matches that of the gradient). With suitable choice of the initial gradient, the species will spatially separate by density, at which point they can be removed by a process known as fractionation.

For DGU to be successful for sorting SWNTs, the buoyant density of a SWNT must be directly related to its physical and electronic structure. Since a SWNT is a hollow cylinder, all of its mass is located on its surface. Consequently, the buoyant density (mass-to-volume ratio) of a SWNT will be proportional to the surface area-to-volume ratio for a cylinder, which is inversely proportional to diameter. If DGU occurred in vacuum, then the SWNT buoyant density would follow this simple inverse relationship with its diameter. However, since DGU occurs in aqueous solution and SWNTs are strongly hydrophobic, amphiphilic surfactants must be used to disperse the SWNTs. Consequently, the actual buoyant density of a SWNT in a DGU experiment will be a function both of the geometry of the SWNT and the thickness and hydration of the amphiphilic surfactant coating. When a surfactant is chosen that uniformly and identically encapsulates all of the SWNTs in solution, then the buoyant density will remain only a function of the SWNT diameter. On the other hand, if a surfactant or combination of surfactants is chosen that inequivalently encapsulate SWNTs as a function of their electronic structure (e.g., metal versus semiconducting), then DGU can be used to sort SWNTs by properties beyond simple geometrical parameters. Ultimately, the combination of clever surfactant chemistry and DGU enables wide tunability for sorting SWNTs.

Figure 11.8 outlines the DGU process for SWNTs produced by the CoMoCAT® growth strategy (Kittiyanan et al. 2000). The CoMoCAT method produces SWNTs by carbon monoxide disproportionation using a proprietary cobalt/molybdenum catalyst. Even though CoMoCAT SWNTs possess a relatively narrow diameter distribution (0.7–1.1 nm), a number of distinct chiralities can be identified from optical absorption spectra. The first step in the DGU process is to disperse the SWNTs in aqueous solution using an amphiphilic surfactant such as sodium cholate. Although ultrasonication leads to a high yield of individually encapsulated SWNTs, some small bundles of SWNTs remain as indicated in Figure 11.8a. Since the bundles possess a higher density than individually encapsulated SWNTs, they simply sediment to the bottom of the density gradient during DGU.

In the second step, the dispersed SWNT aqueous solution is injected into a linear density gradient that is formed from a solution of water and iodixanol. Iodixanol, C35H44I6N6O5, is a water-soluble molecule that possesses a higher density than water. Therefore, by varying the concentration of iodixanol in the aqueous solution, a density gradient can be formed. Figure 11.8b schematically shows the initial density gradient profile and the starting position of SWNTs. By injecting the SWNTs near their isopycnic point in the gradient, the distance that they need to travel, and thus the ultracentrifugation time, are minimized.

Figure 11.8b also shows schematics and corresponding photographs of the ultracentrifuge tube at different points in the DGU process. After 3 hours of DGU at a centripetal acceleration of 288,000 g, the SWNTs have begun to sediment but have not yet reached their equilibrium position in the density gradient. Then, after 6 hours of DGU, layering of the SWNTs by their physical and electronic structure becomes apparent. Finally, after 12 hours of DGU, the SWNTs have clearly layered to the point where fractionation can commence. Evidence for a successful DGU run includes the formation of visibly colored bands, as can be seen in Figure 11.8b. Using one of several fractionation methods, these colored bands can then be removed.
from the centrifuge tube and collected sequentially in optical cuvettes. Optical purity of the resulting SWNT solutions is a direct indicator of monodispersity in the SWNT physical structure and electronic properties.

![Image](image1.png)

Figure 11.8. (a) Cross-sectional schematic of surfactant-encapsulated SWNTs; three specific SWNT chiral vectors and respective diameters are identified. (b) Schematic representation and corresponding photographs of an ultracentrifuge tube at four different points in the DGU process (courtesy of Mark Hersam, Northwestern University).

Figure 11.9 contains a photograph of five distinct, monodisperse SWNT fractions produced from one DGU run.

![Image](image2.png)

Figure 11.9. Following DGU and subsequent fractionation, optically pure SWNT samples are isolated into distinct cuvettes. The color differences between these vials provide clear visual evidence for the success of the DGU process in sorting SWNTs by their physical and electronic structure (courtesy of Mark Hersam, Northwestern University).

The positive attributes of DGU are multifold. Easily controlled parameters such as surfactant chemistry, initial density gradient profile, and ultracentrifugation acceleration and time provide sufficient flexibility to accommodate a broad range of SWNT raw materials. In addition, the use of non-covalent and reversible surfactant chemistry implies that the
encapsulating molecules can be easily removed via dialysis or copious rinsing, thus returning the SWNTs to their native state. The ability to remove the surfactants is particularly important for electronic applications where functionalization chemistry can compromise electrical contacts. Another advantage of DGU is that it can be iteratively repeated. In particular, following the first round of DGU, the best fraction can be removed and placed into a second gradient, at which point the DGU process can be repeated. In this manner, nearly arbitrary levels of purity can be achieved through multiple iterations of DGU. Finally, because DGU has already had widespread use in the pharmaceutical industry, the scalability and economic viability of DGU have already been demonstrated.

The future prospects are promising for SWNTs prepared by DGU. Commercialization of this approach has already been initiated by a start-up company called NanoIntegris (http://www.nanointegris.com/). In addition, DGU-prepared SWNT samples have successfully been exploited in field-effect transistors (Engel et al. 2008) and metallic coatings (Green and Hersam 2008). In research laboratories, the optical purity of DGU-prepared SWNT samples has also been exploited in time-resolved pump-probe laser spectroscopy studies of ultrafast carrier dynamics (Zhu et al. 2007; Crochet et al. 2007). Additional applications that will likely benefit from monodisperse SWNTs include transparent conductors, high-speed integrated circuits, biosensors, and nanocomposite materials.

11.8.2 Quantum Dot Application in Imaging

Contact person: James Murday, University of Southern California

In the early days of photography, film-based cameras were used to capture images (Figure 11.10, left). In more recent years, charge-coupled device (CCD) cameras replaced film with silicon and ushered in digital photography. Then, as cameras became increasingly portable, the CMOS camera was developed (Figure 11.10, center). The image sensor is produced by a CMOS process (hence is also known as a CMOS sensor), and it has emerged as an alternative to the CCD imager sensor. The CMOS active pixel sensor is most commonly used in cell phone cameras, web cameras, and in some digital single-lens reflex cameras; however, silicon-based image sensors only capture on average 25 percent of visible light.

QuantumFilm (Figure 11.10, right) has been developed by InVisage (http://www.invisageinc.com/) under the guidance of Edward H. Sargent at the University of Toronto. The technology is based on semiconductor quantum dots (Tang et al. 2010) and integrates with standard CMOS manufacturing processes. QuantumFilm captures 90–95
percent of the light, enabling better pictures in even the most challenging lighting conditions. It works by capturing an imprint of a light image and then employing the silicon beneath it to read out the QuantumFilm. The first application—projected for 2011 (Greene 2010)—will enable high pixel count and high performance in tiny form factors, breaking the inherent performance–resolution tradeoff of silicon.

Normally, cameras that are sensitive in the infrared and thus can image at night cannot be made using low-cost silicon processing, because, by virtue of its fixed bandgap, silicon is insensitive to wavelengths longer than 1.1 μm. InVisage spin-coats ~5 nm diameter PbS nanocrystals onto a chip, allowing exceptional device performance to be achieved in the shortwave infrared (SWIR) at a fraction of the cost of epitaxy-based, compound semiconductor IR sensors. InVisage is working to improve the sensitivity of the photodetector technology (Konstantatos et al. 2008) and to integrate it with prefabricated silicon read-out integrated circuits to realize SWIR-sensitive focal arrays (Clifford et al. 2008). This technology has the potential to bring tremendous improvements to security systems and consumer electronics applications, because existing infrared imaging technologies are prohibitively expensive for high-volume civilian security markets. Other potential applications of quantum dot light absorption include medical imaging and solar energy conversion.

11.8.3 Nanotechnology-Based Paradigm Shifts in Aerospace

**Contact person: Michael Meador, NASA**

Nanotechnology has the potential to significantly impact future aircraft and space exploration missions. Use of nanostructured materials can enable the development of new aircraft and spacecraft that are significantly lighter than current vehicles and have enhanced performance, increased durability, and improved safety. Nanoelectronics can lead to new devices that are more radiation- and fault-tolerant and have built-in redundancies necessary for use in long-duration space exploration missions. Use of quantum dots and other nanostructures can enable the fabrication of lightweight, flexible, and durable photovoltaic devices to power future exploration missions. Nanoscale electrode materials can lead to new fuel cells and batteries with higher specific power and energy for use in both aircraft and spacecraft. A few examples of where nanotechnology developments are likely to impact future missions are given below.

**Aircraft**

Concerns about the environment will drive the design of new aircraft that have reduced fuel consumption, lower noise, and reduced emissions. Future aircraft designs, such as the Blended Wing Body concept (Figure 11.11) currently being evaluated by the NASA, will be radical departures from the conventional “tube and wing” construction that has been used in aircraft for more than 100 years. Nanotechnology-derived materials will be used heavily in these vehicles. Carbon-nanotube-enhanced fibers (Chae and Kumar 2008) could enable the development of new lightweight composite materials that will reduce the weight of these vehicles by as much as 40%. In addition, these new nanocomposites will have higher electrical and thermal conductivity than conventional composites.
Lightning strike is a major concern in composite aircraft such as the Boeing 787. Typically, a thin copper or aluminum mesh is applied to the surface of these aircraft to improve their conductivity and provide for lightning strike protection. This mesh adds a significant amount of weight to the aircraft and requires additional labor (and expense) to apply. Use of carbon nanotube wire in place of copper wire in the aircraft power distribution system will lead to significant weight reductions. More than 4000 lb. of wire is used in a conventional commercial aircraft such as the Boeing 747. Carbon nanotube wires, such as those currently under development at Nanocomp Technologies, Inc., have higher current-carrying capability than copper at one-seventh the density, are more mechanically robust than copper, and are not susceptible to oxidation.

**Space Exploration**

Nanotechnology has the potential to positively impact space exploration missions. Carbon nanotube–enhanced fibers can enable significant reductions in spacecraft weight. Cryogenic propellant tanks can also benefit from nanotechnology. Cryotanks account for more than 50% of the dry weight (weight without propellant) of a spacecraft. Use of composites in place of metal alloys in these tanks can lead to weight reductions on the order of 30%. However, composites have had mixed success in cryotank applications as a result of the inherent permeability of polymers and composites to low molecular weight gases (e.g., hydrogen), the incompatibility of organic materials with liquid oxygen, and the propensity of composites to microcrack due to thermal cycling during use. Typical approaches to mitigate these issues involve the use of a metal liner on the inner wall of the tank, but this strategy increases weight, complexity, and cost of tank manufacturing, and the liner can delaminate from the tank wall due to the mismatch in coefficients of thermal expansion between the metal liner and composite tank substrate. Recent work has shown that the addition of organically modified clays to toughened epoxy resins leads to a 60% reduction in hydrogen permeability, enhanced compatibility with liquid oxygen, and improved resistance to microcracking (Miller and Meador 2007). Use of these nanocomposites could enable the fabrication of linerless nanocomposite cryotanks.

Increasing the capability of future robotic exploration missions will require instrumentation that is lighter in weight, more compact, and lower power than currently available. Carbon
nanotube emitters have been utilized to develop compact, low-power mass spectrometers for use in exploration missions (Getty et al. 2007).

11.8.4 Developments in Nanofluidics

Contact person: John Rogers, University of Illinois at Urbana-Champaign

The field of nanofluidics, like other areas of nanoscience, derives its driving force from four principal features: (a) accessing new physical phenomena on the nanoscale; (b) enormous increases in the importance of surfaces; (c) the elevation of diffusion to a practical method of mass transport; and (d) the ability to build structures that are commensurate in size with molecular assemblies and even single molecules. Important developments in the past decade have exploited all of these.

New Phenomena

Concentration polarization. An interesting phenomenon that has been reported when ion-selective nanofluidic channels are connected to microfluidic channels is enrichment/depletion of ions at micro/nanofluidic junctions. Referred to as concentration polarization, the phenomenon has been exploited for applications such as water desalination.

Fluidic diodes/active elements. By controlling the spatial distribution of surface charge density on the interior of a nanopore and using a gate electrode, nanopores have been shown to function as diodes, bipolar, and metal oxide semiconductor (MOS)-like devices, opening up opportunities for nanofluidics-based logic circuitry.

3D fluidic switches. Nanocapillary array membranes, consisting of arrays of high-aspect-ratio cylindrical nanopores connecting the opposing surfaces of micrometer thick membranes, can function as electrically addressable fluidic switches supporting 3D integration of microfluidics with no moving parts (Figure 11.12).

Electroosmotic flow (EOF) of the 2nd kind/fluidic vortices/convection. When nanopores are interfaced with microchannels, the net space charge at the micro/nanofluidic junction has been shown to give rise to nonlinear electrokinetic transport due to induced pressure,
induced electroosmotic flow of the second kind, and complex flow circulations. These mechanisms can be exploited for numerous applications, including rapid mixing of species, which can enable the analog of stopped-flow reactors on the femtoliter-picoliter volume scale.

Rotation-translation coupling. When the rotational motion of a molecule, e.g., of water, is severely restricted, such as in single-file water in a nanopore, the frustrated rotational motions have been shown to be coupled to translational motions, leading to a preference for water molecules to move in the direction of the dipole. This phenomenon has been exploited for enhanced molecular transport.

Surfaces

Surface conduction. A much greater understanding of the role of surface conduction in the overall current conduction process in nanopores, especially at low ionic strength, has been obtained through various quantitative experiments.

Structured water. Water confined in nanopores of a critical size under ambient conditions has been shown to undergo a transition into a state having ice-like mobility with an amount of hydrogen bonding similar to that in liquid water. Thus, nanopores can provide an environment in which the dynamics of phase changes may be studied directly.

Diffusive Transport

Reactive mixing. Entrained flow microfluidic geometry has been used to illustrate the possibilities for reactive mixing using only diffusion for mass transport at sufficiently small distances.

Nanofluidic reactors. Nanofluidic channels have been exploited to confine species for enhanced reactivity. Homogeneous confined DNA has been utilized for restriction enzyme mapping at high efficiency, and heterogeneous molecular recognition (anti-insulin) and enzymatic (oxidoreductases) species exhibit enhanced reactivity in nanofluidic channels.

Commensurate Molecular Structures

Entropic DNA separations. The microfluidic-nanofluidic interface constitutes an entropic barrier that has been elegantly exploited for DNA separations. Confinement-induced entropic forces have been realized in a number of different nanofluidic geometries.

Resistive pulse sensing. The generic reduction in current in a nanopore can be exploited to observe the passage of chemical species that either occupy a significant fraction of the pore volume or alter the pore conductivity in other ways.

Stochastic sensing. The resistive pulse idea has been coupled to the presence of single biological ion channels with stochastic blockage elements that respond to the binding/unbinding of analytes. Monitoring the on/off statistics can then be used to assay for the concentration of analytes.

Nanopore sequencing. A promising methodology for DNA sequencing is to electrophoretically transport DNA through nanopores. Recent results have shown that nanopores have been used for sequencing DNA, identify defective DNA structures, and separate single-stranded DNA from double-stranded DNA structures.

Single-molecule studies/zero-mode-waveguides. Ultrasmall-volume (zL) pores in thin opaque metal films can be irradiated in order to produce non-propagating (cut-off) optical modes that can be used to interrogate chemistry within the pores. The ultrasmall volumes access single-molecule dynamics for macromolecules (e.g., enzymes) that have µM to mM dissociation constant values.
11. Applications: High-Performance Materials and Emerging Areas

Technical Advances

Concentration polarization desalting. By placing a nanofluidic interface in one of the arms of a Y-shaped microfluidic element, concentration polarization has been exploited to divide a stream of sea water into desalted and concentrated-salted streams. This approach can be effective for small-scale to medium-scale desalinization systems with battery powered operation.

Multidimensional chemical analysis. Using nanofluidic elements to control flow in multilevel microfluidic architectures, multidimensional chemical analysis (e.g., two-dimensional separations coupling electrophoresis and micellar electrokinetic chromatography) has been accomplished.

11.8.5 Polymer Nanocomposites

Contact person: Richard Siegel, Rensselaer Polytechnic Institute

During the past decade, significant advances have been made in both creating and understanding a wide range of polymer nanocomposites with greatly improved properties (Winey and Vaia 2007; Vaia and Maguire 2007). These include a variety of synthetic and natural polymer matrices combined with a host of nanoscale building blocks (e.g., nanoparticles, nanotubes, or nanolayers). Such nanostructured fillers, with their extremely high specific surface areas, are able to very strongly influence, and even dominate, the bulk properties of these nanocomposites by means of their interaction with the polymer chains of the matrix. Learning to specify and control these interactions has led over the past ten years to the capability to now create polymer nanocomposites with individual properties, and even multifunctional sets of properties, that are desirable for many commercial applications.

For example, as shown in Figure 11.13, it has recently been possible to tailor the surfaces of SiO₂ nanoparticles by means of reversible addition-fragmentation chain transfer (RAFT) polymerization and click chemistry (Li and Benicewicz 2008), attaching an inner functional polymer layer and an outer matrix compatible layer to the nanoparticles, to greatly improve the properties of epoxy insulation material (J. Gao, S. Zhao, L.S. Schadler, and H. Hillborg, private communications).

![Figure 11.13](image)

Figure 11.13. Improved epoxy nanocomposites for electrical insulation have increased strain-to-failure, fatigue resistance, electrical breakdown strength (30%), thermal conductivity, and endurance strength (x10), and lower constant of thermal expansion (CTE).

It has also become possible to theoretically model (Jayaraman and Schweizer 2008a, 2008b) the organization of these nanoparticle-polymer systems in terms of the number density and
length of such grafted, brush-like polymers and then to experimentally demonstrate the predictive nature of these models (Acora et al. 2009). Such capabilities for structure and property control, as they are developed and expanded, will enable broad future applications of polymer nanocomposites.

11.9 INTERNATIONAL PERSPECTIVES FROM SITE VISITS ABROAD

11.9.1 United States-European Union Workshop (Hamburg, Germany)

Panel members/discussants

H. Peter Degischer (co-chair), University of Technology, Wien (Vienna), Austria
Mark Hersam (co-chair), Northwestern University, United States
Costas Charitidis, National Technical University of Athens, Greece
Michael Moseler, Fraunhofer Institute for Mechanics of Materials (IWM), Germany
Inge Genné, VITO NV (Flemish Institute for Technological Research), Belgium

The field encompassed by the term “nanomaterials” has changed dramatically over the past ten years. The vision from 2000 to produce cost-efficient structural materials for automotive, consumer appliance, tooling, and container industries has been transferred in 2010 to advanced high-tech niche products. The opportunities for significant improvements in structural materials with nanoscopic reinforcements of extraordinary properties and the exploitation of nanoscale grain size in inorganic materials are seen more specifically to have the potential for multifunctionality. Enabling impacts were expected of high surface and interface areas at the nanoscale, novel chemical reactivity and/or physical interactions, and biochemical properties exploitable in medical implants. Actually, engineered materials are required that offer property profiles that cannot be fulfilled by existing materials, e.g., the combination of high strength/stiffness and toughness at elevated temperatures, wear and corrosion resistance provided by lightweight materials, etc. Such challenging mechanical performance is mostly required in combination with physical properties such as high thermal conductivity and stability, and/or optical transparency.

Extensive research has been dedicated to processing of nanocomposites and nano-grained materials. Laboratory-scale processing of nanoparticles, nanotubes, and nanowires is available. Dispersion-strengthened metals and polymers with sub-micrometer-scale fillers existed already but have been further improved in an incremental manner. The distribution of the nanoscopic reinforcement and the consolidation with polymer, metal, or ceramic matrices, combined with the design of interfaces between the constituents to transfer properties, remain fertile areas of research. Hybrid nanocomposites of different materials at various length scales are considered for the design of unique property profiles. Interconnected reinforcements and interpenetrating nanocomposites provide significant thermal stability.

Sub-µm aluminum grains with natural nanoscopic oxide skin compacted to a network of flexible ceramic closed cells filled with ductile aluminum exhibit extraordinary elevated temperature strength and toughness. Inorganic particles in biopolymers have been developed for nanocontainers for targeted drug delivery. Methods to render self-assembling molecules creating periodic polymer structures have been developed. Nanoporous materials have been produced for physico-chemical applications. Embedding of conducting nanoparticles into polymer matrices has been achieved to provide transparent conducting foils of considerable strength. Sub-µm coatings of all material categories are being developed by embedding nanoscale constituents to improve physical, chemical, and
mechanical surface performance. Nano-grained metals produced by various processing methods of severe plastic deformation achieve macroscopic components surpassing the exploitation of the Hall-Petch relation for strength by maintaining the disordered crystalline state up to appreciable temperatures.

In addition, significant advancement has occurred in the field of microstructural characterization of size, morphology, and spatial distribution of constituents of heterogeneous materials, including three-dimensional methods at the sub-µm scale (e.g., focused ion beam sectioning, 3D high-resolution TEM, and third-generation focused synchrotron radiation sources). The reliable determination of properties at the nanoscale with high accuracy deserves further improvement and standardization. The incorporation of microsensors made of functional nanomaterials into extremely loaded structural components could be used for health monitoring.

The number of publications on the afore-mentioned topics is still increasing. Solutions are sought for uniform dispersion of significant volume fractions, increased interface bonding, and reduction of porosities. It is evident that the interfaces in nanocomposites play a dominant role in the achievable property profiles. The unsatisfactory distribution and the limited transferability of the attractive properties of nanotubes to the matrix represent the main limitation for the exploitation of such nanoscopic reinforcements.

Enabling features of nanocomposites are not yet found, and conventional composites with matrices of polymers, metals, or ceramics can be identified that outperform the mechanical properties of nanocomposites. More emphasis is required to predict the potential of achieving previously unrealizable property profiles. Based on the acquired knowhow, modeling and simulation can be applied to assess the multitude of material combinations from producible architectures of nanoconstituents.

Processing research should aim to give realistic visions of the variability of technologies to achieve structures controlling size-dependent interactions of the nanocomposite constituents by interface design strategies. Assemblies with tunable performance are demanded. Estimations of the required efforts to produce nanomaterials are required to assess the competitiveness of “nano” solutions. Process developments are to be combined with quality control methods applicable to successful up-scaling of the technology. Opportunities are envisaged in self-assembling methods, in situ methods to create hierarchical structures, and in building-block architectures.

Methods for structural characterization are available, but standardized property definitions and methods of determination would be required in each production phase. Therefore, research is required to correlate multiscale structural features with properties. Advancements should be pursued in the combination of properties for structural applications that are not achieved by existing materials.

Scientific knowledge-based calls should be sent out asking for interdisciplinary research proposals combining theory, modeling, simulation, processing, characterization, and experimental verification of a hypothesis submitted to critical evaluations. Boards consisting of scientists, industrial researchers, market experts, and funding agencies should work on the analysis of the strengths, weaknesses, and opportunities of a proposed solution as well as on the market tendencies (SWOT analysis) of the project objectives. Funding conditions should attract the best researchers in the field and allow them to work efficiently with as little bureaucratic burden as possible. Critical scientific reviewing of publications by experts needs to be enhanced to avoid diversion down unproductive tracks.
Business models are required to assess the market tendencies as well as the benefits expectable by applying nanomaterials. The up-scaling from successful laboratory samples to industrially reproducible products requires a promising profitable prognosis and reasonable access to venture [and other] capital resources, particularly for the development of small-scale niche products. Environmental, health, and safety (EHS) concerns must be considered in the context of life-cycle assessments for promising products. Regulations shall be globally agreed upon to replace the existing uncertainty regarding health and safety concerns.

Over the next ten years, researchers will focus on a range of issues to improve the performance, multifunctionality, integration, and sustainability of nanostructured and hybrid material systems for structural applications. Functional nanomaterials also require certain mechanical property profiles, where research on structural materials can contribute to the development of reliable products. In particular, the field requires technologies for scaling-up high-quality nanomaterial production, designed to achieve independent tunability of previously coupled properties. Examples of desirable properties of new nanostructured materials include high stiffness and strength combined with toughness and low weight, complemented with elevated temperature and fatigue resistance, possibly combined with conductivity.

11.9.2 United States-Japan-Korea-Taiwan Workshop (Tsukuba, Japan)

Panel members/discussants

Sang-Hee Suh (co-chair), Korea Institute of Science & Technology
Mark Hersam (co-chair), Northwestern University, United States
Takuzo Aida, University of Tokyo, Japan
Hideo Hosono, Tokyo Institute of Technology, Japan
Soo Ho Kim, Korea Institute of Materials Science
Li-Chyong Chen, National Taiwan University
Hidenori Takagi, University of Tokyo, Japan

In the last ten years, major advances with broad technological impact have been achieved in almost all categories of materials, including the following:

- **Polymer materials**, e.g., controlled radical polymerization, block copolymers, polymer brushes, dendrimers, supramolecular one-dimensional polymers, and metal-oxide frameworks
- **Structural materials**, e.g., high-strength, high-functionality, lightweight, automotive materials (achieved but not economically feasible); wear-resistant materials (3–4x improvement); and corrosion-resistant coatings for cutting tools and semiconductor processing equipment
- **Electronic materials**, e.g., electronic, optoelectronic, spintronic, energy, phase change materials, correlated electrons for thermoelectrics; nanostructured silicon for light-harvesting (anti-reflection improved by 10x, also broadband); GaN nanomaterials with 1000x improvement in photoconductivity; transparent amorphous oxide semiconductors for high-mobility electronics (LCD/OLED back plane)
- **Carbon-fiber-based materials**, e.g., aircraft/aerospace (a $1 billion industry); carbon-fiber-based nanomaterials used in the Chevy Corvette (high-performance, high-cost); carbon-based nanomaterials (e.g., graphene), which present promise for transparent conductors
• **Catalysts**, e.g., Pt nanoparticle/CNT/graphene nanocomposite for fuel cells requires 1/10 Pt level with better performance; self-cleaning materials represent a $1B market (mainly titanium oxide, which is also present in cosmetics, textiles, and paints)

A wide range of goals have been identified for the next 5–10 years in the area of high-performance materials:

• Low-cost manufacturing processes are required to bring high-performance materials to the marketplace.

• New functionality needs to be realized from materials based on earth-abundant elements.

• Renewable resources should be used as raw materials (e.g., biofibers, plants, wood, etc.).

• Specific focus should be devoted to green nanotechnology (e.g., new catalysts, energy conversion/transport/storage (entropic materials), and water-based plastics [aquamaterials]).

• Computational design will become increasingly important to save time and money in developing nanomaterials.

• Self-healing materials, biomimetic materials, and bionanomaterials have been demonstrated but need to be transitioned to real applications (e.g., paints, implants, regenerative medicine).

In addition to technological drivers, a range of fundamental issues remain, including the needs for:

• Improved understanding and control of surfaces/interfaces (especially organic/inorganic interfaces)

• Development of computational approaches for electron correlation

• Realization of properties/materials by design using combined computational/combinatorial approaches

These goals require improvements in the scientific and technological infrastructure and innovative R&D investment and implementation strategies. From the infrastructure perspective, a variety of specific items are needed, including:

• Characterization/observation methods for interfaces/surfaces in the operating state (e.g., next-generation neutron and synchrotron sources)

• Nanofabrication user facilities (including ongoing support)

• Human resource training

R&D investment and implementation recommendations include:

• Long-term funding (5 years guaranteed + 5 year renewal)

• International funding

• Continuation of fundamental research, funded by government

• Government-funded R&D focused on social issues (energy, environment, water, food, health)

• Cross-cutting, multidisciplinary funding opportunities

• Applications/commercialization funded with contributions from industry and private investors
11.9.3 United States-Australia-China-India-Saudi Arabia-Singapore Workshop (Singapore)

Panel members/discussants

Jan Ma (co-chair), Nanyang Technological University, Singapore
Mark Hersam (co-chair), Northwestern University, United States
Rose Amal, University of New South Wales, Australia
Julian Gale, Curtin University of Technology, Australia
Zhongfan Liu, Peking University, China
Koon Gee Neoh, National University of Singapore
Yee Yan Tay, Nanyang Technological University, Singapore

Over the past decade, the idea of manipulating materials at the nanoscale has been intriguing researchers globally. In 2000, researchers were focused on novel methodologies to control the size of different materials while attempting to explore many unique and distinctive size-dependent properties. The intensive study of nanoparticles, nanowires, and nanotubes is a good example. In particular, this early work attempted to develop an understanding of the chemical and physical properties of individual nanoconstituents. The nanomaterials were also effectively incorporated into coatings and bulk nanocomposites with clearly identifiable applications making use of the spatial anisotropy, morphology, and the relative proximity of nanoconstituents with respect to each other and the host matrix. Specific examples include nano-bio interfacing in the field of biotechnology, where nanomaterials are interfaced with a biological component for biosensing and drug delivery applications. The photocatalytic feature of materials at the nanoscale dimension is useful for self-cleaning surface applications, which has been successfully commercialized in the paint industry. In addition, the metal-organic framework emerged for many state-of-the-art applications such as hydrogen storage.

Over the next 10 years, we anticipate new directions for various aspects of nanomaterials, built on these early achievements. For example, the study of two-dimensional and three-dimensional open structure architectures at the nanometer length scale will attract significant attention. A specific aspect of this work in the next ten years will be the development of nanoporous membranes with ballistic selective water transport, which could impact technologies such as water purification. While various unique nanostructures have been emphasized, it is also necessary to address the physical properties of nanocomposites, where interfaces are expected to play a dominant role. In particular, the optimization of internal interfaces will likely allow fluxes such as charge, energy, spin, etc., to be controlled independently. The introduction of computational guidance on realistic nanomaterials will also provide many useful predictive properties that are essential for the design of nanoscale devices.

The realization of these goals will require essential supporting aspects. For example, it is necessary to develop advanced characterization techniques that are capable of in situ and in vivo studies with concurrent time and spatial resolution. This type of instrumentation will facilitate the development of fundamental concepts, thus inviting new views of complex system at short time and length scales. It is also important to establish affordable shared facilities with stable funding for recurring costs. While it has been highlighted previously that methodologies for scaling-up should be emphasized, it is also critical that the requisite infrastructure be in place to facilitate cost reduction in early-stage manufacturing. Multidisciplinary research will ultimately drive future innovation; thus, funding agencies need to provide ample proposal opportunities along these lines.
11.10 REFERENCES


