Taylor & Francis
Taylor & Francis Group

Journal of the Air & Waste Management Association

ISSN: 1096-2247 (Print) 2162-2906 (Online) Journal homepage: http://www.tandfonline.com/loi/uawm20

Nanoparticles and the Environment

Pratim Biswas & Chang-Yu Wu

To cite this article: Pratim Biswas & Chang-Yu Wu (2005) Nanoparticles and the Environment, Journal of the Air & Waste Management Association, 55:6, 708-746, DOI: 10.1080/10473289.2005.10464656

To link to this article: http://dx.doi.org/10.1080/10473289.2005.10464656

Published online: 01 Mar 2012.

Submit your article to this journal

Article views: 2630

View related articles

Citing articles: 214 View citing articles

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=uawm20

Download by: [University of North Texas] **Date:** 21 January 2017, At: 01:33

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **55**:708–746
Copyright 2005 Air & Waste Management Association

Pratim Biswas

Chang-Yu Wu

Nanoparticles and the Environment

Pratim Biswas
Environmental Engineering Science Program, Department of Chemical Engineering, Washington University, St. Louis, MO

Chang-Yu Wu
Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL

ABSTRACT

Nanoparticles are a class of materials with properties distinctively different from their bulk and molecular counterparts. A critical review of the very broad topic of environmental nanoparticles is presented. Because of the vast nature of the topic, the review is focused primarily on gas-borne nanoparticles. The "life history of nanoparticles" is presented, tracking it from its formation to its potential use and eventual fate in the environment. Nanoparticle sources, anthropogenic emissions from industrial and occupational settings, and conversion and formation in the atmosphere are discussed. The ability to characterize and capture these nanoparticles (as would be necessary in a nanoparticle production system), as well as their control (of emissions from an industrial source) is discussed. A description on the use of nanoparticles in environmental technologies and the potential impact on the energy sector is provided. The potential effects on human health and the environment, both adverse and beneficial, are important aspects that need to be considered. As will be evident, the study of "environmental nanoparticles" is a new and fast-growing field. Much work remains to be done before we can fully harness the advantages of nanoparticles and ensure that there are no potential adverse consequences. A set of recommendations for additional work in each area is provided.

IMPLICATIONS

The mushrooming field of nanotechnology is finding applicability in the field of environmental protection. However, there is also a growing concern that nanoparticles could be potentially detrimental to the environment and to human health. To avoid mistakes made by the biotechnology food industry and the past practices of the chemical industry, research in environmental and health impacts needs to go hand in hand. Proper design of products and materials from nanotechnologies is needed to ensure that they have a minimal environmental footprint.

INTRODUCTION

Nanotechnology has been defined as research and development at the atomic, molecular or macromolecular scales.[1] Nanoparticles are considered to be the building blocks for nanotechnology, and are referred to particles with at least one dimension <100 nm. Particles in these size ranges have been used by several industries and humankind for thousands of years; however, there has been a recent resurgence because of the ability to synthesize and manipulate such materials. Nanoscale materials find use in a variety of different areas, such as electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic, and materials applications. Because of the potential of this technology, there has been a worldwide increase in investment in nanotechnology research and development.[2] The investment for nanotechnology research by the federal government in the United States will be approximately $1 billion, in Western Europe about $600 million, in Japan $800 million, in Korea $200 million, and other countries totaling about $800 million in 2005. This is a 7-fold increase in nanotechnology research and funding since 1999. Major emphasis is also being put on ensuring broader societal improvements and sustainable development.[3]

Nanotechnology has great potential in improving air, water, and soil quality in the environment. It can improve detection and sensing of pollutants and help in the development of new technologies for remediation. Understanding the formation and growth dynamic processes of nanoparticles (e.g., in the combustion system) allows the development of efficient methodologies for minimizing the formation of pollutants in the first place and for reducing their emissions. Although nanotechnology has the potential to improve environmental quality, there are

concerns that it can also lead to a new class of environmental hazards.[4,5] Such concerns are associated with practically all new technologies, and they need to be addressed upfront. With proper attention, careful research, and incorporation of findings at an early stage, the safety of nanotechnology can be ensured.[1]

Although the above concerns are relevant, appropriate, and justified, there are many other reports in the popular literature that probably should be classified in the "fiction" category. The book *Prey*[6] is an example and explains how a failed experiment resulted in emissions of nanoparticles (a major aspect of this review) that self-replicate to form robots that become deadly and cannot be destroyed, and human beings become the "prey." Although one cannot doubt that such books are very effective at bringing awareness of the subject matter to the lay reader, it is unfortunate that the statements are misconstrued (even by the Prince of Wales). For example, certain groups have called for a moratorium on nanotechnology research.[7] Facing such incorrect interpretation and understanding by the public, scientists are the ones who have the responsibility to raise the questions, design studies to answer them, and effectively communicate the results to both the public and the policy makers.

The subject of nanoparticles and the environment is very broad, and justice cannot be done in a simple review as presented herewith. With increased funding, there has been a mushrooming of research and development projects and with it a great increase in the number of publications. Coverage of all articles cannot be provided here. Therefore, a brief description of the many scientific and technological challenges and opportunities is provided with an illustration of the need for multidisciplinary efforts to further our understanding.

Figure 1 provides an overview of environmental nanoparticles, as will be discussed in this review. First, there are several sources that result in nanoparticle formation: stationary industrial sources,[8] such as coal fired combustion systems and incinerators; mobile sources,[9] such as automobiles and diesel powered vehicles; and occupational environments,[10] such as those where welding processes are prevalent and those where engineered nanoparticles are deliberately synthesized. There are several natural sources and nanoparticles of biological origin[11] that also need significant attention. For example, pollen fragments are potential causes of allergies, and viral nanoparticles can be used as vaccines or can play a significant role in the spread of disease. Once nanoparticles are emitted to the atmosphere,

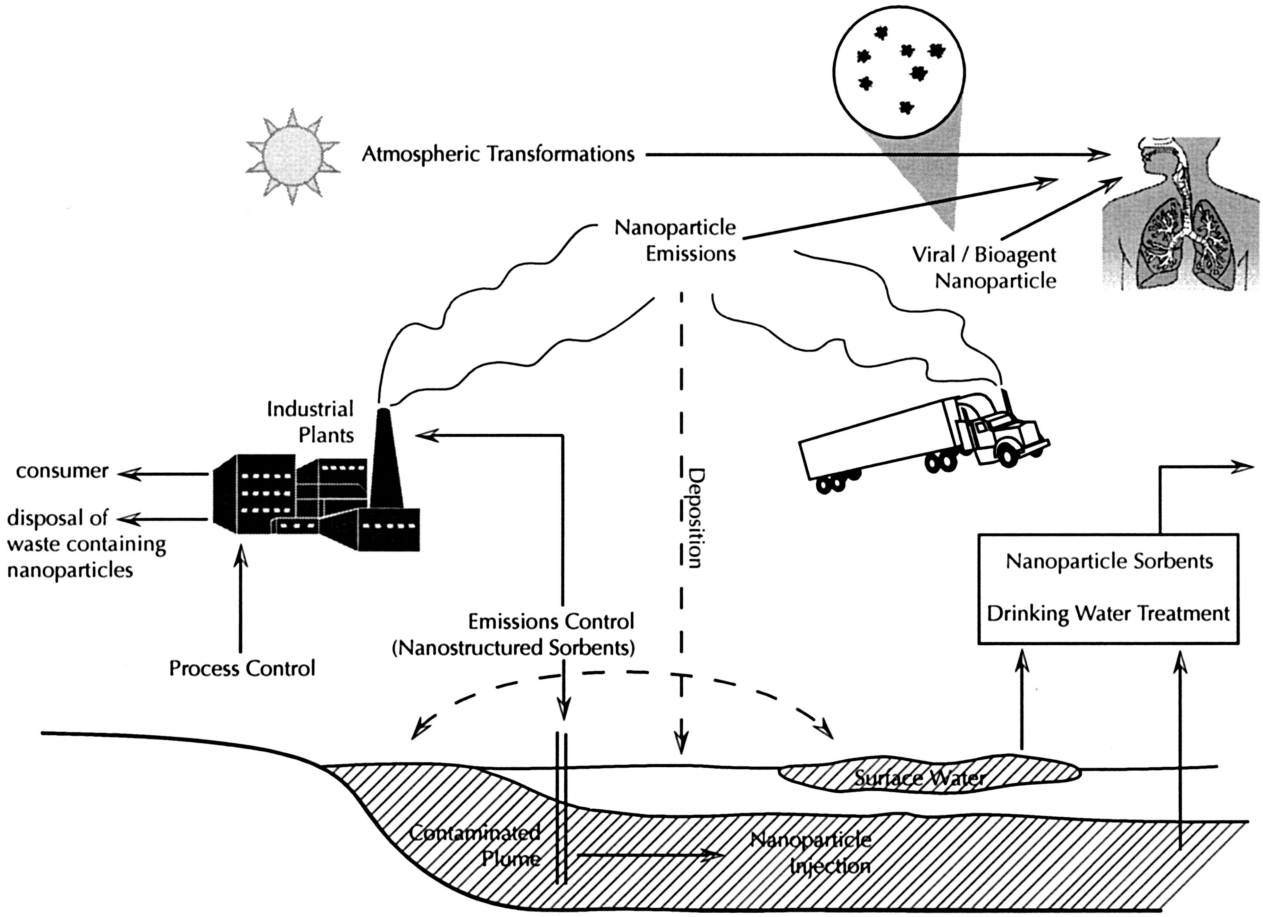

Figure 1. Schematic diagram illustrating nanoparticles in the environment.

they are readily transformed, and this may result in alterations in size and composition from their point of origin. Furthermore, nanoparticles are also formed in the atmosphere by nucleation events[12] arising out of photochemical processes. These nanoparticles are important to cloud formation, but they can also be transported in the atmosphere over large distances and can eventually result in human exposure via inhalation routes.[13] Nanoparticles can also be deposited onto the soil and water bodies and result in secondary contamination or other environmental effects.

Also illustrated in Figure 1 are several environmental nanotechnologies. Nanoparticle science and technology can improve the processes to reduce formation and emissions of pollutants. Nanostructured sorbents can capture noxious gases in an exhaust plume.[14] Nanomaterials can be used as catalysts to reduce mobile source emissions.[15] Nanoparticles can be injected into subsurface groundwater to remediate contaminated plumes.[16] Being of a size and with certain surface characteristics, nanoparticles can travel to contaminated zones and can be carried to great distances with the groundwater plumes.[17] Adsorbents made of nanoparticles can be used to purify drinking water, for example, in the removal of arsenic.[18,19]

Figure 2 summarizes the nanoparticle system. The objective of this review is to track the "life history of nanoparticles" from their formation to their use and fate and transport in the environment. Human activities and industrial and environmental processes are viewed as nanoparticle generation systems. In some systems, processes result in the formation of unwanted nanoparticle emissions. In others, the processes create useful and functional nanoparticles, including nanomedicine. In many instances, the source or the process is a high-temperature operation. In both cases, there is a control/collection and measurement/characterization device. If the nanoparticles are unwanted byproducts, efforts are made to remove them from the effluent before disposal. If nanoparticles are deliberately synthesized, the objective is the same: to collect them efficiently as a useful product. In many instances, unwanted nanoparticle emissions can be converted to a useful byproduct. Other features of the system are the resultant exposure if uncaptured followed by potential environmental or health impacts. The development and advancement of environmental technology will improve environmental quality by material substitution, better sensing, emission control, and waste treatment, although by itself it can be a new source of nanoparticles to the environment. Because many pollutants are formed from fossil fuel combustion for energy production, alternative

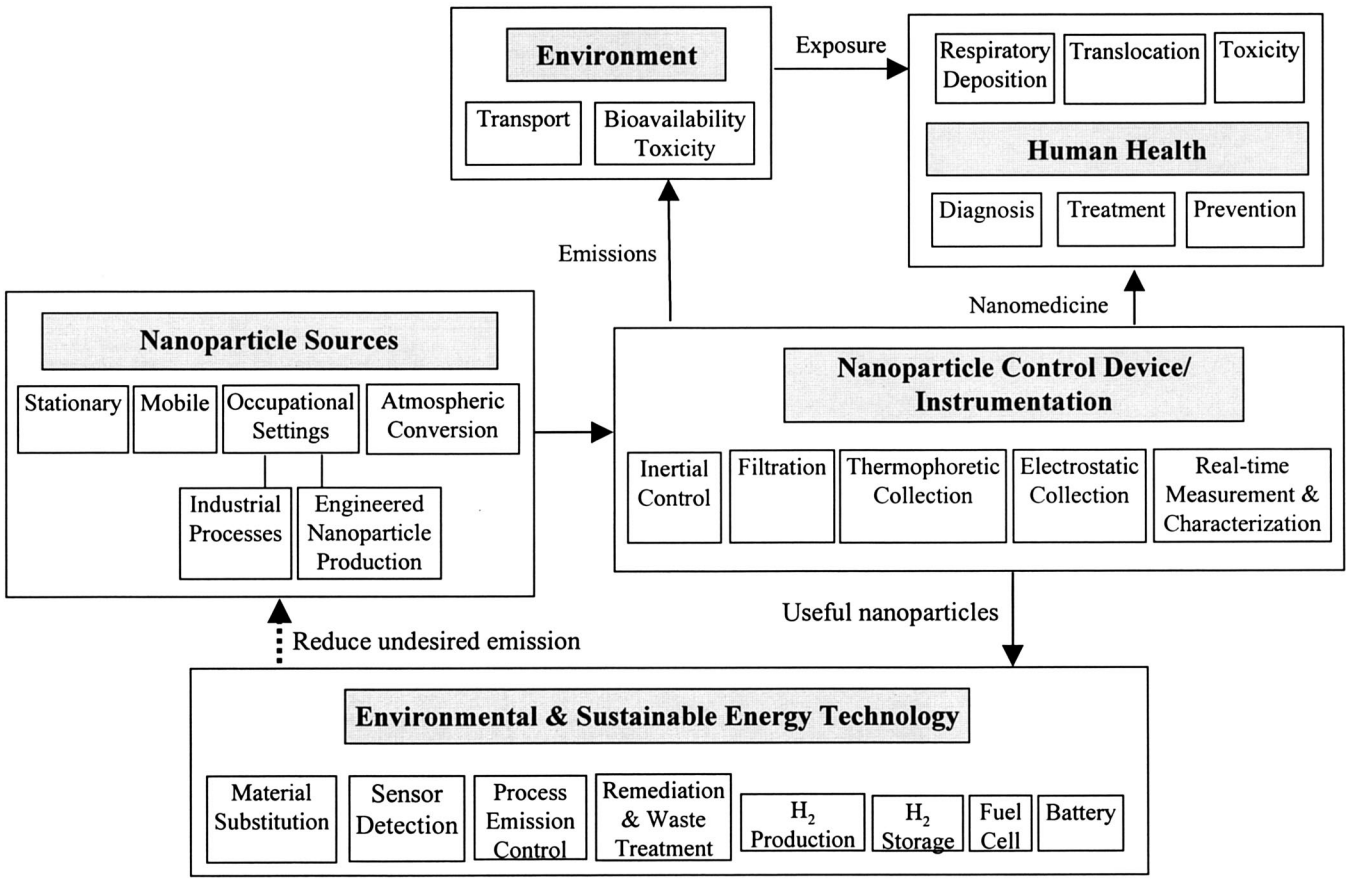

Figure 2. Nanoparticle system reviewed in this paper.

energy generation enabled by nanoparticle science and technology has the potential to reduce the emissions. Care, however, should be exercised for different types of environmental and health consequences resulting from alternative energy sources. A feedback loop as in a "life cycle analysis"[20] should provide guidance to the front end of the system.

Whereas the use of the term nanoparticles is currently in vogue, the atmospheric sciences research community has used terms such as ultrafine particles. Figure 3 outlines the terminology used, and in this review the term nanoparticle has been used interchangeably with ultrafine particles. It should be noted that as the size of the particle decreases, the fraction of molecules that are present in the outer layer close to the surface with respect to the total number in the particle increases. This characteristic is an important aspect that results in properties of nanoparticles being different from their bulk counterparts. Furthermore, when the particle size is less than approximately 10 nm, quantum effects begin to play an important role, resulting in alteration of the properties of the particle.

There have been excellent reviews of some of these aspects.[21,22] The field of nanoparticle aerosol science and technology has received significant attention in recent years, and detailed review documents have been prepared that outline research needs.[23] This review elaborates those with a more holistic and critical treatment of the different features of gas-borne nanoparticles and their applications related to the protection of the environment and human health. The review starts with a discussion of nanoparticle sources–industrial and occupational–and conversion and formation in the atmosphere. The ability to capture these nanoparticles (as would be necessary in a nanoparticle synthesis system) and their control (e.g., of emissions from an industrial source) is discussed next. This is followed by a brief review of nanoparticle instrumentation and characterization methods. The use of nanoparticles in a few environmental technologies and the potential impact on the energy sector is addressed. The environmental impact and potential health effects are summarized. Each section provides a review of selected past studies; identification of research gaps; and a summary table of key references, findings, and recommendations. As will be evident, much work remains to be done before we can fully harness the advantages of nanoparticles and ensure that there are no potential adverse consequences.

NANOPARTICLE SOURCES

The sources of nanoparticles are numerous. A summary of some of the important nanoparticle source categories is provided in Table 1. In addition, the key features are outlined along with a set of recommendations for additional research that needs to be done.

Nanoparticles can be directly emitted from combustion processes that include both stationary[8] and mobile[9] sources. They can be formed in the atmosphere through reaction and/or nucleation of vapor precursors or by radioactive decay.[24,25] In industrial settings, nanoparticles are also commonly produced. With the recent advancement of nanotechnology, the presence and potential emissions of engineered nanoparticles has become an emerging issue.

Combustion processes play an important role in the economy, but they are also responsible for many emissions. Hildemann et al.[26] characterized aerosol size distributions of emissions from industrial boilers, fireplaces, automobiles, diesel trucks, and meat-cooking operations. The predominant peak in the mass distribution was observed to be at or below ~0.2 μm (200 nm). On examining the number distribution, many of these sources have their predominant peak much below 100 nm. Many of these sources also have distinctive bimodal distributions, with a nuclei mode peak between 20 and 60 nm (even in the mass distributions). This indicates clearly the occurrence and importance of nucleation.

An interesting phenomenon observed for the different types of sources (stationary,

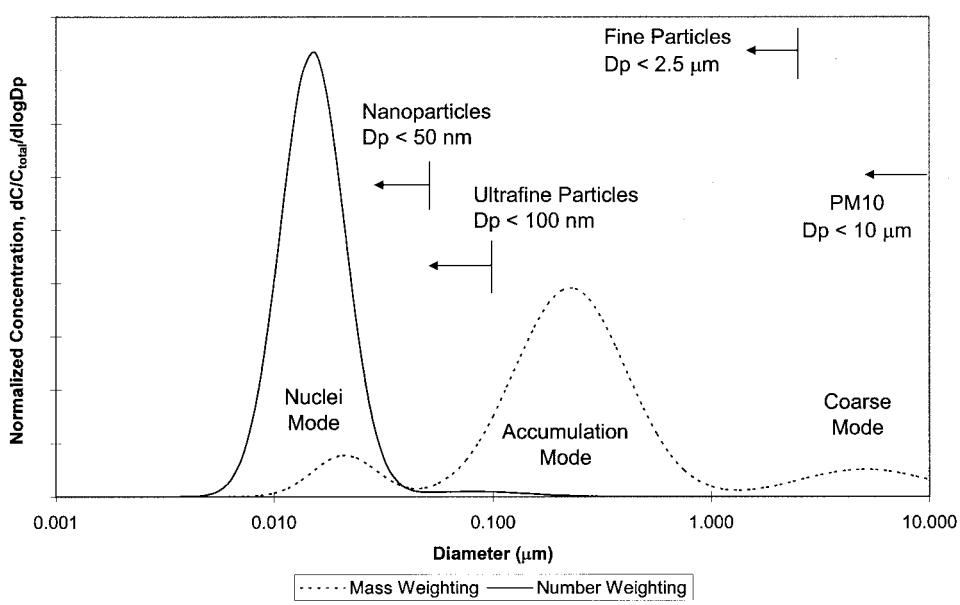

Figure 3. Typical engine exhaust size distribution: both in mass and in number. (Reprinted from Kittelson[9] with permission from Elsevier.)

Table 1. Sources of nanoparticles.

Category	Key References	Summary of Findings	Recommendations
Stationary emissions (coal/oil/gas boilers, incinerators, smelters, cooking, cigarette, residential combustors)	Hildemann et al.[26]; Ebelt et al.[30]; Lipsky et al.[31]; Maguhn et al.[27]; Chang et al.[8]; Utsunomiya et al.[37]; Tolocka et al.[34]; Wallace et al.[40]	• Ultrafine particles formed in combustion systems vary by fuel types. They grow out of ultrafine by coagulation and condensation. • Ultrafine particle emission may increase after effective removal of coarse and fine particles in system, a process similar to that in the ambient. • Important indoor ultrafine sources also from combustion.	• Develop control techniques that can reduce mass concentration of larger particles and prevent formation of high number of ultrafine particles. • Develop pertinent sampling methods. • Characterize metals in ultrafine. • Correlate outdoor and indoor ultrafine particles. Characterize indoor sources.
Mobile emissions (diesel/gasoline/LPG/CNG vehicles, metals in catalytic converters/fuel cells)	Hildemann et al.[26]; Rickeard et al.[48]; Kittelson[9]; Burtscher et al.[46]; Ristovski et al.[51]; Artelt et al.[57]; Tobias et al.[44]; Harris and Maricq[50]; Shi et al.[49]; Wehner et al.[53]; Kim et al.[55]; Zhu et al.[54]; Sakurai et al.[45]; McDonald et al.[47]; Luther[22]; Mathis et al.[59]; Zhang and Wexler[32]	• Nuclei mode nanoparticles dominate the number concentration. Sulfate and hydrocarbons are major composition. • Nucleation also occurs after emission. • Noble metal ultrafine particles may be potentially emitted.	• Develop control techniques that can reduce mass concentration of larger particles and prevent formation of high number of ultrafine particles. • Examine emission of noble metals in catalytic converts. • Assess the potential of nanocatalysts emission for the future use of fuel cells.
Atmospheric conversion (urban, rural, remote area)	Clarke[78]; Koutsenogii and Jaenicke[83]; McGovern et al.[84]; Covert et al.[70,73]; Wiedensohler et al.[75,77]; Weber et al.[74,85]; Eisele and McMurry[86]; Mäkela et al.[76]; Seinfeld and Pandis[62]; Hughes et al.[80]; Clarke et al.[79]; Birmili and Wiedensohler[69]; Yakovleva et al.[94]; McMurry et al.[12]; Shi et al.[49]; Chung et al.[81]; McMurry and Woo[66]; Laakso et al.[82]; Stanier et al.[67]; Park et al.[72]; Jimenez et al.[88]; Fine et al.[90]; Cabada et al.[92]; Tolocka et al.[93]; Hussein et al.[68]; Herner et al.[89]	• A new nucleation mode (3–10 nm) of ultrafine particles is identified, which is universal in urban and remote areas. • Ultrafine composition is different from that of fine and coarse particles due to different formation processes. • Fine mode mass concentration and ultrafine mode number concentration are not always correlated. • Nucleation mode formation follows the diurnal pattern or atmospheric perturbation. • Sulfuric acid is key to the nucleation mode formation. • Nucleation formation varies geographically and seasonally, depending on the types of reactants.	• Develop real-time measurement techniques for size fractionated composition down to a few nanometer. • Characterize geographical variations. • Understand the dynamic interaction with fine and coarse mode particles. • Assess if successful reduction of fine and coarse mode mass concentration will result in the increase in ultrafine mode number concentration.
Occupational settings: industrial processes (hot process, combustion process, bioaerosol, high energy mechanical process)	Knight et al.[376]; Rendall et al.[377]; Hewett[378]; Hämeri et al.[379]; Camata et al.[380]; Vincent and Clement[10]; Zimmer and Biswas[381]; Zimmer et al.[382]; Zimmer and Maynard[383]; Luther[22]; Wheatley and Sadhra[384]; Brouwer et al.[95]	• Varieties of sources for nanoparticles from industrial processes not intended to produce engineered nanoparticles have been identified. • High spikes of number concentrations during active operation and then decay over time.	• Develop instrumentation for measuring personal exposure on a routine basis. • Develop pertinent sampling protocols for true assessment of exposure.
Occupational settings: engineered nanoparticle production (cleaning, disposal, conditioning application)	Zhang and Wang[16]; Schmid et al.[96]; Dahn et al.[97]; Cheng and Jenkins[385]; Luther[22]; Maynard et al.[98]; Lecoanet et al.[100]; Kuhlbusch et al.[99]	• Exposure is more likely to happen after the manufacturing process, including cleaning, waste/wastewater disposal, handling, and commercial/consumer application. • Certain types of nanoparticles are intentionally released.	• Expand investigation of source strengths of all production processes and exposure after the production. • The distribution and fate of nanoparticles after production is currently not assessed for most cases. • Set up protocols for handling and disposal of nanoparticle containing products in workplace and for consumers.

mobile, atmospheric conversion, and occupational setting) is the disappearance of nanoparticles (those <100 nm) when high concentrations of larger particles are present. Larger particles can serve as a sink for scavenging ultrafine particles or their vapor precursors. This phenomenon raises an important and challenging question on the establishment of standards for regulation, especially if the concentration of ultrafine particles is to be controlled on a number basis. An important point that has not been extensively researched is the control of condensable species and/or vapor precursors at the source, with the eventual intent to reduce the resultant ultrafine or nanoparticle concentrations. Detailed discussions on each source category that is listed above are provided below.

Stationary Sources

Stationary combustion systems have long been known to be an important source of fine particle emissions. However, ultrafine or nanometer-sized particulate matter emission characterization is only now starting to receive attention. Maguhn et al.[27] analyzed ultrafine particles in the flue gas and in the stack of a municipal waste incinerator. The peak size was found to be ~90 nm at 700 °C (in the combustor). The particles grew to larger sizes in the cooler downstream regions, and grew up by coagulation, condensation, and reactive bonding of gaseous chemicals onto the nucleated particulate matter. Intermittent periods of high emissions of ultrafine particles <40 nm after the wet electrostatic precipitator (ESP) were observed, probably formed by nucleation of gas-phase constituents in cooler regions downstream of the ESP (because of the absence of particle surfaces on which to condense, which would have resulted in larger particles). The number of ultrafine particles at exit of the wet ESP was correlated with the SO_2 concentration in the effluent. The use of back-up oil burners also resulted in the formation of a dominant peak of 30-nm particles. Chang et al.[8] reported ultrafine particle size distributions from coal-, oil-, and gas fired stationary combustion sources. Peaks in particle size (in the number distribution) were observed at 40–50, 70–100, and 15–25 nm on combusting medium sulfur bituminous coal, No. 6 fuel oil, and natural gas, respectively. Clearly, the composition of the fuel plays an important role in the resultant size distribution. Laboratory scale studies on understanding the emissions from coal combustors have been conducted, and pathways of transformation of metallic species have been established to determine nanoparticle formation.[28,29] The high ash content in coal results in the presence of an aerosol that may provide a large surface area for vapor condensation and coagulation with smaller particles, thereby potentially reducing nanoparticle formation.

With advanced instrumentation, measurements are helping to point out the role of aerosol formation and growth dynamics on resultant particle size distributions. However, very little theoretical work has been conducted to create process parameter maps that would indicate a relationship of particle emissions to operating conditions. This is partly because of the complexity of the systems and the aerosol growth dynamics models. Biswas and Wu[14] proposed methods to estimate characteristic times for different particle growth processes, such as coagulation and condensation. Such tools could be used to provide guidance and to establish conditions under which different size distributions would be dominant. An important consideration is also the adoption of regulations for the reduction of fine and ultrafine particles and whether the reduction of the mass concentrations of the larger particles actually enhance the ultrafine particle concentrations in the emissions.[30]

The sampling of ultrafine particles at high temperatures is challenging because of the dilution process that affects nucleation, coagulation, and condensational growth. Lipsky et al.[31] reported that residence time and dilution rates did not influence particle mass emission rates from coal combustion, but they affect the size distributions and number concentrations (ultrafine particle concentration increased as the dilution ratio increased). Zhang and Wexler[32] show that if dilution is sufficient, gas concentration falls below the supersaturation level, and nucleation rates decline. Chang et al.[8] reported an aging time of 10 sec and a dilution ratio of 20 to be sufficient to obtain representative primary particle emission samples from such sources. The needed aging times were longer for hot gas that had lower initial particle number concentration and discouraged condensation. Several dilution probes and sampling systems have been designed for unbiased measurement.[33]

Metals can serve as markers for specific emission sources (e.g. selenium [Se] for coal combustion, vanadium [V] and nickel [Ni] for oil combustion, and zinc [Zn] for municipal waste incineration), and some of them adversely affect human health. Tolocka et al.[34] measured the real time concentration of metal species in ultrafine ambient aerosols. In Baltimore, MD, the number concentrations of ambient particles containing metals were found to be as high as 10^4 cm^{-3}. Vanadium was observed to originate from all wind directions; lead (Pb) and iron (Fe) were observed to have a common emission source, whereas arsenic (As) and Pb came from different sources. In the past, trace metals in particulate matter $(PM)_{10}$ and $PM_{2.5}$ have been used to determine the contributions of various emission sources by using receptor models.[35,36] Similar chemical mass balance modeling of the nanometer fraction of the ambient aerosol has not been done and

would provide rather useful results. The dynamic nature of nanometer-sized particles may cause their chemical profiles and size distributions to change between source and receptor. Utsunomiya et al.[37] identified trace metals in fine and ultrafine particles in Detroit, MI. Many trace metals were observed mainly as individual particles, with some as small as 10 nm. Strong correlations between certain metals were used to infer the emission sources.

In modern times, people spend more time indoors than outdoors, and there are many sources in the indoor environment. In assessing the effects of air quality to human health, characterization of the indoor aerosol and its correlation with the outdoor aerosol is essential. Cigarette smoke has long been recognized to be a primary source for particulate matter indoors, and it is a contributor to ultrafine particles.[38,39] Cooking, especially frying and sautéing, is also an important source for indoor ultrafine particles. Wallace et al.[40] reported that >90% of the particles by number were in the ultrafine fraction during cooking, with a primary peak at 60 nm and a secondary peak <10 nm. A gas burner or an electric stovetop heating element alone (i.e., without pot or food being cooked) resulted in up to 1.1×10^5 cm^{-3} ultrafine particle concentrations.[41,42] Candles, residential wood, coal combustors, tobacco smoke, incense, and mosquito-coils in Asian countries also contribute to indoor nanoparticle levels. Venkataraman et al.[43] characterized soot emissions on the combustion of biofuels used for cooking in the Indian subcontinent; and the measured emission factors ranged from 0.38 to 0.62 g kg^{-1} from wood combustion for varying burn rates (0.9–2.0 kg hr^{-1}) and from 0.12 to 0.17 g kg^{-1} from straw and dried cattle manure. Measured organic carbon (OC) emission factors ranged from 0.17 to 4.69 g kg^{-1}. Black carbon and OC emission factors from kerosene and liquefied petroleum gas (LPG) stoves were lower than biofuel stoves by a factor of 3–50. They also concluded that these cooking stove emissions could have a significant impact on climate change in the South Asia region.

Mobile Sources

Diesel engines are major sources of nanoparticles (<50 nm), which dominate by number concentration, whereas the mass distribution is dominated by the accumulation mode (50 nm < particle diameter < 1 μm), as shown in Figure 3.[9] Recent advances in instrumentation have also revealed a nucleation mode (<10 nm) for freshly formed particles. Nanoparticles from diesel engines are typically hydrocarbons (soluble organic fraction) or sulfate particles formed by nucleation, whereas the accumulation mode particles are primarily carbonaceous soot aggregates. Tobias et al.[44] reported that diesel exhaust nanoparticles are comprised primarily of unburned fuel and lubricating oil. Sulfuric acid accounted for a small percent, but played a critical role as nuclei that provide a surface for condensation of organic species. Sakurai et al.[45] carried out online measurements of diesel exhaust nanoparticle composition and reported the volatile component to be comprised of ≥95% unburned lubricating oil. Lower emission standards for diesel engines reduce particle mass emissions, but nanoparticle number concentrations may increase because of the lower availability of condensation surfaces. Burtscher et al.[46] examined emissions from a diesel engine and reported a mode diameter ~60 nm measured at ambient temperature. They reported that the volatile fraction decreased, whereas polycyclic aromatic hydrocarbons on the particle surface increased as the load increased. Catalysts can be used to enhance oxidation of organic compounds, and effective use in after-engine exhaust treatment will help reduce both the mass concentrations and the potential to form the nuclei mode downstream. McDonald et al.[47] studied the impact of diesel truck emissions on the ambient aerosol in the vicinity of highways. The mass concentration was reported not to be a function of distance from the highway, whereas the number concentrations showed clear peaks in the ultrafine range in the near vicinity of the highway, decreasing to upwind levels within 50 m of the downwind roadside.

Spark-ignition (SI) engines are reported to generally emit a lower total number concentration of particles than diesel engines.[9] However, under high-speed highway cruise conditions, it has been found that they emit at levels equivalent to diesel engine exhausts.[48] Studies conducted by Shi et al.[49] have reported that SI engines emit higher number concentrations of the nucleation mode particles (<10 nm) than diesel engines. Emissions from SI engines have a number-based mode size of 20–40 nm,[50] and these particles primarily contain a high fraction of volatile material,[46] one that vaporizes below 300 °C. Ristovski et al.[51] reported that both unleaded and leaded gasoline engine emissions have a number or count median diameter (CMD) ~45 nm, with the number concentration 200 times higher for the leaded gasoline engine exhaust (1.8×10^6 cm^{-3} vs. 8×10^4 cm^{-3}). LPG, which is considered to be a cleaner fuel,[52] results in larger nanoparticle emissions than those of unleaded gasoline (CMD = 60 nm, N = 2.6×10^5 cm^{-3}). In New Delhi, India, there have been regulatory changes that replaced diesel fuels with LPG and compressed natural gas fuels. Whereas the mass concentration of PM has decreased, there is no clear understanding as to how the nanoparticle emissions have changed. Wehner et al.[53] measured nanoparticle size distribution from traffic in a street canyon. The mode size (15 nm) was smaller than those directly measured in vehicle exhausts in laboratory dynamometer tests (50 nm), suggesting the nucleation of emitted vapors. Zhu et al.[54] characterized ultrafine particles near a major highway in Los Angeles, CA, and reported three distinctive ultrafine modes (13, 27, and 65 nm) at 30 m

downstream the highway. At another Southern California site,[55] the ultrafine particles were reported to have a mode size ~30–40 nm. The size distribution changes as a function of distance to the road: mode size increases, whereas number concentration decreases, indicating aerosol growth by coagulation and condensation and a reduction by dilution and evaporation. In addition to the fuels and lubricating oils contributing to particle formation in engine exhausts, metal parts from engines and catalytic converters, including platinum (Pt), are believed to be emitted as ultrafine particles.[56] Artelt et al.[57] reported that nanocrystalline platinum was observed, and was almost exclusively attached to micron-sized alumina. However, their impactor sampling method was not designed for studying ultrafine particles, and, hence, more studies will be needed to identify these emission characteristics. Other noble metals, such as palladium (Pd) and rhodium (Rh), may potentially be emitted as nanoparticles. Recent studies have suggested the use of transition metals, such as cobalt (Co) and barium (Ba), to replace Pt in nitrogen oxides (NO_x) storage and reduction catalysts[58] for lean burn engines. Whereas most catalysts are selected based on their performance for the reduction of gaseous pollutants, no life cycle-type analysis or potential re-entrainment and emissions have yet been considered.

Two-stroke engine vehicles are common in developing nations, and they have high emissions. However, no studies were found in the literature that measured nanoparticle emissions from two-stroke engines.

Similar to sampling under conditions of high temperatures and particle concentrations in stationary sources, measurement in vehicle exhausts is equally or more challenging. Various parameters in the sampling process, such as dilution temperature, dilution ratio, residence time, and relative humidity,[59] may affect the formation and growth of ultrafine particles and result in varying observations. The effects of different dilution ratios on the measurement of mobile source emissions are additionally complicated because of a variety of operating cycles of the engine. Only when clear protocols are developed for measurement of nanoparticle emissions from these sources can comparisons be made among various studies and clear trends derived for eventual exposure and environmental impact assessments.

Outdoor mobile sources have also contributed to the indoor aerosol.[60] Although it is expected that the ultrafine particles would penetrate and enter the indoor environment, detailed studies were not found for this review that can firmly quantify this relationship.

Atmospheric Conversion

Nucleation has long been known as a process that results in the formation of ultrafine particles in the atmosphere. Aiken[61] in the late part of the nineteenth century reported the observation of the nuclei mode particles, typically in the range of 20–50 nm, which are now also known as the Aiken mode. The key species in the atmosphere are sulfuric acid, nitric acid, and organic gases.[62] With the advances in instrumentation in recent years for the detection of ultrafine particles,[63–65] the formation of a new mode of atmospheric particles of sizes of a few nanometers has been reported. This phenomenon has been observed in urban Atlanta, GA;[12,66] the Pittsburgh, PA, area;[67] urban Birmingham, AL;[49] urban Helsinki, Finland;[68] and moderately polluted continental air in Germany,[69] as well as remote atmospheric regions, such as the North Pole,[70,71] South Pole,[72] Mauna Loa,[73] high mountains,[74,75] and in a Finnish forest.[76] Figure 4 displays the size distribution of the nucleation mode particles along with the larger mode measured at the South Pole. Researchers have also argued that nucleation mode particles can be produced aloft in the free troposphere cloud outflows that are then transported to the surface.[70,73,77] Ultrafine particle formation in the upper troposphere is a source of global atmospheric particles.[78,79] These nucleation mode particles can continue to grow by coagulation and vapor condensation to become the Aiken mode and accumulation mode particles, which result in atmospheric optical effects and, subsequently, climate change on a global scale. The lifetime of ultrafine particles in the atmosphere is typically short (15 min for 10-nm particles[9]), but they can become fine particles that can be

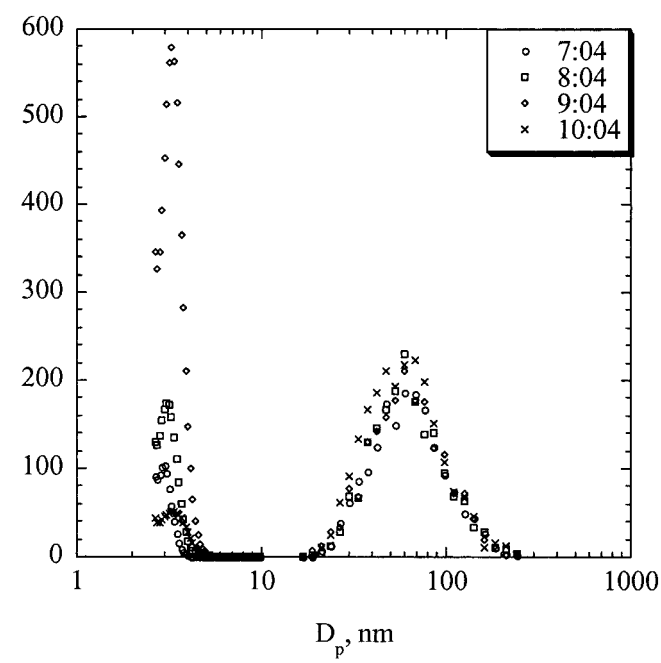

Figure 4. Size distribution measured during a "nucleation event" in South Pole. (Reprinted from Park et al.[72] with permission from Elsevier.)

transported over long distances adding regional air quality degradation. The number concentration of ultrafine particles and $PM_{2.5}$ mass concentration are not necessarily correlated,[67,80–82] in other words, $PM_{2.5}$ mass concentration is not a consistent surrogate for health effect end points that are associated with number concentration.

The nucleation mode particles can follow regular diurnal patterns with peak production around noon when the sunlight is most intense,[49,83] from traffic emissions,[49,67,68,82] and from stationary sources.[49] Figure 5 shows examples of nanoparticle formation around noontime. Such production of small nanoparticles has also been reported during the morning rush hours instead of noon in Finland.[68,82] An annual pattern was observed with higher concentrations in winter and spring, whereas lower concentrations were observed in summer. Geographic locations seem to have a strong influence on the observed particle formation patterns. The formation of nucleation mode particles also occurs during atmospheric perturbations (e.g., the removal of pre-existing aerosol[79] and the addition of gas phase reactants from a surface source[84]). Nucleation has also been observed in the remote marine atmosphere downwind of penguin colonies where the reaction of ammonia and sulfuric acid was speculated to be the source of the ammonium sulfate particles.[85] Sulfuric acid has been reported to play a critical role in many nucleation events.[49,67,79,86] The measured size distributions in urban Atlanta are consistent with a collision-controlled nucleation process, as would be expected for a highly supersaturated system.[12] Photo-oxidation of diiodomethane (CH_2I_2) and its derivatives have also been shown to result in ultrafine particle formation in coastal areas.[87,88] Meanwhile, it should be pointed out that the presence of high concentrations of fine mode particles serves as a sink for nanoparticles, because it results in the suppression of particle formation.[68]

There have been many studies on particle size distribution of ultrafine particles, and reports of the composition are also emerging. To study the transient and rapidly changing nature of nanoparticles, real-time measuring instruments are a must to provide the necessary data. However, current analytical capabilities are limited, and only recently have single particle mass spectrometers been used, and these have also been limited in their capabilities in the ultrafine particle size ranges (see "Nanoparticle Control and Instrumentation" section below). Many studies have relied on the use of high-velocity impactor stages for the collection of the ultrafine particles on a time-weighted average basis (e.g., 24 hr average). Hughes et al.[80] analyzed the ultrafine particles collected by micro-orifice uniform deposit impactors (MOUDIs) in Los Angeles, CA, in winter. Organic compounds were found to be the largest constituents in the ultrafine mass with a small amount of sulfate. The most abundant catalytic metal was iron. The ultrafine composition was different from the co-collected fine particle composition. Similar results were observed in the PM study carried out in Northern California (Herner et al.[89]). Chung et al.[81] carried out the analysis of ultrafine particles collected by MOUDIs in Bakersfield, CA, in winter. OC accounted for 20% of the mass. There were also significant amounts of water-soluble cations and anions with water-soluble calcium (Ca^{2+}) as the dominant cation (20%) and nitrate (11%) and sulfate (5%) as the dominating anions. The particle acidity was a function of particle size, and ultrafine particles were more alkaline. Similar to the Los Angeles study, the ultrafine composition was different from the fine particle composition (nitrate, ammonium, and OC; neutral acidity). Fine et al.[90] analyzed ultrafine particles (<0.18 μm) for organic compounds in Los Angeles and identified vehicular emission markers, such as hopanes,[91] in the ultrafine mode. In the eastern United States, Cabada et al.[92] analyzed the ultrafine particles ($PM_{0.056}$ and $PM_{0.1}$), which were also collected by MOUDIs at the Pittsburgh supersite. Ultrafine particles accounted for $<5\%$ of the $PM_{2.5}$ mass. During summer, the ultrafine mass was 50% carbonaceous material and 50% inorganic sulfate and ammonium. In winter, the percentages were 70% and 30%, respectively. Tolocka et al.[93] analyzed ultrafine particles at the Aiken mode at the Baltimore supersite using a real-time single particle mass spectrometer and reported that nitrate played the dominant role in the formation with condensational growth of ammonium nitrate. The nucleation event occurred in cold and humid weather and followed a diurnal pattern with the peak in the early morning hours. However, these studies did not target the nucleation mode of the ultrafine particles because of instrumentation limitation in this mode. Size-classified and real-time chemical speciation for these ultrafine particles, especially the nucleation mode particles, is critical in determining the sources of precursors and in evaluating the effects on climate, health, and the environment.[94] Therefore, the composition of ultrafine particles should be additionally investigated, which no doubt will depend on the advances in instrumentation. Another aspect, where information is lacking, is the long-term pattern (at least >5 years) data set, which is not sensitive to episodal weather or emission conditions.[68]

Occupational Settings

Industrial Processes. There are a variety of industrial processes that are sources of unwanted nanoparticles. Vincent and Clement[10] categorized ultrafine particles in the workplace as the following: (1) fumes from hot processes (e.g., smelting, refining, and welding), (2) fumes from (incomplete) combustion processes (e.g., transportation and carbon black manufacture), and (3) bioaerosols (e.g.,

viruses and endotoxins). They also summarized the "favorable" conditions required for the generation of ultrafine particles in a workplace: (1) presence of vaporizable material, (2) sufficiently high temperature to produce enough vapor, followed by condensation to form an independent aerosol, and (3) rapid cooling and a large temperature gradient.

There has been a long history of occupational exposure to ultrafine particles, which is summarized in Table 2. In many of these studies, high spikes of ultrafine particle number concentration were observed during active operations, followed by a gradual decay after the operation, primarily because of coagulation, evaporation, dilution, and/or deposition. The fraction of the total ultrafine particle number

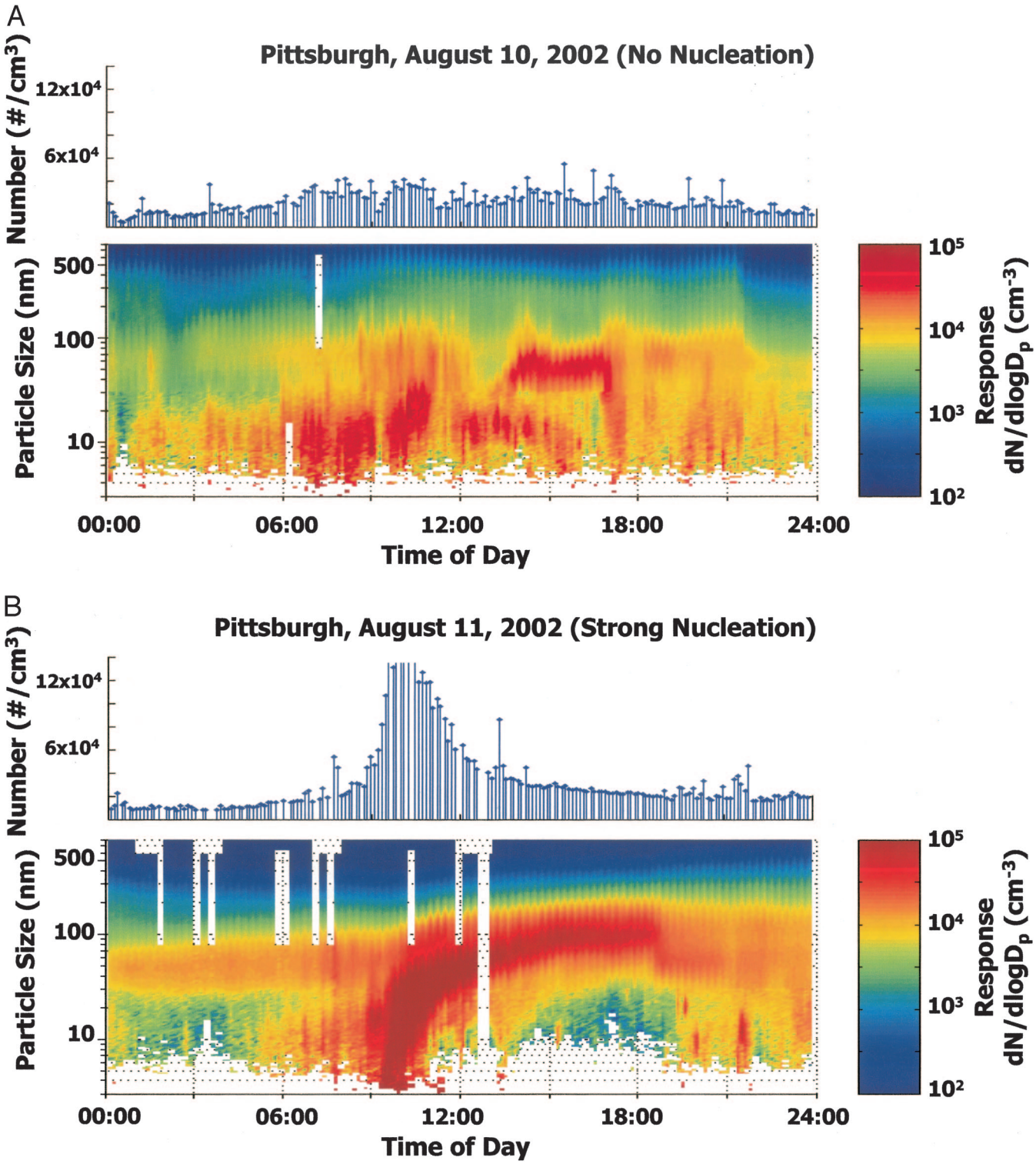

Figure 5. Diurnal pattern of number concentration of ultrafine particles at Pittsburgh. (Courtesy of Drs. Charles Stanier and Spyros Pandis.)

concentrations generally decreases, whereas that of the fine particle number concentrations increases with time and distance from the point of emission. To accurately estimate exposure, the effects of spatial and temporal changes will need to be evaluated. It is also important to identify the time needed for the concentration to decline to the normal or background levels. There are a spectrum of other industrial settings that have the potential to generate ultrafine particles that have not been investigated yet, including plasma cutting, milling, powder coating, printing, copying, baking, and cooking.[22]

The instrumentation used in some of these studies did not accurately target the ultrafine range (i.e., 1–100 nm). Pertinent design of the sampling instrument, procedures, and protocols are needed to truly assess the exposure of ultrafine particles in an occupational setting.[95] There are instruments available to conduct this assessment. For example, condensation nuclei counters can be used as screening devices to determine ultrafine particle emission sources; low-pressure impactors for collecting ultrafine particles for subsequent analysis and characterization; and scanning mobility particle sizers or electrical low-pressure impactors can be used to measure number-weighted size distributions. Distance from the source and time of measurement also need to be factored in the sampling protocols. Eventually, personal exposure monitors need to be developed and routinely used to track exposure to ultrafine particles.

Engineered Nanoparticle Production. The production of engineered nanoparticles can be generally categorized into two approaches.[96] The first is a top down approach that starts with a bulk material and then breaks it into smaller pieces using some form of energy. Processes that can be listed in this "top-down" category include high-energy ball milling, mechanochemical processing, etching, electroexplosion, sonication, sputtering, and laser ablation. The second approach is to synthesize materials from the atomic or molecular level by growth and assembly to form the desired nanoparticles. Processes included in this "bottom-up" category are sol-gel, aerosol routes, chemical vapor deposition, plasma or flame spraying, laser pyrolysis, atomic or molecular condensation, supercritical fluid, spinning, and self-assembly. Most of these processes are performed in a closed reaction chamber. Human exposure to these engineered particles does not occur during synthesis unless there is an unexpected system failure (e.g., rupture of a seal) or during the starting and stopping of continuous processes. Human exposure is more likely to occur after the manufacturing process[22] when opening the reaction chamber, drying the product, or in the post-process handling of the products.

The collection of produced nanoparticles also poses increased risks, especially in a dry form. Because of their small sizes, gravity has negligible effects on nanoparticles. The lack of gravitational settling results in a long lifetime in the air, increasing the chances of human exposure and health risks. The risk of dust explosion arises, especially for metal powders, which have high pyrophoricity. Figure 6 summarizes the conditions under which dust explosions could occur.[97] The handling of nanoparticles as aerosols in the ventilation/filtration system also requires extra caution, including respirators, to avoid entrained particles.

The release of nanoparticles during cleaning operations of the production chamber is another critical point. Cleaning typically involves using water or some solvent, resulting in wastewater containing nanoparticles. Brushes, sponges, or tissues used in the cleaning will carry nanoparticles into the waste stream. Other items that will enter the waste stream include filters that were used to collect the nanoparticles. Disposal of the waste and wastewater may become a source of nanoparticle release into the environment.

Conditioning (e.g., compression, coating, and composition) of nanoparticles to form final products may also result in the release to the environment and resultant

Table 2. Occupational exposure to nanoparticles.

Reference	Setting	Concentration (cm^{-3})
Knight et al. [376]	Diesel-powered vehicles in confined industrial spaces (*e.g.*, mining)	
Hämeri et al. [379]	Ski hot-waxing using fluor powder	5×10^4
Cunningham et al. [386]	Silicon from smelter	N/A (TEM analysis)[a]
Rendall et al. [377]	Arc spraying	382 mg/m^3; 50 nm
Hewett[378]; Zimmer and Biswas[381]; Zimmer[387]; Zimmer et al. [382]; Brouwer et al. [95]	Gas metal arc welding operation	$10^5 - 10^7$
Zimmer and Maynard[383]	High-speed grinding	$6.5–800 \times 10^3$
Camata et al. [380]	Laser ablation	N/A (only size distribution)
Wheatley and Sadhra[384]	Diesel exhaust fumes in bus/truck distribution depots	$58–231 \times 10^3$

[a]TEM = transmission electron microscopy.

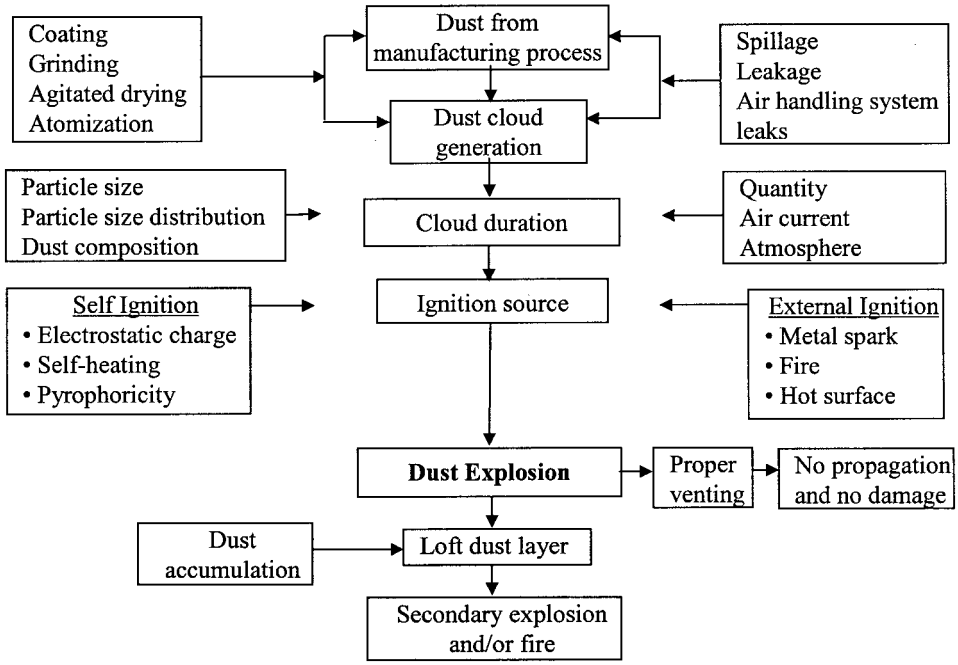

Figure 6. Summary of conditions for dust explosions. (Reprinted from Dahn et el.[97] with permission.)

exposure, although very few studies have been carried out on this subject. Recent studies[98] to evaluate the aerosol release during the handling of carbon nanotubes showed that the generation of ultrafine particles occurred under vacuum to remove spilled nanotube material or vigorous mechanical agitation; however, they reported that the concentrations were very low. Measurements of ultrafine particle levels during the bagging of carbon black showed no increases in nearby air.[99] There are many current consumer products that have nanoparticle ingredients,[100] such as sunscreens and paints (nanostructured titanium dioxide and zinc oxide), additives in tires (fumed silica, carbon fibers, and nanotubes in the future), lubricants and chemical mechanical polishing slurries (nanosized silica), and shampoos and detergents (nanosized alumina). Self-cleaning surfaces made out of coatings of nanostructured titanium oxides are being used in window panes and ceramic tiles. With the additional advancement of nanotechnology, the use of nanoparticles will increase. The use in pharmaceutical products is a good example. There may be several pathways for nanoparticles in the products to enter the environment by mechanical release from the product or when the consumer product is disposed.

Whereas most engineered nanoparticles are not designed to be released into the environment, there are certain types of nanoparticles that are inevitably or intentionally released in their applications. Examples include nanoenergetic materials/explosives,[101] high obscurance nanoflakes, and nanoscale metals for groundwater dechlorination.[16] Exposure potential of nanoexplosives exists in the postdetonation environment in the testing chamber or in battlefield applications. They are intentionally released in large quantities and may stay in the environment for a long time, although their lifetime in the environment has not been accurately assessed. Residue from explosives may contain unreacted chemicals that make their effective removal hazardous.

NANOPARTICLE CONTROL AND INSTRUMENTATION

The capture and control of nanoparticles are important to prevent unwanted emissions into the environment, to understand design of devices for respiratory protection, and to collect engineered (useful) nanoparticles that are synthesized in processing systems. The fundamental behavior of particles in air streams has been explained in several textbooks, such as, Friedlander,[102] Seinfeld and Pandis,[62] and Hinds.[103] The following discussion emphasizes new developments in cyclones (operating at low pressures), filters, thermophoretic deposition, and electrical precipitators. A brief review of nanoparticle instrumentation for size distribution measurement and characterization is also provided.

Inertial Control Devices

Pioneering work on the drag force acting on fine particles was done by Stokes[104] and Cunningham.[105] The relaxation time (time required for the velocity of a particle to equal that of the fluid it is carried in or the time to come to rest with respect to the fluid) for a particle in the nanometer size range is rather small (8.6×10^{-8} sec for a 100-nm particle of unit density and 6.5×10^{-10} sec for a 1-nm particle), and, hence, it tends to follow the airstream lines. Therefore, methods, such as inertial separation, are not expected to be as effective unless high velocities are used (such as in high-velocity impactors[106]) or low-pressure conditions (such as in low-pressure cyclones to collect nanoparticles). When operating inertial devices at high-fluid velocities, scaling parameters (such as Stokes number) that determine particle collection efficiency may be altered. Biswas and Flagan[106] conducted a study to examine scaling criteria for high-velocity impactors operating at low downstream pressures. They found that the same scaling criteria (impaction efficiency and Stokes number relationships) could be used, provided that property

values were determined at stagnation point (in an impactor, this would be where the center line from the nozzle intersects the collection plate) conditions. Steep curves for the nanoparticle collection efficiencies as a function of the Stokes number were obtained for impactor operating conditions wherein the jet velocities equaled the speed of sound (highest jet velocity possible). Hillamo and Kauppinen[107] have demonstrated the viability of a multistage impactor operating several stages at high velocities where the flow was compressible. Different designs, such as virtual impactors and particle trap impactors, have also been designed for nanoparticle collection.[108] Whereas laboratory scale impactors are good for establishing the scaling criteria for inertial collection at lower pressures, they are not control devices per se, other than designs such as the particle trap impactor.[109] However, cyclones, which also operate on inertial collection principles, are particle control devices that are extensively used because of their simplicity in design, low cost, and ease of operation.[110] A key advantage is the low pressure drop through the unit. However, the collection efficiency is a function of the Stokes number, and it drops for particles in the nanometer-size regime. Tsai et al.[111] have successfully demonstrated that axial flow cyclones can be operated at low pressures to remove particles <100 nm. An expression for the collection efficiency of the cyclone operating at low pressures (<20 Torr) was derived. In addition to correctly estimating the Cunningham slip correction factor at low pressures (because of altered mean-free paths), they determined that the aerodynamic cutoff size was also a function of the flow Reynolds number. The collection efficiency of the device therefore depends on the Stokes number and an additional parameter, the Reynolds number. The results suggested that such devices could be operated under low-pressure conditions (6–20 Torr). At a pressure of 6 Torr and a flow rate of 0.5 liters/min, the collection efficiency of 100 nm particles was close to 100%, with a 50% cutoff size of ~50 nm. Such cyclones could be used for preventing emissions of nanoparticles from exhaust gases of reaction chambers prevalent in the semiconductor and optoelectronic industries. Other designs of cyclones have used additional forces on the nanoparticles, such as electrical fields for overcoming the low capture efficiencies in these size ranges.[112] Clearly, more developmental work is necessary for designing simplistic inertial devices for the capture of nanoparticles.

Filtration Systems

Filtration devices are also used for particle control, and there are various designs for nanoparticle collection. Baron and Willeke,[113] Friedlander,[102] and Hinds[103] provide detailed information on approaches to determine the total collection efficiency of filtration systems. The first step involves determining the single target collector efficiency and then combining it in a packed configuration of certain porosity to establish the overall collection efficiency. An intriguing feature in such systems is the transition point when a very small particle can be considered to behave like a gas molecule. It is well known that gas molecules pass through filters, and the only effect is an associated pressure drop. Whereas the diffusional transport of nanometer-sized particles are expected to result in capture on the filter elements, it is not clear at what size the particles will behave like molecules and slip through. Fundamental research needs to be conducted in this arena to clearly answer the above questions.

High-efficiency particulate air (HEPA) filters have been constructed and are widely used for the capture and removal of fine particles from airstreams. Disadvantages of such systems are that they have high-pressure drops and require frequent maintenance and replacement. Whereas conventional HEPA-rated and ultra-low particulate air-rated filters have high capture efficiencies for airborne nanometer-sized particles (99.97% at 7300 nm and 99.9999% at 100 nm, respectively), alternate methodologies have been developed to overcome the major limitation of the associated high-pressure drop. For example, electrostatically augmented air filters[114–117] and dielectric screens[118] attain high collection efficiencies (>99.9%) with a smaller associated pressure drop that is one-eighth that of HEPA filters.[116] These filters are used only in specialized applications, such as ultraclean rooms for microelectronics component assembly or surgical rooms in hospitals, primarily because of their high capital and operating costs.

There are large-scale designs of filters, such as bag configurations, for capture of particles in industrial scale operations. Such systems have also been used to collect deliberately produced nanoparticles at the exit of engineered reactors. However, the operational details (such as collection efficiency as a function of size and operating costs because of high pressure drops) of such systems purely for collecting nanoparticles are not known. After operation for a length of time, the bags are vibrated mechanically, acoustically, or with reverse air-pulse jets, to drop the collected particles onto hoppers. The removal of particles by these means often shortens the life span of the bag filter system. The process streams where these are used are often at elevated temperatures, which also reduce the life span of the bags.

Thermophoretic Collection Systems

Thermophoretic forces act on particles because of the presence of a temperature gradient causing them to move

from a high to low temperature region.[102] The thermophoretic velocity arises because of the differences in molecular energies at the different temperatures and their resultant interaction with the nanoparticles. Expressions for the thermophoretic velocity have been derived by Waldman and Schmitt[119] using the kinetic theory of gases. In the nanoparticle size regimes, the thermophoretic velocity is independent of particle size and, hence, a good method for collection without a bias toward size selectivity.

Many synthesis systems operate at high temperatures to promote chemical reactions that result in formation of the desired molecular state from which nanoparticles are formed by nucleation. To promote nucleation (the conversion of the gaseous molecular state to nanoparticles), there is often a quench zone with a high-temperature gradient in nanoparticle synthesis reactors. High-temperature gradients are often also necessary to promote preferential crystallization of a desired state, such as the anatase phase of titanium dioxide or the magnetic (γ) phase of iron oxide.[120,121] Because of the presence of temperature gradients in nanoparticle synthesis systems, thermophoretic forces can be used for the collection of nanoparticles. Thermophoretic collectors have been used in many laboratory scale studies with flame and furnace reactors.[120,122–124] Thermophoretic phenomena have also been successfully used in the deposition of particles to form nanostructured films.[125]

Electrostatic Collection Methods

The best methodology to collect nanoparticles in systems with low pressure drops is the use of electrical fields. In these devices, the particles that enter are typically charged using unipolar ions generated in a corona (most often created by applying a voltage that generates a localized electrical field greater than the breakdown level for the gas; for industrial scale units, the voltages applied are on the order of 60 kV, whereas in smaller scale units for indoor air cleaning, the voltage applied is 8–15 kV). Several researchers have studied the charging behavior of nanoparticles.[126–128] Once the particles are charged, they experience a force because of the electrical field causing them to migrate to the collector walls that result in their removal from the gas stream. Studies conducted for the capture and collection of nanoparticles in such systems have revealed that a certain fraction remains uncharged, resulting in lower capture efficiencies.[129–131] The collection efficiency dropped from ~90% for 60-nm-sized particles to <10% for 10-nm-sized particles. Similar trends have also been observed in industrial scale ESPs, wherein a drop in collection efficiency was observed for nanometer-sized particles.[132,133] The co-use of soft X-ray irradiation and unipolar coronas has resulted in a dramatic improvement in the charging efficiencies of nanoparticles.[131] Using a device with both a soft X-ray and unipolar corona source, a very high capture efficiency (> 99.99%) for nanometer-sized (5–100 nm) particles was obtained because of effective charging of nanoparticles by increased ion concentrations and direct photocharging of the particles.

The capture of nanoparticles with high efficiencies is important in several air cleaning and bioagent inactivation devices. For example, it is desirable to remove biological particles, such as viruses in aircraft cabins, to prevent spread of infections (such as colds and Severe Acute Respiratory Syndrome). Because of increased concerns of bioterrorism, there is a need for robust air cleaning units in building ventilation systems that will remove agents, such as small pox and other nanoparticle-sized viruses. HEPA filters are effective at trapping such particles; however, they do not inactivate them. Once captured, biological particles can give out endotoxins, and these would continuously be released from the surface of the filter and entrained in the airstream.[134] Biological particles, such as pollen and bacteria, may fragment, resulting in the release of constituents that can be potentially harmful to health.[135] Hogan et al.[11] have designed a soft X-ray-enhanced corona system that has been demonstrated to have >4 logs removal (>99.99% collection efficiency) of such viral bioagents, with an inactivation (kill) rate >7 logs (> 99.99999%). Corona-based systems are now being used in commercial room air cleaning systems (Ionic Breeze, Orcek Inc.). These rely on the concept of ionic wind to generate a flow, and, hence, no external pumping devices, such as fans, are needed. However, the particle capture efficiencies of such devices for nanoparticle capture have not been rigorously tested and are mostly unknown.

Real-Time Nanoparticle Instrumentation and Characterization

There are several instruments for real-time measurement of gas-borne nanoparticles. The design of the instruments is based on the same principles as the collection devices, with stricter control of operating parameters. There are many reports in the literature and excellent descriptions of aerosol instrumentation.[113]

Electrical Instruments. Chen et al.[64] developed a nanodifferential mobility analyzer that measures on a real-time basis the size distribution of particles down to 3 nm. After acquiring a charge, the particles are passed through a classification section where they are classified by mobility. Improvements in design have been possible because of the use of transport models to determine diffusional

losses[136] and accordingly to redesign the unit. Single-mobility classified particles are then introduced into a condensation particle counter to obtain the number concentrations. Developments are currently under way to now extend the operational range of these instruments down to smaller sizes (<1 nm) by overcoming limitations in the counting device.[137,138] Another important consideration is the effective charging of nanoparticles, and it is desirable to have a larger fraction charged to improve sensitivity and reduce counting errors. Chen and Pui[65] have designed an effective nanoparticle charger using unipolar ions in a well-designed electrical field to prevent loss of both ions and charged nanoparticles. The combination of soft X-ray with the corona chargers[131] may also be effective in charging larger number fractions of nanoparticles. Kumar et al.[139] have used a modified nanodifferential mobility analyzer system with a high throughput for the collection of nanoparticles in their flame aerosol reactors in narrow size regimes.

Real-Time Inertial Impactor. The only commercially available real-time nanoparticle measurement device based on inertial principles is the Electrical Low Pressure Impactor.[140,141] It consists of a corona charging system and a cascade impactor. The principle of operation is similar to the impactors described in the previous section; however, an electrometer at each stage allows for the real-time monitoring of the deposited particles. Steep collection efficiency characteristics as a function of particle size have been obtained, with better performance in the smaller size ranges.

Dynamic Light Scattering. Light scattering methodologies allow for both real-time and in situ monitoring of aerosols. The intensity of the elastically scattered light varies as the sixth power of diameter for nanoparticles. Because of this, the scattered light signals from nanoparticles are very small and cannot be detected reliably. Nonelastic light scattering methodologies, such as dynamic light scattering, have been used for measuring nanoparticles.[113,142] Dynamic light scattering, also called photon correlation spectroscopy, is the spectral broadening of the signal because of Brownian motion of the particles. In this method, the diffusion coefficient of the particles is determined by interpretation of the dynamically scattered light signal, and with knowledge of the temperature, an estimate of the particle size can be obtained. Clearly, this poses challenges because of difficulties in accurate determination of temperature, for example, in combustion systems. Moreover, the optics are rather complicated, and, hence, the technique is not extensively used in situ. However, there are several commercial instruments that are used offline to determine the fractional size distributions of particles in the nanometer-size regime.[143]

Characterization. Along with size distribution measurements, determining chemical composition and other properties of nanoparticles are also important. Developments in single particle mass spectrometers[144,145] allow the determination of composition as a function of size. In a single particle mass spectrometer, a size-classified particle is irradiated and fragmented with a high-intensity laser (optical targeting), and the molecular and atomic constituents are then introduced into a conventional mass spectrometer. Whereas previous designs of these instruments were not effective in the nanoparticle-size regimes, development of the aerodynamic lens[146–148] has resulted in better optical targeting to overcome the limitation.[149] Single-particle mass spectrometers have been primarily used for determining the composition of the atmospheric aerosols.[93] These devices have been used in a few laboratory studies to examine emissions from combustion systems;[150] however, more needs to be done with full-scale combustors, such as coal-fired power plants, smelters, incinerators, and other mobile sources. There is a need for the development of robust measurement and characterization methodologies for nanoparticles in full-scale industrial systems.

Some of the other characterization tools that are routinely used for nanoparticles are summarized in Table 3. Interesting features are observed in the nanoparticle size ranges. For example, broadening of X-ray diffraction peaks are observed, and the Scherrer equation can be used to determine crystal sizes.[151] Line shifts are observed in Raman spectra as has been demonstrated by Xu et al.[152] and Almquist and Biswas[153] for nanostructured titanium dioxide. Quantum effects in small nanoparticles also result in the separation of energy levels and increase of band gaps, which are correlated to particle sizes.[153,154]

A summary of important characteristics of several collection methods is provided in Table 4. Recommendations for the development of improved collection efficiency devices for the different methods are also provided.

ENVIRONMENTAL NANOTECHNOLOGIES

Nanoparticle-based technologies find applications in several environmental areas,[4,155] and some of these are listed in Figure 2. The applications of nanoparticles in environmental technologies are collectively referred to as "environmental nanotechnology." Because nanoparticles have enhanced structural, magnetic, electrical, and optical properties, they have a significant potential to replace existing materials. Because of their superior

Table 3. Nanoparticle characterization techniques.

Method	Observable
Electron microscopy (transmission and scanning)	Real space structure–particle size and morphology; particle morphology
X-ray diffraction	Phase and crystallite size measurements in the 4–40 nm range from Bragg peak linewidths using Scherrer formula[120]
BET surface area	Surface area and porosity of nanoparticles
UV-vis absorption spectroscopy	Fundamental optical gap; interpretation of band gap energies
Raman scattering	Phase analysis by phonons, crystallite size measurements by phonon linewidths; shifts as a function of size because of relaxation of selection rules
Mössbauer spectroscopy	Identification of magnetic behavior through internal fields: superparamagnetism by blocking temperature; identification of chemical shifts and quadrupole effects
FTIR spectroscopy	Vibrational spectra in infrared region. Analysis of surface adsorbed species such as OH radicals
Nuclear magnetic resonance	Localized bonding states (chemical shift and coupling constants) by detecting presence of specific nuclei
X-ray absorption spectroscopy EXAFS, XANES	Element-specific information on coordination environment to determine structure of nanocrystalline domains

Notes: BET = Brunauer-Emme H-Teller; FTIR = Fourtier transform infrared; EXAFS = edge X-ray absorption near edge structure; XANES = X-ray absorption fine structure.

properties, lower quantities will be used that will not only lower costs but also leave a reduced environmental footprint. Nanoparticles are finding applications in newer sensing technologies to detect pollutants at lower concentrations with greater selectivity and precision. Because of inherent size advantages they can be used to probe more difficult-to-reach regions, such as in the subsurface environment or complex engineered systems. Nanomaterials also find great applicability in existing processes to reduce or prevent emissions or to convert effluents to useful byproducts. Nanoparticles can also be used to clean up contaminants that are present in the environment because of deleterious past practices.

Table 4. Comparison of collection devices for capture of airborne nanoparticles.

Device	Operational Principle	Size Range (Efficiency)	Configurations	Key Advantages	Recommendations
Low-pressure cyclone	Inertia (although enhanced by other methods)	100–60 nm (>98%), 50 nm (~50%)	Axial, tangential, low pressure	Low pressure drop; ease of operation and low cost	• Improve capture efficiencies for nanoparticles by using additional force fields
Filtration	Diffusion and inertia	Up to 5 nm (>95%)	HEPA, packed bed, bag	High capture efficiencies	• Fundamental study of filtration (understanding transition between molecules and nanoparticle behavior) • Develop low pressure drop filters with high capture efficiencies
Thermal precipitators	Thermophoresis	1–100 nm (>99%)	Plate	Capture independent of particle size	• Determine scale up criteria (used only for small scale applications)
Electrostatic precipitators	Electrical mobility	60–100 nm (>95%) efficiency drops below 60%	Tubular, parallel plate	High capture efficiency with low pressure drop; low operating costs	• Understand charging of nanoparticles • Design of systems with other forms of radiation to enhance capture • More detailed studies of pathways of inactivation of biological particles • Compact high voltage sources, reduce cost

Material Substitution

Hazardous materials in manufacturing can be replaced by the more functional nanomaterials that are designed for specific, targeted functions resulting in reduced production of wastes. The more mature field of "green chemistry and green engineering" can guide the increased usage of nanomaterials.[156] For example, nanomaterial-based catalysts can be used in place of more harsh catalysts for the synthesis of compounds. Film reactors with environmentally benign nanostructured photocatalyst films have been demonstrated to be effective in the synthesis of partial oxygenates from different precursors.[125] In contrast to conventional processes that use harsh operating conditions and toxic materials, these processes are environmentally benign. For more effective implementation of such processes, a multiscale approach needs to be adopted. Such an approach includes developments at the molecular level, linking of these to fluid dynamics/transport, and reactor models at the micro- and macroscales. Studies at such disparate length and time scales are only possible by interdisciplinary research and collaborations among theoretical and computational specialists, engineers, chemists, and industrial partners (with experience in plant scale perspectives).[157] New classes of nanomaterials can also replace conventional materials with less toxicity and better performance.[4] As an example, field emission displays constructed with carbon nanotubes can provide better functionality than the conventional cathode ray tubes that contain many toxic metals.[158] The field emission displays use only 0.5 g of carbon nanotubes per monitor compared with the large amount of lead in cathode ray tubes.

Nanoparticle Sensors and Detectors

The need of sensing of pollutants and other compounds is of immense importance not only for public health protection but also in the design of safe and effective manufacturing processes. With the increase in potential terrorism acts, there is an increased need for effective sensors, and they are finding use in many homeland security applications. Developments in sensor technology have been under way for the last 2 decades, with an emphasis on miniaturization. Various nanostructured materials have been used in sensors. Upon exposure to gases such as NO_x, the electrical resistance of single-walled carbon nanotubes (SWCNTs) has been found to change dramatically. A chemically functionalized SWCNT with covalently attached poly m-aminobenzene sulfonic acid has been demonstrated to have improved sensor performance for detection of ammonia,[159] thus allowing higher sensitivity (as low as 5 ppm) than existing solid-state sensors.[160] Boron-doped silicon nanowires have been developed that are highly sensitive sensors for chemical and biological species.[161] Kennedy et al.[162] have developed a fully automated gas sensing and electronic parameter measurement system for testing miniaturized nanoparticle-based gas sensors. Such systems allow for the quick optimization of gas sensor configurations and for the understanding of their size-dependent properties. Gas sensing properties of zinc oxide (ZnO) nanostructures were found to have a sensitive response, good selectivity, and very short response time to very low concentrations of ethyl alcohol. Single crystal ZnO nanowires synthesized by gas-phase routes have been shown to be very sensitive to oxygen concentrations, with increased sensitivity at lower-wire radii.[163] The detection sensitivity of these nanowires could be modulated by altering the gate voltage of the n-type semiconductor to extend the concentration range over which oxygen could be detected.

Nanostructured Sorbents for Process Emissions Control

Understanding particle formation and growth dynamics in combustion systems would allow developing strategies to minimize emissions.[14] Several methods have been proposed for the control of toxic metal emissions from combustors.[14,164] The capture of heavy metal species in combustion systems by bulk sorbents has been demonstrated.[165,166] However, once the outer surface has chemisorbed the metallic species, the inner volume is rendered ineffective, thus requiring a large volume of bulk sorbent to trace metal that is being captured. Furthermore, the bulk sorbents have been ineffective in certain environments, for example, when chlorine is present.[167] They do not effectively suppress the nucleation of the heavy metal species that result in the formation of the submicrometer-sized aerosol that is difficult to capture in conventional particle control devices. An alternative is the use of a nanostructured sorbent agglomerate process to capture the heavy metals in combustion environments.[168–170] Several studies have been conducted to understand the effectiveness of this process for heavy metals, such as lead.[171] Capture efficiencies of lead exceeded 95% in a high-temperature environment on injection of a precursor that resulted in the formation of a nanostructured silica sorbent particle.

The understanding of metallic species formation and growth pathways has resulted in the use of sorbent injection methods to control and prevent the release of toxic metal species, such as lead, cadmium, and arsenic, from a variety of combustion systems.[165,168,169,172,173] The objective of the sorbent process is to suppress the homogenous nucleation pathway (to prevent eventual formation of the difficult-to-capture submicrometer-sized particles) and promote chemisorption of the metallic species vapors (to firmly bind the metal species to the sorbent to prevent

leaching into the water body when disposed), as illustrated in Figure 7. This is promoted by a large available specific surface area (increasing with decreasing particle size) of the sorbent material. It is essential that the sorbent particle is in a size range (preferably >500 nm[129,174]) that would result in its effective capture in a particle control device. These contrasting requirements are overcome by using a nanostructured agglomerate, which has a large specific surface area and is in an overall size range that would be effectively captured in a conventional particle control device.

Several sorbent materials, such as calcium, silica, and other oxides, complexes of aluminum-silicon, are effective in reacting and capturing heavy metal species.[14,169,175–180] As outlined earlier, there are several factors that determine the effectiveness of the sorbent for capture of the heavy metal species. Equilibrium calculations provide a feasibility determination and temperature range for the choice of sorbents.[181,182] These also allow qualitative comparisons of various types of sorbents and their effectiveness under a variety of combustion system conditions, such as temperature, equivalence ratios, and presence of other reactive species.

Mercury, a toxic element, primarily emitted from coal combustion systems, is a pollutant transported on a global scale. Brown et al.[183] have discussed several methods for mercury control. One of the most touted methods is that of activated and other forms of carbon. The carbon sorbents have been found to be most effective when they are impregnated at the nanoscale with functional groups that have a high affinity for mercury, such as halogens and other chelating groups.[184] Whereas carbonaceous species in various forms have been proven to be effective in the capture of mercury, there remains a problem of its low temperature applicability and problem of disposal when mixed with fly ash.[173] The use in packed or fluidized beds would result in additional costs because of the large flows that need to be treated in a typical full-scale coal combustor. Thus, significant research and development is currently under way to develop inorganic sorbents.[185–189]

To effectively design and scale up nanoparticle-based sorbent processes, the following need to be studied: (1) interaction of the metal species with sorbent compounds to elucidate pathways of capture and determine rates of chemisorption, (2) growth dynamics of the sorbent particles to determine injection locations to maximize the surface area of the agglomerate and its size, (3) pilot testing of these methodologies, and (4) cost comparisons with bulk sorbent methods.

Byproducts of value can sometimes be synthesized from nanoparticle effluents, thereby reducing emissions to the environment while offsetting control and disposal costs. Biswas et al.[190] proposed the injection of titanium-based precursor compounds into lead-enriched exhaust streams, such as that from a lead smelter to produce ferroelectric materials. This was successfully demonstrated in laboratory-scale studies. Zimmer and Biswas[191] suggested the use of magnetic fields to capture magnetic nanoparticles in a welding plume. This would protect the workers in an occupational setting, and at the same time produce high-value magnetic oxides. Zimmer[192] demonstrated the viability of using captured welding-generated aerosol particles for the treatment of contaminated water streams.

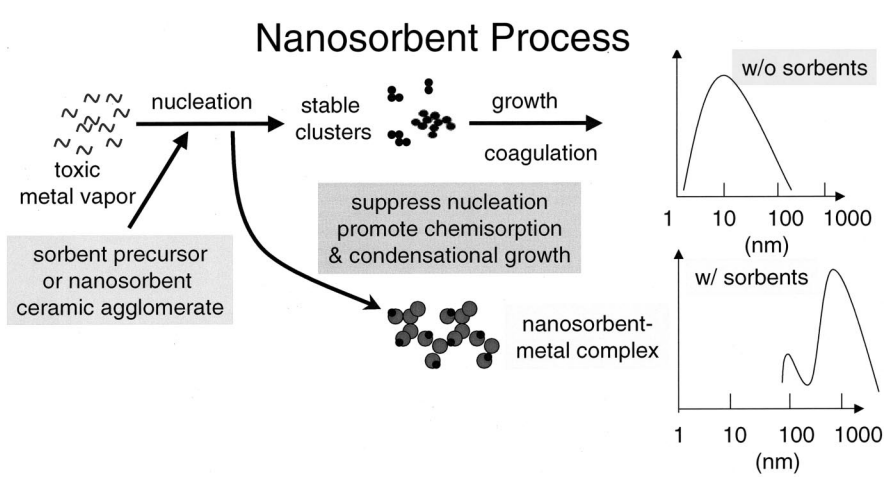

Figure 7. Mechanistic pathway of toxic metal species in combustion system resulting in particle formation. In the absence of the nanosorbent agglomerate, the resultant particles are in the difficult-to-capture submicrometer sizes. In the presence of nanosorbent agglomerates, nucleation is suppressed resulting in association of the metal species with the larger agglomerate particles that are readily captured.

Remediation and Waste Treatment

Groundwater is often contaminated by spills, agricultural practices, past waste disposal practices, and leaking underground storage tanks. Contaminated groundwater poses threats to human health by entering drinking water source streams, and it also damages ecosystems. Restoration of contaminated sites in the United States alone has been estimated to be a multibillion dollar industry.[193] Remediation is often difficult because of inaccessibility and slow mass transfer rates from nonaqueous phases. Nanoscale science and engineering may provide cost-effective and environmentally friendly options to restore such contaminated sites, both by direct conversion of contaminants by reaction on nanoparticle surfaces and by artificial enhancement of naturally

occurring biogeochemical reduction processes. Because of their high-specific surface area, nanoparticles exhibit enhanced reactivity with respect to their bulk counterparts. Size effects on reactivity at the solid-liquid interface are due to various reasons, such as the proportion of surface sites at edges or corners, the presence of distorted high-energy sites, contributions of interfacial free energies to chemical thermodynamics, the effects of altered surface regions, and quantum effects.[21,194]

Effective in situ remediation is possible by transporting nanoparticles through porous media. Injection of iron nanoparticles into the subsurface has been demonstrated to be effective in the degradation of chlorinated organic compounds to benign forms.[17,195,196] Fundamental studies have also been conducted on the transport of nanoparticles in porous media[100] and deposition onto surfaces.[197,198]

Nanoparticles can also be anchored onto substrates for the remediation of contaminated air and water streams.[199] Various methods of anchoring onto substrates, such as carbon,[200] zeolites,[201] silica gel,[188] and membranes,[202] have been demonstrated for the treatment of contaminated streams. The use of nanostructured film reactors has also been demonstrated to be effective at remediation. Different deposition techniques have been studied to control film characteristics to obtain optimal reactor performance.[125,203–205]

Various configurations of nanoparticles in different geometries have been proposed to adsorb species, such as organics and heavy metals. It has been reported that carbon nanotubes are more effective than activated carbon in sorption of various organics.[206,207] Onyango et al.[18] have demonstrated the effective adsorption of arsenic on zeolite active surfaces. The trapping and removal of heavy metals from contaminated water is a challenging problem, and just recently the National Academy of Engineering has announced an award of $1 million to inventors who come up with a system for the effective removal of arsenic from drinking water supplies.

Nanoparticles have been used in the field of catalysis for many decades. The best-known example is that of precious metal nanoparticles, such as Pt, Pd, and Rh, in catalytic converters to treat engine exhaust. The development of better nanoparticle synthesis methods and characterization tools, along with molecular design, has resulted in better catalytic materials. Bimetallics of nanoscale materials, such as iron/platinum and iron/palladium, have been demonstrated to be effective in the degradation of organic environmental contaminants.[208,209] Gold nanoparticles have been used for a variety of catalytic applications.[210] Schlogl and Hamid[211] examined whether the science of nanoparticles was really new or just being revisited and concluded that it is a new scientific arena with a lot more work to be done to fully realize the potential of nanocatalysts.

A class of compounds, the wide-band gap semiconductors, are finding applicability in remediation systems.[212,213] Optimum conditions for degrading specific compounds have been determined.[153,214–216] There are key factors that still need research and development before such wide-band gap semiconductors can be used effectively in remediation technologies. The first is the ability to synthesize these nanostructured materials with controlled size, composition, and morphology in scalable processes. Gas phase processes allow the scaling up of production methods with the ability to control these characteristics.[217] The second is the understanding of the fundamental reaction steps and relating them to the characteristics of the nanoparticles. The third is the ability to alter the band gap energies to increase the photoactivation at visible light frequencies. Methods such as nitrogen doping, transition metal doping, and dye sensitization are being researched (discussed in the "Nanoparticles and the Energy Sector" section, below).

NANOPARTICLES AND THE ENERGY SECTOR

In 2000, oil, natural gas, and coal accounted for 39, 24, and 22% of the U.S. energy supply, which totaled 3.3 tetrawatts.[218] Two-thirds of the oil was consumed by the transportation sector. By 2020, total consumption is projected to increase by 32% with roughly the same distribution among the fossil fuels. Fossil fuels are limited, because they are produced on geological time scales, whereas human beings consume them over shorter time scales. The rapid growth of secure energy needs coupled with the increasing demands for clean energy sources that do not increase the atmospheric loading of carbon dioxide and other pollutants have called for increased global attention to a "hydrogen economy," which is a potentially sustainable solution to future energy needs.[219] As outlined in Figure 8, the transition to a hydrogen economy is anticipated to take place over a few decades. Nanotechnology has a major role to play over this entire period. With our current reliance on fossil fuels, nanoparticle technologies should be used to minimize hazardous emissions (as described in the "Environmental Nanotechnologies" section, above). In the transition period, fossil fuel-based fuel cells, hybrid fuel cells, and hybrid electric vehicles will rely on the development of new nanomaterials. In the future, energy generation maybe distributed, and the development of more efficient solar cells and other nanomaterial-based technologies will be important. The adoption and eventual transition to the hydrogen economy will be dependent on the rapid development of the field of nanotechnology. As just one example, a sustainable method of hydrogen production is

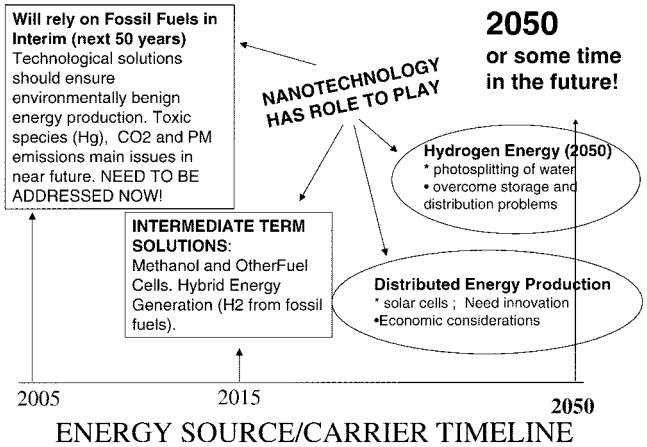

Figure 8. Role of nanotechnology in the transition to the hydrogen economy.

by photosplitting water using nanocatalysts that are activated by sunlight.

To accomplish this goal, the U.S. Department of Energy has initiated a National Hydrogen Vision and Roadmap.[220] Though hydrogen itself is not an energy source (because there is no natural hydrogen reserve), it can serve as an energy carrier. On a mass basis, the chemical energy of hydrogen (142 MJ/kg) is at least three times larger than that of other chemical fuels (e.g., 47 MJ/kg for gasoline). In addition to the reduction in carbon dioxide and other pollutants, there are numerous benefits of the hydrogen economy, including an abundant and sustainable supply, a diversity of end uses, convenient storage for load leveling, and flexible interchange with existing energy media. However, scientific and technical challenges in hydrogen production, storage, and use must be overcome to realize the hydrogen economy.[218]

Catalyst nanoparticles play a central role in the pursuit of the hydrogen economy because of the capability in converting solar energy to chemical energy, producing hydrogen from water or hydrocarbon-based fuels, and producing electricity from hydrogen in fuel cells. They also improve the efficiency of upload/release of stored hydrogen with reduced requirement of thermal activation. The extraordinary improvements in catalytic activity that depend on the nanoscale size and shape have enabled advances in these areas.[219] Understanding and controlling nanoscale processes at the interface of hydrogen with materials will dictate how fast the hydrogen economy will evolve.

Hydrogen Production

Current industrial-scale hydrogen production is by steam reforming of natural gas. However, carbon-neutral hydrogen production will rely on sun-energized resources (solar, biomass, and wind), nuclear energy, and geothermal resources. The power from the sun that is intercepted by Earth is $\sim 1.8 \times 10^{11}$ MW, many thousand times that of the current usage rate.[221] The key problems are the dilute nature of the incident radiation (not exceeding 1000 W m^{-2} as a highest) and the spatiotemporal variation. Efficient harvesting of solar energy for hydrogen generation by splitting water through photovoltaic (PV) cells or through direct photocatalysis at energy costs competitive with fossil fuels is a major enabling milestone for a viable hydrogen economy. Hydrogen produced in this way would be readily available for use without additional purification.

The economic viability of solar hydrogen depends on a high efficiency and a low cost of solar energy conversion. The sequential processes of light collection, charge separation, and transport in PV cells and photocatalytic devices are all key steps, and nanoscale architectural control will play a key role by improving the efficiency.[222] Currently, single crystal silicon PV cells have an efficiency ~25%, close to the theoretical solar energy conversion limit of 32%, although the cost/efficiency is too high for widespread use. Fujishima and Honda[223] demonstrated semiconductor oxides to photoelectrochemically split water. Grain boundary recombination reduces the quantum yield of light-to-electrical energy conversion. By doping metal ions (Fe, V, Mo, and Ru), researchers have successfully produced nanophotocatalysts with increased photoreactivity.[154,224,225] Nanoparticle materials with gradient composition also exhibit better electronic transfer properties than abrupt-type materials.[226,227] Grätzel cell[228] is a dye-sensitized photoelectrochemical cell that consists of a highly porous thin layer of nanocrystal TiO_2 aggregates coated with an organic dye. Under irradiation, the dye becomes energized and injects electrons into the TiO_2 thin film, which are then transmitted to a conducting glass electrode connected to an external circuit. The organic dye extends the absorption of wavelengths into the visible range, compared with the ultraviolet range by the TiO_2 nanocrystal itself, thus increasing solar conversion efficiency (~10%). The advantage of separation of optical absorption and charge-generation functions also includes resistance to photocorrosion. Khan et al.[229] doped carbon atoms into TiO_2 nanocrystals and reported a similar effect. Extremely thin absorber solar cells are based on a similar concept, except that the molecular dye is replaced by a 2–3-nm thin layer of a small-band gap semiconductor.[230] Tandem cells that connect two photosystems in series, one capturing the blue part of the solar spectrum and the other absorbing green and red light similar to the photosynthesis in green plants, have also been proposed.[228] Nanostructured organic conducting polymers (e.g., polymer/fullerene blends[231,232]) present another category of materials with potential for solar cells, although their efficiency and stability need improvement.

Multicomponent nanoparticles containing more than one absorber in various structures (e.g., core-shell, and strips in nanowires or branches) may additionally improve the energy conversion efficiency. Nanomaterials that absorb at multiple wavelengths prevent electron-hole recombination, provide short connection lengths between the excitation and collection points, and provide possible energy conversion improvement.

As the transition to widescale use of hydrogen as a fuel is under way, fossil or other hydrocarbon fuel resources will play an important role in hydrogen production. Nanocatalysts are needed for more efficient water-gas shift reactions (eq 1[233–236]), which can operate at a low temperature, are less susceptible to poisoning and fouling and are more stable.

$$CO + H_2O \xrightarrow{nanocatalyst} CO_2 + H_2 \quad (1)$$

Another important process is autothermal reforming,[237–239] where nanocatalysts also enhance the conversion. Chen and Goodman[240] reported that bilayer gold clusters on oxides exhibits high catalytic activity for CO oxidation, although gold in its bulk form is inert.

Hydrogen Storage

Hydrogen, produced from various sources and intended for diverse uses, needs to be effectively stored and delivered to the point of use. Depending on the application, there are different requirements for storage which are as follows: appropriate thermodynamic for hydrogen charge/discharge, fast kinetics, high storage capacity, gravimetric/volume densities, effective heat transfer, long cyclic lifetime, and high mechanical strength/durability/safety.[218] Mobile storage requirements are far more stringent and difficult than those for stationary systems. Onboard hydrogen storage is one of the most challenging obstacles to be overcome for realizing the widespread use as a fuel for the transportation sector. Table 5 summarizes mobile storage system requirements.

Hydrogen can be stored as a high pressure gas, liquid, or solid. Gaseous and liquid hydrogen storage systems are more mature techniques at present. However, they will not meet the FreedomCar[220] criteria because of their low energy density (4.4 MJ/L at 10 kpsi for gaseous storage and 8.4 MJ/L for liquid storage, compared with 31.6 MJ/L for gasoline). A large tank will be needed to run such a vehicle (e.g., 225 L at 200 bar for high pressure tanks to run 400 km). Additionally, the amount of energy required for pressurization and liquefaction is one-third of the energy value of the hydrogen stored. Solid storage in the form of metal hydrides, chemical storage materials, and nanostructured materials are considered to have the best opportunity to meet the requirements for onboard storage.

Table 5. FreedomCar hydrogen storage system targets.

Targeted Factor	2007	2010	2015
Specific energy (kWhr/kg)	1.5	2	3
Hydrogen (wt %)	4.5	6.0	9.0
Energy density (kWhr/L)	1.2	1.5	2.7
System cost ($/kWhr/system)	6	4	2
Fuel cost ($/gallon of gasoline equivalent)	3	1.5	1.3
Operating temperature (°C)	−20/50	−30/50	−40/60
Cycle life-time (absorption/desorption cycles)	500	1000	1500
Minimum flow rate (g/sec/kW)	0.02	0.02	0.02
Min/max delivery pressure (atmosphere)	8/100	4/100	3/100
Transit response (sec)	1.75	0.75	0.5
System fill time for 5 kg H_2 (min)	10	3.0	2.5
Loss of useable H_2 (g/hr/H_2 stored)	1	0.1	0.05

Note: Adapted from U.S. Department of Energy.[220]

Reversible metal hydrides may represent ideal storage systems.[241] Metal hydrides have comparable volume density to hydrocarbon fuels, although they are heavier. A database[242] lists more than 2000 elements, compounds, and alloys that form metal hydrides and reversibly release hydrogen. In metal hydrides, hydrogen atoms fill in tetrahedral or octahedral interstitial sites of the metal matrix. Upon release, atomic hydrogen recombines at particle surfaces to form molecular hydrogen. Magnesium (Mg), a light metal, has a promising storage level (7.6 wt %) and releases hydrogen at high temperature (300 °C at 1 bar). Other light elements (lithium [Li], boron [B], sodium [Na] and aluminum [Al]) and their alloys are also candidates. The alanates (e.g., $NaAlH_4$ and Na_3AlH_6) or borohydrides (e.g., $LiBH_4$) have even higher densities (7.4 and 18 wt %, respectively). Hydrogen release from these storage materials can start at a lower temperature than release from Mg and continue at several temperature stages. These materials still need to have significant improvement of storage capacity, energy density, hydrogen uptake, release kinetics, and cycling durability to meet FreedomCar targets. The improvement can be accomplished by nanostructuring the metals. Ball milling is the most commonly used method to prepare such materials, because it can reduce grain size, increase defect concentration that facilitates hydrogen transport, shorten hydrogen diffusion distance, and reduce heat.[243–245] Hydrogen storage improvement can also be achieved by adding transition metal nanocatalysts (e.g., V, Ti, Mn, Fe, and Ni[246]), their oxides,[247,248] or Pd.[249] Interactions between nonhydride-forming catalysts (e.g., Ni and Fe) and hydride-forming elements (e.g., Mg) alter the bond strengths and enhance kinetics and thermodynamics.[250] Mixing

hydrides to make multicomponent complex hydrides have also been proposed.[218] In such a system, the ionic bonding of hydrogen-rich anions with light element cations can bridge the gap between hydrogen-poor intermatellic hydrides and hydrogen-rich compounds with slower kinetics.

Nanoscale materials can be classified into two categories: atomic/dissociative and molecular/nondissociative. For the first category, hydrogen molecules are split into hydrogen atoms that are then bonded within the lattice of the material (similar to the metal hydrides discussed above with improved kinetics). For the second category, hydrogen in the molecular state is stored via molecular-surface interactions (van der Waals force). Hydrogen stored in carbon materials has been correlated well with the material's surface area.[251–253] Numerical simulations show that hydrogen can be adsorbed both inside and on the surface of carbon nanotubes.[254] Nanostructured materials relying on physical adsorption (e.g., carbon nanotubes, graphite, zeolite, aerogels, or xerogels) have low hydrogen storage capacity and require low temperatures for storage. Carbon-based material may need to prevent the formation of hydrocarbons if chemisorption does occur.[255]

Fuel Cells

Fuel cells transform chemical energy into electrical energy, and nanocatalysts enhance the transformation. Alkaline fuel cells have provided energy for space missions since the 1960s. A fuel cell is an electrochemical cell consisting of two electrodes separated by an ionically conducting medium (electrolyte). Good efficiency comes from close contact of the electrolyte, gaseous reactants, electrocatalyst, and current collector (a triple-phase-boundary interface). Because fuel cells do not rely on the heat of combustion, the energy conversion efficiency is much higher than that of conventional internal combustion engines or boilers. Materials used for fuel cells are determined by their operating temperature: low (polymer and alkaline), medium (phosphoric acid), and high (solid oxide and molten carbonate). Nanomaterials that are stable and durable in rigorous chemical environments and under varying thermal cycles are needed.

The electrodes are electronically conductive and electrocatalytically facilitate the reaction of fuel (at the anode) and of oxygen (at the cathode). The U.S. Department of Energy[256] has set a 2010 goal of fuel-cell demonstration vehicles with 480-km (300-mi) range, a lifetime of 2000 hr, and a cost of $125 per kW. Most recent research and development efforts focus on low-temperature polymer proton exchange membrane fuel cells (PEMFCs) and high-temperature solid oxide fuel cells (SOFCs). The PEMFC is the primary type expected to be used for the transportation segment. For low-temperature fuel cells, fluoropolymer conductors (Teflon with metal or carbon powders that provide the electronic pathways) are used with Nafion being the workhorse. Highly dispersed Pt nanoparticles as the electrocatalyst are embedded in porous composites of ionic/electronic conductors. Because Pt supply is expensive, an alternative is sought for large-scale automotive applications, such as a submonolayer/monolayer amount of Pt coated on polymer particles.[257–260] Other challenges for PEMFCs include (1) durability, (2) selective transport of hydrogen and oxygen that can eliminate critical contaminants or prevent leakage transport between fuel cell compartments, (3) proton conduction properties at elevated temperatures, (4) ability to operate at a lower relative humidity, (5) tolerance of impurity in the fuel, and (6) minimal polymer degradation over the long operating life. Nanostructured materials other than fluoropolymer are also emerging, including hydrocarbon-based and polybenzimidazole-based nanocomposite membranes.[261,262] Besides PEMFC, direct methanol fuel cell (DMFC) is also a viable technology (e.g., radiografted membranes[263]). It does not require fuel processing equipment, and therefore avoids humidification and thermal management problems associated with the PEMFC. One main issue with the DMFC is that methanol behaves like water and will penetrate through membrane materials resulting in a loss of fuel. The development of innovative membrane materials can solve this problem. In pure hydrogen and air, Pt is the most active material. However, oxidation of adsorbed CO species on Pt is slow and, therefore, it cannot be used in a system where CO may be present or in a DMFC. Binary nanoparticles that have enhanced CO oxidation by higher oxygen storage (e.g., Ru/Pt[264] and ceria[265]) are being developed to address this issue.

SOFCs rely on solid oxides to transport oxygen ions from the cathode to the anode that typically operate between 500 and 1000 °C. The advantages of SOFCs include the use of a wide range of fuels, long lifetime, and long runtime. The barriers are lower power density, inability to withstand thermal cycles, and material corrosion. The most common materials used are yttria-stabilized zirconia for the anode as well as the electrolyte, and lanthanum-strontium manganese oxide ($LaSrMnO_3$) for the cathode. For the anode, Ni nanoparticles are used as electrocatalysts, although coking is an issue. During material preparation, the key challenge is to select compounds for the electrodes and the electrolyte that do not react with each other and have no thermal expansion mismatch. There is a strong interest in the development of intermediate temperature SOFCs, and new nanomaterials are being sought for this purpose. $Ce_{0.9}Gd_{0.1}O_{1.95}$ and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ are such candidates for the

intermediate temperature anode and electrolyte.[266,267] Because materials for the cathode also need to function at lower temperature (<500 °C), some ceramic components need to be replaced with metals. Anode catalysts that can process fuels other than hydrogen are also sought (e.g., formic acid by a PtBi-ordered intermetallic electrode[268]).

Environmental Impact

Although the primary benefits of the hydrogen economy on the environment are rather clear, it is important that we recognize the possibility of indirect effects of anthropogenic hydrogen emissions on the complex and dynamic environment. Preliminary modeling results show that an increased concentration of hydrogen in the atmosphere can potentially do the following: (1) influence the atmosphere's oxidizing capacity (e.g., by scavenging OH radicals[269]), (2) interfere with the stratospheric ozone (by increasing the moisture[270]), (3) alter the pace of climate change (by indirectly increasing the lifetime of methane), and (4) influence the hydrogen-consuming microbial ecosystems in subsurface soils.[271,272] Similar to nanoparticles, the potential release of hydrogen into the environment should also be assessed for its impact.

Several nanocatalysts are used in a hydrogen system. During the repeated charging/discharging cycles of reversible metal hydrides, high-volume change (expansion/shrinkage) induced by the metal/hydride transformation may result in the release (emission) of the nanocatalysts. Such a release from the matrix should be considered in the design of the metal hydride materials and should be assessed before practical applications are implemented. Another scenario where nanoparticles may be released is when the materials are in sudden contact with air or water (e.g., rupture of the safety packaging). This is aggravated by the high-specific surface area combined with the high exothermal potential of the metals.[22]

Batteries

Batteries play an important role in energy storage.[273] Lead acid batteries are common in automotive and stationary markets, whereas Li ion cells have dominated the portable batteries market (63% in 2001) in recent years. Research and development efforts are seeking engineered materials that can electrochemically provide the energy that meet the gravimetric and volumetric capacity requirements. Among several routes taken, nanostructuring the material to obtain high porosity and surface area constitute an unexploited opportunity. Vanadia (V_2O_5) aerogels, networks with nanometer domains, have been reported to improve the storage capacity 100% over its powder counterpart.[274,275] Transition metal nanoparticles (Co, Ni, Fe, Cu, or Mn) enhance the kinetics of Li_2O formation and decomposition and, therefore, can improve the capacity of Li batteries two- or three-fold.[276] Nanoparticle fillers, such as Al_2O_3 or TiO_2, are added to a polymer electrolyte (e.g., polyethylene oxide) to increase the electrolyte conductivity several-fold; these fillers also prevent the crystallization of the polymer. Both are important to increased Li transport.[277]

HEALTH AND ENVIRONMENTAL EFFECTS

The determination of exposure to nanoparticles is an important aspect before eventual health impacts can be established. Although there are many studies on the exposure to chemicals and particles in occupational environments, data on the exposure to nanoparticles are just emerging. Limited data and guidelines are available for handling and dealing with nanoparticles, not only in occupational settings but also in research laboratories. Because of the lack of knowledge, there are no adequate guidelines for respiratory protection selection for specific nanoparticle system applications.

Fine ($PM_{2.5}$) particle mass has been demonstrated to be associated with increased symptoms and deaths from cardiovascular and respiratory causes.[278–282] Results for such effects due to ultrafine particles are also emerging in a few studies.[283–288] In some studies, fine particles have been reported to be more strongly related to certain symptoms than ultrafine particles (e.g., De Hartog et al.[288]), whereas in others ultrafine particles are reported to have stronger effects (e.g., Peters et al.[289] and Penttinen et al.[285]). More investigations are needed to have a better and clearer understanding of the health effects of nanoparticles, one of the causes for greatest concern of the public. Because this subject spans many dimensions, organized and integrated efforts from various government agencies and researchers are needed. A holistic picture of the key subjects to be studied in terms of health and environmental effects along with the federal agencies responsible for each subject is summarized in Figure 9. However, it should be noted that resources allocated for assessing environmental impact are pretty low. In fiscal year 2003, only $200,000 out of the $700 million investment in nanotechnology research was provided to address environmental impacts[290] in the United States. Significantly greater investment in research is essential in the near future, and this will help answer the vital questions and derive solutions that will enable society to rapidly adopt and implement nanotechnologies.

The human body has three major contacts with the environment: the skin, the lungs, and the gastrointestinal tract. The uptake through the gastrointestinal tract has been reviewed by Hussain et al.[291] A complex mix of compounds in the gastrointestinal tract can interact with the nanoparticles and reduce the adverse effects of ingested toxins. The most critical concern with regard to

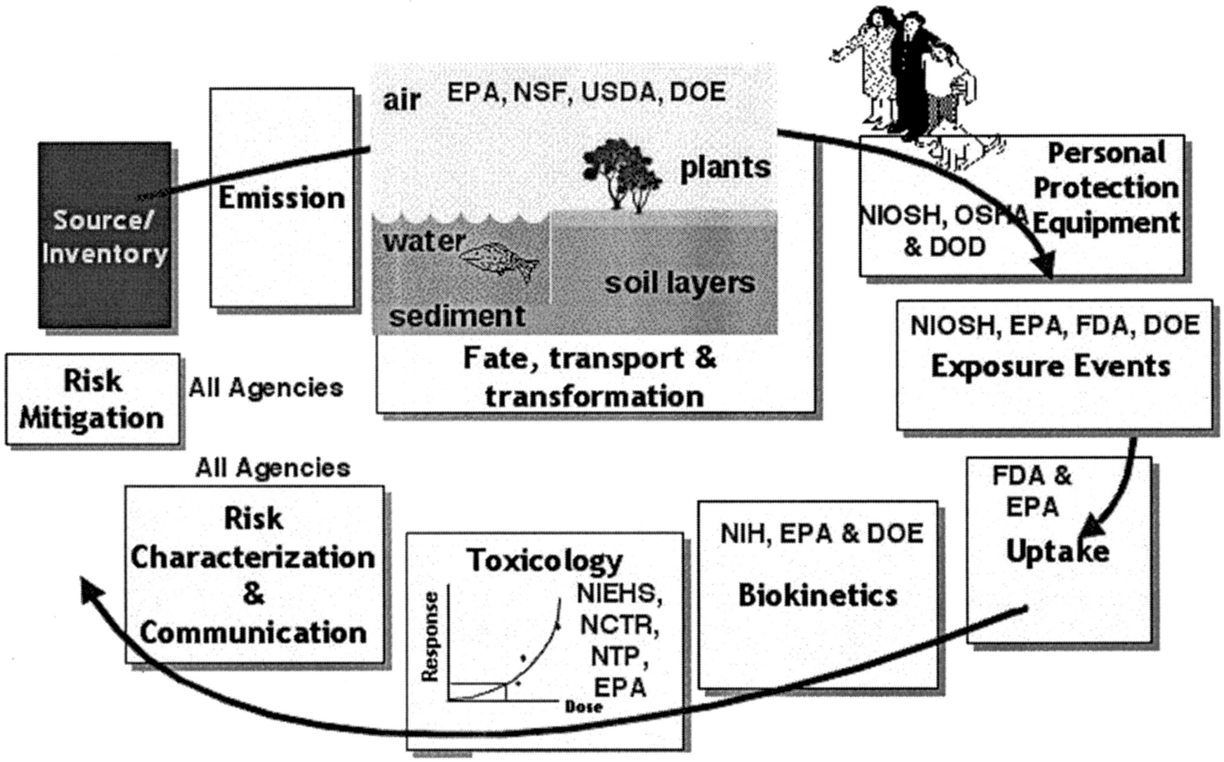

Figure 9. Key subjects in the health and environmental of nanoparticles. (Adapted from Luster[330].)

potential health and environmental effects of nanoparticles are when they are gas-borne as aerosols. Nanoparticles in the air have a high mobility and can enter into the human body through the inhalation route. Although there are some defense mechanisms, the alveolar tissue is not as well protected against environmental damages as the skin and gastrointestinal tract and is, therefore, the most vulnerable contact site. Human lungs have adapted to function and fulfill their work under natural exposure to particles,[22] so the challenge lies in understanding the effects of manmade nanoparticles, especially from traffic, energy production, or industrial processes.

Several hypotheses concerning physiochemical characteristics of particles responsible for adverse health effects have been proposed.[292,293] These include general properties, such as surface area or size, and also more specific chemical properties, such as acidity or metal content.[292,294] Particle number and surface area[10,289] may cause larger effects than mass concentration. Nanoparticles also act synergistically with other pollutants, such as O_3 or NO_x.[287,295,296] The complex interactions between particles and gaseous components complicate the assessment of the nanoparticle effects.

It should be emphasized, however, that nanoparticles have also provided a wide spectrum of opportunities for better quality of life by advancing our capability in diagnosis and treating diseases. Various agencies (e.g., National Institutes of Health) have placed significant sources and efforts to develop nanotechnologies for improving human health.

Respiratory Deposition

The deposition and clearance rate of ultrafine particles is a critical factor in assessing their health effects. Inhaled ultrafine particles can effectively deposit in human lungs (40–50% deposition fraction of 40-nm particles[297]) primarily by diffusion, and a large fraction deposits in the alveoli.[298] Fine submicrometer particles, which account for most of the $PM_{2.5}$, have a lower deposition rate and a smaller fraction deposit in the alveoli. Nanoparticles decrease the ability of alveolar macrophages to clear out foreign particles, because their large numbers are overwhelming.[299,300] This results in an increased contact time between particles and lung epithelial cells.

Cheng et al.[301–303] measured the deposition of ultrafine particles in the human nasal/oral region, finding that nasal deposition increased with decreasing human age. The results agreed with turbulent diffusion deposition models. However, variability among individuals was observed, implying the need for population-wide dosimetry. Cohen et al.[304] measured the deposition of 40-nm particles in adult human tracheobronchial (TB) airways and reported higher deposition (by a factor of 9) than the theoretical prediction for laminar flow. Deposition in other regions was two times higher than predicted. Smith et al.[305] examined the deposition of ultrafine particles

(1.75, 10, and 40 nm) in TB airways of humans of various ages (3, 16, and 23 years old). The results showed that deposition models for diffusion from laminar, parabolic flow underestimated aerosol deposition, whereas the plug flow deposition models overestimated TB deposition. Deposition in the 3-year-old was higher than that for the others, and deposition of 1.75-nm particles was substantially higher than the larger diameters. An important factor reported by Cohen et al.[306,307] was the influence of electrostatic charge of the ultrafine particles. Charged particles have higher deposition efficiencies as compared with neutral particles. Most studies have focused on spherical nanoparticles. Many engineered nanomaterials, such as carbon nanotubes, are nonspherical, or nanoparticles in an agglomerated state[308] and have not received full evaluation yet.

Mathematical models to describe respiratory deposition, clearance, and retention (i.e., biokinetic information) of aerosols are available (e.g., the International Commission on Radiological Protection model[309,310] and the National Council on Radiation Protection and Measurement model[311]). These models have been developed based on an experimental database of elements with isotopes, and they have been assumed to be applicable to nonradioactive substances as well, because they rely on the same physical mechanisms for deposition and clearance. These models have been validated for nanoparticles <5 nm (by measurement of radon progeny) and for particles >100 nm (by attaching radioactive labels). However, the model parameter values are interpolated for particle sizes between 5 and 100 nm, and this needs to be validated. The biokinetic database, currently available only for elements with isotopes, also needs to be established for nonelemental compounds, because nanoparticle biochemistry is a function of size and composition. Mathematical modeling on a theoretical basis (instead of fitting experimental data) can provide insights into the mechanisms. Such models have started to emerge (e.g. Broday[312]), although theoretical predictions only qualitatively explain experimental data trends. The difference indicates a lack of understanding of the mechanisms involved.

Translocation

Because of their small size and, therefore, high diffusivity, inhaled nanoparticles are effectively deposited in all of the respiratory regions (nasal, TB, and alveolar). The mucociliary escalator is an efficient transport system to clear particles in the upper airways, whereas macrophage phagocytosis is the dominant clearance mechanism in the deep lung. However, these mechanisms may not work for nanoparticles. Nanoparticles can be translocated to interstitial sites in the respiratory tract (defined as "biopersistent"). Alternatively, they penetrate the alveolar epithelial barrier and enter the blood stream and lymphatic system for transport to extrapulmonary organs.[298] Using different testing materials, researchers have observed translocations to various organs: graphite carbon to the liver within 4–24 hr of exposure,[313,314] 30-nm gold in platelet,[315] or 60-nm polystyrene causing thrombus.[316,317] Comparing fine (250 nm) and ultrafine (20 nm) TiO_2 particles, Oberdörster et al.[299] observed much more translocation of the ultrafine to the pulmonary interstitium and persistence than the fine. In a study using 18- and 60-nm (CMD) iridium in rats, Kreyling et al.[318] found only minimal translocation (<1%) into secondary organs. However, there was 10 times more translocation for 15-nm-sized particles compared with 80-nm-sized particles. Protein binding was suspected to be the mechanism. Different materials may have different fates depending on their physical, chemical, and biological properties. A systematic study of translocation covering a range of materials would provide a true picture.

The influence of ultrafine particles on extrapulmonary organs has been recognized.[319] Most studies focus on the effect on the cardiovascular system (e.g., low heart rate variability because of the effects on cardiac autonomic control).[320,321] The fact that ultrafine particles can be translocated certainly infers the potential impact on other systems, such as liver and kidney. There are two hypotheses for the effects on extrapulmonary systems: (1) strong pulmonary inflammatory reactions in the lungs lead to the release of mediators that can influence the heart or other cardiovascular end points, and (2) translocation of nanoparticles from the lungs into systemic circulation directly impacts the cardiovascular system. Nemmar et al.[322] reported lung inflammation and thrombosis by ultrafine particles (60 nm) but only lung inflammation by fine particles (400 nm), suggesting the importance of systemic translocation from the lung into the blood. There may be several factors that determine the contribution from each mechanism, although currently the factors are not clearly characterized yet. The understanding of these mechanisms will also help manage in the administration of macromolecular or nanosized drugs by inhalation.

Translocation not only occurs from nanoparticles deposited in the lung, but also from those in the nasal region (e.g., olfactory pathway). Oberdörster et al.[323] observed a persistent accumulation of ultrafine graphite rods (CMD = 30 nm, concentration = 170 $\mu g/m^3$) in the olfactory bulb of rats. Olfactory pathways in mammals have been reported to be the responsible mechanism for selective transport of xenobiotics to the brain.[324] The same pathways have been reported for viruses (30-nm

Polio virus[325]), colloidal gold (50 nm[326]), and microspheres (40 nm[327]).

Toxicity: Particle-Cell Interactions

Much of our knowledge of the health effects of particles has originated from pharmaceutical research, such as drug delivery, toxicology (xenobiotics), and pharmacotoxico kinetics. Donaldson et al.[13] discuss mechanisms of particle-lung cell interactions as shown in Figure 10. Failed clearance may result from the following: (1) overloading, and (2) particle-mediated macrophage toxicity or impairment of motility. Prolonged interaction between the particles and cells is an important factor in stimulating inflammation and interstitial transfer of the particles. A large number of deposited particles per unit of mass exceed the maximum ability of macrophages to phagocytose them. The responses are different depending on whether the particles are intrinsically toxic (such as quartz) or not (such as carbon and TiO_2). For nontoxic materials, the effective dose that mediates toxicity correlates well with particle surface area. Many materials regarded as inert have demonstrated strong responses when they are in the form of nanoparticles (e.g., 30-nm Teflon fume[328]). For toxic materials, surface chemistry resulting from the high surface area of nanoparticles has a profound effect. Transition metals in many nanoparticles can generate free radicals leading to oxidative damage and cell stimulation. Nanoparticles introduced into other organs also induce oxidative stress (e.g., liver[329]). Figure 11 shows the important pathways and mechanisms regarding toxicity of nanoparticles that should be investigated.[330]

There are numerous types of nanoparticles: TiO_2, carbon (carbon black and nanotubes), and transition metals are some of the commonly used or prevalent nanomaterials, and their health impacts are discussed below.

Toxicity: TiO_2

TiO_2, a commonly used photocatalyst, is one of the candidates of great interest. Ferin et al.[331] pointed out the issue of inhalation toxicity of TiO_2 ultrafine particles to be related to number of particles, particle size, delivered dose, and delivered dose rate. Donaldson et al.[332] suggested that the TiO_2 nanoparticle surface might be more reactive than their larger particle counterparts. In many experimental studies[13,278,300,332,333] where particles were inhaled or instilled, a great inflammatory response was observed for nanoparticles compared with fine particles. The role of surface area, however, was not evaluated in these studies. In a comparison of exposure (10 mg/m^3) of 20-nm particles[334] and of 500-nm particles,[335] higher lung tumor incidence was found in the nanoparticles case, suggesting the importance of small particle size or high number concentration. Oberdörster[298] instilled TiO_2 particles into rat lungs and found different results. For the same mass of particles, nanoparticles (d_p = 20 nm) yielded a greater inflammatory response than fine particles (d_p = 250 nm). However, when normalized to particle

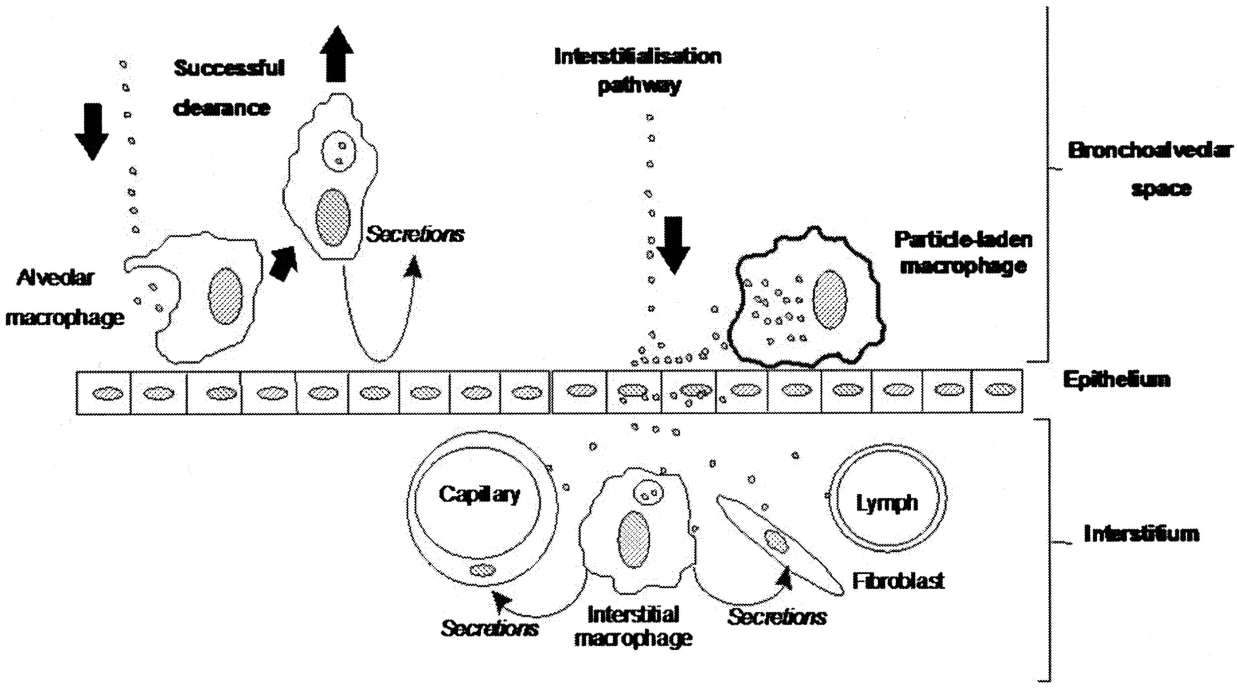

Figure 10. Fate of particles (left) cleared by the normal pathway and (right) those that enter the interstitial compartment of the lung. (Reprinted from Donaldson et al.[13] with permission from Elsevier.)

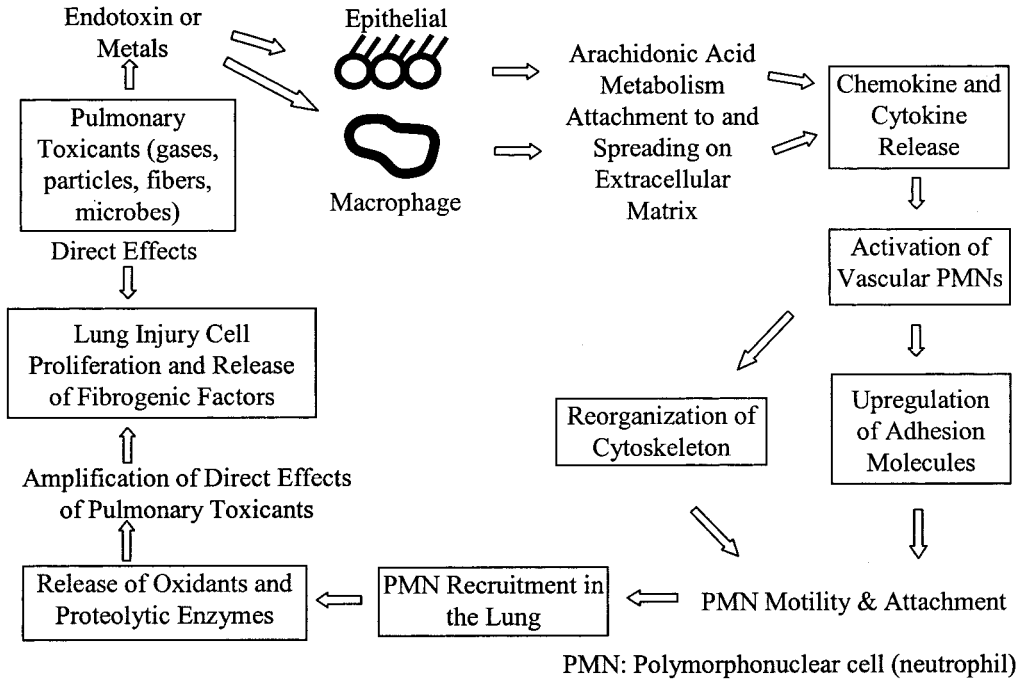

Figure 11. Pathways and mechanisms of nanoparticle toxicity. (Adapted from Luster[330] with permission from Dr. Michael Luster.)

surface area, there was no difference in the response. Their results suggest no special reactivity for TiO_2 nanoparticles.[336] Bermudez et al.[337] examined pulmonary responses of mice, rats, and hamsters exposed to ultrafine TiO_2 (P25, Degussa) and found species-based differences. Rats developed more inflammatory response and, subsequently, progressive epithelial and fibroproliferative changes. Interstitial accumulation and alveolar septal fibrosis were also observed. Particle clearance from lungs was impaired in mice and rats at 10 mg/m^3 concentration levels, whereas hamsters did not appear to be affected. The differences imply different biological mechanisms in different species and question the extrapolation of rodent sensitivity to human responses.

Because of its presence in sunscreen, TiO_2 has been studied for effects of dermal contact. Ultrafine TiO_2 particles (20–100 nm) were observed on the outermost surface of the stratum corneum and follicle areas but not detected in deeper layers of the human epidermis and dermis.[338–340] TiO_2 particles in sunscreen have also been observed in the deeper parts of the hair bulb and papilla, but this does not represent penetration into skin layers because of a barrier horny layer that covers the follicular channel.

Toxicity: Carbon Black and Carbon Nanotube

Arts et al.[341] exposed rats and mice to carbon black nanoparticles (CMD ~30 nm; 10^5-10^6cm^{-3}; 5–13 μg/m^3) and observed no signs of lung injury. Larger particles with greater masses (aggregate CMD ~450 nm; 10^4-10^5 cm^{-3}; 2–6 mg/m^3) resulted in early signs of lung injury, although these aggregates were composed of 30–100-nm primary particles. Gilmour et al.,[342] on the other hand, showed proinflammatory effects (an increase in total bronchoalveolar lavage leukocytes, total number of leukocytes, and macrophage inflammatory protein-2 mRNA) of exposure to ultrafine (primary d_p of 14 nm with agglomerate CMD of 114 nm; 1.7 mg/m^3; 5×10^4 cm^{-3}) that exceeded carbon black particles (CMD = 268 nm; 1.4 mg/m^3; 4×10^3 cm^{-3}).

In testing SWCNT in rats and mice, toxicity was found in the form of granuloma and inflammation.[343,344] Shvedova et al.[345,346] exposed immortalized human epidermal keratinocytes and bronchial epithelial cells to SWCNT for 18 hr. They observed the formation of free radicals, including the accumulation of peroxidative products, antioxidant depletion, and loss of cell viability. The exposure also caused ultrastructural and morphological changes in these cells. They attributed the damages to SWCNT-associated ferrous iron that produced free radicals in cells and biological fluids. Mechanisms of nanotube-specific toxicity of refined CNT that has no transition metals, however, have not been evaluated. The association of toxicity with particle size, surface area, and surface reactivity needs to be established.

Sayes et al.[347] examined the cytotoxicity of water-soluble fullerenes (nano-C_{60}) using human dermal fibroblasts and human liver carcinoma cells (HepG2). Toxicity changed with relatively minor alterations in fullerene structure. The formation of superoxide anions was

thought to be responsible for membrane damage, whereas water-soluble functional groups on the surface decreased toxicity.

Toxicity: Transition Metals

The importance of iron is evidenced by the increased risk of respiratory-tract cancers in industrial workers exposed to excessive airborne ferrous materials.[348,349] Iron is also a risk factor for many infections and inflammatory dermatological diseases.[350–352] The toxicity of iron nanoparticles results from its ability to generate OH radicals, which are highly oxidizing and, therefore, damaging to biological systems through the Fenton reaction.[13,353–355] Shvedova et al.[346] reported the role of SWCNT-associated ferrous iron in cells and biological fluids through the following reactions:

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \quad (2)$$

$$Fe_{3+} + A_{\mathrm{red}}^- \rightarrow Fe^{2+} + A_{\mathrm{ox}} \quad (3)$$

$$O_2^- + O_2^- + 2H^+ \rightarrow O_2 + H_2O_2 \quad (4)$$

$$Fe^{2\,+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (5)$$

$$LOOH + Fe^{2+} \rightarrow Fe^{3+} + \cdot LO + OH^- \quad (6)$$

where A_{red}^- is a physiological relevant reductant, A_{ox} is the oxidized product, and *LOOH* is a lipid peroxide. Atmospheric reactions can reduce particulate Fe^{3+} to Fe^{2+}, enhancing the impact of Fe^{2+}.

Other transition metals, such as nickel, cobalt, zinc, and copper, also cause health effects. Ultrafine nickel and cobalt have been demonstrated for their ability to enhanced inflammation resulting from free radicals.[208,356] Studies[357–359] demonstrated the pulmonary effects of zinc oxide and copper oxide ultrafine particles from smelters and coal combustors. Sulfur oxides coating on the particles increased the effect.

Nanomedicine

Numerous research studies have embarked to harness the power of nanoparticles to improve human health, such as the treatment of cancer. Nanotechnology is a multifunctional tool for cancer diagnosis, prevention, and treatment.[360] Because of their similarity in size to large biological macromolecules, such as enzymes and receptors, nanoparticles can readily interact with biomolecules both on the cell surface and within the cell without altering the behavior and properties of the molecules. Multicomponent magnetic nanorods for high sensitivity and high selectivity biodetection with separation and purification capabilities have been developed.[361,362] Chan and Nie[363] prepared bioconjugated quantum dots by chemically binding quantum dots to particular genes and proteins. Based on the different colors, the quantum dots absorb or emit at different wavelengths as their sizes change. Multifunctional nanoparticles can serve as fluorescent contrast agents in magnetic resonance imaging for cancer diagnosis or to monitor the performance of drug therapy. Multifunctional nanoparticles with a magnetic core, silica shell, optical probes, and cell-surface receptor ligands have also been proposed.[360] The ligands bind specifically to molecules found on the surface of cancer cells, thus allowing the delivery of anticancer drugs directly to tumor cells and their supporting endothelial cells without unpalatable side effects. Another research front is the development of "smart" nanostructures that are capable of detecting malignant cells in vivo, finding out the cell location in the body, destroying the cells, and reporting back the accomplishment of their task. One design[364,365] coats the surface of the "nanoclinics" with a tumor-homing monoclonal antibody for cancer cell detection and polyethylene glycol to shield it from immune system detection. The matrix is loaded with contrast agents to provide enhanced sensitivity for locating the cells and with therapeutic agents that activate when a malignant cell is detected.

Impact on the Environment

Unintentional nanoparticle release into the environment can lead to unknown consequences (e.g., nanomedicine as a new class of toxins). The environmental impact is determined by numerous factors, the first one being the residence time. Particles in the 0.1–10 μm range have the longest residence time in the atmosphere. Nanoparticles have short residence times because of their fast diffusion to and deposition on surfaces, coagulation with larger particles, and evaporation of their semivolatile components. However, nanoparticles attached to the accumulation mode particles remain in the atmosphere for essentially as long as the accumulation mode particles and participate in the atmospheric chemistry and physics. Jakab et al.[366] reported the specific surface area of diesel exhaust particles to be in the range of 100 m^2/g, which corresponds to the specific surface area of 30-nm carbon spheres. This implies that essentially all the surface area of individual primary particles that comprise the aggregates is available for surface interactions, such as reaction and adsorption. The optical properties of particles affect atmospheric visibility and building soiling. Diesel particles can

strongly absorb light because of their black carbon content, which can contribute to global warming. Nanoparticles are not efficient light scatters, because they are much smaller than the 400–700-nm visible light spectra.

Once engineered nanomaterials are released into the environment, their transport is the critical parameter in assessing the exposure/impact. Systems of concern include underground aquifers and water treatment plant filters, among others. It is desired to have low mobility for nanomaterials that are not intended to be released, but high mobility is desired for nanomaterials that are designed to be dispersed into the environment (e.g., Zhang and Wang[16]). Transport of nanoparticles is dominated by Brownian diffusion, whereas forces such as the London-van der Waals and double-layered forces are responsible for attachment that ultimately determines the mobility.[197] Water-soluble fullerol (C_{60} hydroxide, or $C_{60}[OH]_m$, m = 22–26) and SWCNT have the highest mobility, whereas colloidal aggregates of insoluble $C_{60,}$ anatase TiO_2, and ferroxane are the least mobile.[100,367] The hydrophobicity of a material is responsible for the difference in the mobility, implying the influence of naturally occurring polyelectrolytes in the environment as surfactants.

Bioavailability and toxicity of nanoparticles are largely unknown. Transport in cells is an important mechanism to be understood for assessing these impacts. Silver nanoparticles of different sizes were used to study the transport of nanoparticles through cell membranes of *Pseudomonas aeruginosa* in real time.[368] Nanoparticles can be taken up by bacteria and living cells, and this is an entry point into the food chain leading to bioaccumulation. Oberdörster[369] observed increased levels of lipid peroxidation in the brains of large-mouth bass after 48 hr of exposure to 0.5 ppm of uncoated fullerenes (nC_{60}, 30–100-nm aggregates) but decreased levels in gills and livers. Selective transport to the brain[324] and better antioxidant defense in the other organs were suspected to be the reason. No changes in the total protein oxidation in any of the tissues were observed. Also observed was improved water clarity, possibly because of the interference with bacterial growth.

Impact on Future Regulations and Research

The $PM_{2.5}$ standard of the U.S. Environmental Protection Agency is based on mass concentration.[370] Number and mass concentrations are not always related.[371,372] Control of $PM_{2.5}$ mass may have little impact on nanoparticle number concentrations and, thus, may be ineffective in preventing any potential adverse health effects posed by nanoparticles. However, particle number concentration is not conserved, can change by homogeneous nucleation and coagulation, and maybe difficult to use as a basis for a standard.

Nanoparticles in the aerosol form typically are in the agglomerated form. An important question to be answered in future research is whether particle-size-dependent phenomena, like cell barrier crossing are valid, especially for engineered nanoparticles. Investigations need to be performed to examine the role of particle morphology and whether or not agglomerates can disintegrate in the lung fluid or other biological fluids.[22] Systematic investigation of the influence of nanoparticle properties (e.g., size and surface area) and translocation/retention should be conducted and the data compiled. In lieu of the inadequately defined material properties reported in the literature, it has also been suggested that scientific journal editors be urged to require proper characterization of nanoscale materials for all publications in the emerging field of nanotoxicology.[373] Both acute and chronic effects (e.g., at occupational exposure levels) in the lung and other target organs should be assessed via standardized tests. Mechanistic models should be integrated to develop a framework for determining relative toxicity for hazard identification.[374] Because understanding of the subject truly requires a multidisciplinary approach, it is recommended that government agencies explore ways to create and promote linkages among experts in biological sciences, physical sciences, and chemical sciences. Furthermore, government agencies should provide assistance in creating standard reference materials[373] and in defining nomenclature.[375] They should also assist in the development of accreditation programs for laboratories conducting analysis and the characterization of nanoscale materials.[373] Documentation of recommended practices should also be developed for people working with nanomaterials. Finally, resources have to be committed to research the impact on the environment (ranging from transport, distribution, and bioaccumulation, among others). The current knowledge base is rather limited, and the ultimate impact on human society is unknown.

A summary of the various categories describing the health and environmental impacts is outlined in Table 6, along with suggested recommendations.

CONCLUSIONS

The field of nanotechnology has tremendous promise and applicability in a variety of different sectors. The applications in the environmental arena are also extensive as has been illustrated in this review, starting with a fundamental understanding of processes and phenomena (because of improvements in nanoscale science), to sensing pollutants, controlling emissions, and remediation technologies. Nanoparticles are also finding use in alternative energy production, storage, and conversion, and this can greatly reduce the reliance on fossil fuel combustion and

Table 6. Health and environmental effects of nanoparticles.

Category	Key References	Summary of Findings	Recommendations
Respiratory deposition	Cohen et al.[304,306,307]; Cheng et al.[301–303]; Jaques and Kim[297]; Smith et al.[305]; Broday[312]	• Ultrafine particles effectively deposit in all respiratory regions by diffusion. • Dependence on age, gender and activity. • Different mathematical models developed. • More effective for charged particles.	• Integration of measurement and model. • Population-wide dosimetry. • Patterns for nonspherical particles unknown.
Translocation	Tjälve and Henriksson[324]; Oberdörster et al.[313,314,323]; Nemmar et al.[316,320,322]; Yeates and Mauderly[321]; Kreyling et al.[318]	• Translocation occurs locally to interstitial sites in the respiratory tract and systemically to extrapulmonary organs. • Also through olfactory pathway.	• Dependence on physical/chemical/ biological properties. • Aggregates vs. solid spheres. • Other than the respiratory and the cardiovascular systems. • Effects on extrapulmonary systems whether due to the release of mediators in the respiratory system or systemic translocation of nanoparticles or both.
Dermal uptake	Lademann et al.[338]; Pflucker et al.[339]; Schultz et al.[340]	• Insignificant penetration of TiO_2 nanoparticles through the skin layer.	• Other types of materials.
Toxicity - TiO_2	Heinrich et al.[334]; Ferin et al.[331]; Seaton et al.[278]; Donaldson et al.[13,300,332,333]; Lademann et al.[338]; Oberdörster and Yu[336]; Pflucker et al.[339]; Oberdörster[298]; Schultz et al.[340]; Bermudez et al.[337]	• Ultrafine more reactive than larger ones per same mass basis. • No special reactivity for TiO_2 nanoparticles compared to larger particles. • Different biological mechanisms in different species. • Ultrafine particles in sunscreen not penetrating the skin layer.	• Extend to other oxide particles.
Toxicity: carbon	Arts et al.[341]; Warheit et al.[343]; Lam et al.[344]; Shvedova et al.[345,346]; Sayes et al.[347]	• Toxicity varies significantly depending on the type and structure of carbon. • Effects due to iron in SWCNT that generate free radicals	• The mechanisms of nanotube-specific toxicity. • Toxicity association with chemistry of the catalyst vs. particle size, surface area, and surface reactivity.
Toxicity: transition metals	Amdur et al.[357]; Amdur and Chen[358]; Chen et al.[359]; Ghio et al.[353]; Smith and Aust[354]; Zhang et al.[208,356]; Donaldson et al.[13]; van Maanen et al.[355]; Shvedova et al.[345,346]	• Generate free radicals through Fenton reaction. • Acid coated on particles can also cause adverse effects.	• Identify transition metals and their combinations with other materials that may have health effects.
Impact on future regulations and research	• Should air quality regulation be based on number or mass concentration? • What is the pertinent sampling protocol? • Require proper nanomaterials characterization for publications. • Promote linkages between experts in biological, chemical, and physical sciences. • Establish standard reference materials and develop accreditation programs for analytical facilities. • Examine both acute and chronicle effects.		

overall emissions. Recommendations for each of the components addressed in the review have been discussed at the end of the respective sections. Table 7 provides an overall summary of the critical recommendations. There is a paucity of information on sources of nanoparticles, and both the size distributions and chemical compositions need to be identified. Detailed understanding of process parameters and mechanistic pathways of nanoparticle formation need to be developed. This knowledge has to then be used to develop effective control methodologies. The knowledge base should also be used to consider the development and adoption of "number-based" PM regulations. Although advances have been made in real time aerosol instrumentation in recent years, the

Table 7. Summary of overall recommendations.

Sources of nanoparticles	• Fundamental understanding of nanoparticle formation in a spectrum of systems, both natural and man-made
	• Quantitative description (measurement) of nanoparticle size distribution and composition of emissions; Developing guidelines for proper sampling protocols
	• Establishment of number based emission regulations and regulations for nanoparticle precursors (condensable species)
	• Understanding of the life-cycle of engineered nanomaterials
Control of nanoparticle emissions	• Design of high-efficiency nanoparticle emission control systems for specific applications
	• Systematic approaches to modify processes to tailor nanoparticle byproduct so it is readily controllable
Instrumentation and characterization	• Pushing the limits of real-time aerosol instrumentation to measure sub-3 nm (1 nm)-sized particles
	• Real-time composition characterization of nanoparticles
	• Creation of a database of properties of commonly encountered nanoparticles as a function of size
Exposure and health effects	• Development of a database of toxicological properties of nanoparticles as a function of size and composition
	• Accurate exposure and respiratory models need to be developed through integration of theoretical modeling and experimental measurement
	• Guidelines and criteria for workplaces and research laboratories
	• Understanding of transport and bioavailability of nanoparticles in the environment / ecosystem
Environmental nanotechnology	• Development of novel methodologies for remediation and establishing guidelines for implementation so that there is no adverse impact
	• Procedures for timely implementation and adoption of safe nanotechnologies
	• Enabling the development of alternative and sustainable energy sources

"sub-3 nm" barrier needs to be overcome. Databases of information on nanoparticle properties have to be compiled and made readily available along with toxicological properties as a function of size. Safe practices for the occupational environment where engineered nanoparticles are synthesized and handled have to be developed to minimize exposure. Research laboratories should also have strict guidelines regarding nanoparticle systems. Finally, the potential of useful applications of nanoparticles in environmental technologies should be fostered, but care should be taken to use a holistic approach to ensure no adverse side effects.

A few overall statements are made regarding the approach to be taken for effective adoption of nanotechnologies. Before widespread use of this technology, it is important that the environmental and health impacts be understood. Even if some nanomaterials have deleterious impacts, the science is interesting and exciting that it can be used to overcome such problems. For example, if the causes (mechanistic details) of a biological effect are established, the knowledge can be transferred to the nanoparticle synthesis scientists who can research and modify the characteristics to retain functionality and avoid the negative impacts. Although this is easily said, it would require collaborations and interdisciplinary efforts to overcome these challenges. It is strongly recommended that federal agencies provide due attention to this and that enhanced funding is provided at these early stages to determine the true environmental footprints and health impacts. This is the best approach to avoid pitfalls and mistakes made on rapid introduction of a new technology so that other concerns and important questions do not have to be addressed later. Futuristic clean-up costs and remedial action can be avoided, and at the same time more rapid development, deployment, and acceptance of nanotechnology can be promoted.

ACKNOWLEDGMENTS

The authors thank the members of the Critical Review Committee, Judith C. Chow, John Watson, Peter Mueller, Charles McDade, and Thomas Overcamp, for their review and comments on the manuscript. They acknowledge the assistance of Dr. Myong-Hwa Lee and Kuk Cho in formatting the bibliography for this paper. Additionally, the authors thank Holly Franklin at University of Florida Engineering Publications for creating Figure 1 for the manuscript.

Pratim Biswas thanks colleagues at the University of Minnesota, Drs. David Pui, Peter McMurry, and Uwe Kortshagen, for discussion of ideas during development of a collaborative proposal. Support from the Center of Materials Innovation (CMI) at Washington University in St. Louis for work on Environmental Nanotechnology projects is gratefully acknowledged. Partial support from National Science Foundation NIRT 0304649 on nanoparticle synthesis and the Department of Defense-Multidisciplinary University Research Initiative grant UR 523873 on nanoparticle toxicology is also acknowledged. Chang-Yu Wu thanks Drs. Yung-Sung Cheng, David Warheit, and Anna Shvedova for providing insightful information related to health effects. Chang-Yu Wu acknowledges the support from the EPA STAR program

under Grant No. R-82960201 for environmental technology research and General Motors under Contract No. ND0284600 for hydrogen research. He is grateful to his colleague at University of Florida, Dr. Dale Lundgren, for invaluable mentoring on aerosol research.

REFERENCES

1. *National Nanotechnology Initiative*. Available at http://www.nano.gov/html/facts/EHS.htm (accessed 2004).
2. Roco, M.C. Broader Societal Issues of Nanotechnology; *J. Nanopart. Res.* **2003**, *5*, 181-189.
3. Choi, M.; Biswas, P.; Fissan, H.; Pui, D. Y. H. Special Issue on Nanoparticles: Technology and Sustainable Development; *J. Nanopart. Res.* **2003**.
4. Masciangioli, T.; Zhang, W. X. Environmental Technologies at the Nanoscale; *Environ. Sci. Technol.* **2003**, *37*, 102a-108a.
5. Colvin, V. Point of Impact: Where Technology Collides With Society, Business, and Personal Lives; *Technol. Rev.* **2003**, *106*, 71-73.
6. Crichton, M. *Prey*; New York, NY: Harper Collins, 2002.
7. *ETC Group*. Available at http://www.etcgroup.org/documents/TheBigDown.pdf (accessed 2003).
8. Chang, M.C.O., Chow, J.C.; Watson, J.G.; Hopke, P.K.; Yi, S.M.; England, G.C. Measurement of Ultrafine Particle Size Distributions From Coal-, Oil-, and Gas-Fired Stationary Combustion Sources; *J. Air & Waste Manage. Assoc.* **2004**, *54*, 1494-1505.
9. Kittelson, D.B. Engines and Nanoparticles: A Review; *J. Aero. Sci.* **1998**, *29*, 575-588.
10. Vincent, J.H.; Clement, C.F. Ultrafine Particles in Workplace Atmospheres; *Philos. Trans. Royal Soc. Lond. Series a-Math. Phys. Eng. Sci.* **2000**, *358*, 2673-2682.
11. Hogan, C.J.; Lee, M.H.; Biswas, P. Capture of Viral Particles in Soft X-Ray-Enhanced Corona Systems: Charge Distribution and Transport Characteristics; *Aero. Sci. Technol.* **2004**, *38*, 475-486.
12. McMurry, P.H.; Woo, K.S.; Weber, R.; Chen, D.R.; Pui, D.Y.H. Size Distributions of 3–10 nm Atmospheric Particles: Implications for Nucleation Mechanisms; *Philos. Trans. Royal Soc. Lond. Series a-Math. Phys. Eng. Sci.* **2000**, *358*, 2625-2642.
13. Donaldson, K.; Li, X.Y.; MacNee, W. Ultrafine (Nanometre) Particle Mediated Lung Injury; *J. Aero. Sci.* **1998**, *29*, 553-560.
14. Biswas, P.; Wu, C.Y. Control of Toxic Metal Emission From Combustors Using Sorbents: A Review; *J. Air & Waste Manage. Assoc.* **1998**, *48*, 113-127.
15. Lloyd, S.M.; Lave, L.B.; Matthews, H.S. Life Cycle Benefits of Using Nanotechnology to Stabilize Platinum-Group Metal Particles in Automotive Catalysts; *Environ. Sci. Technol.* **2005**, *39*, 1384-1392.
16. Zhang, W.; Wang, C. Nanoscale Metal Particles for Dechlorination of PCE and PCBs; *Environ. Sci. Technol.* **1997**, *31*, 2154-2156.
17. Zhang, W.X. Nanoscale Iron Particles for Environmental Remediation: an Overview; *J. Nanopart. Res.* **2003**, *5*, 323-332.
18. Onyango, M.S.; Kojima, Y.; Matsuda, H.; Ochieng, A. Adsorption Kinetics of Arsenic Removal From Groundwater by Iron-Modified Zeolite; *J. Chem. Eng. Japan* **2003**, *36*, 1516-1522.
19. Peng, X.J.; Luan, Z.K.; Ding, J.; Di, Z.H.; Li, Y.H.; Tian, B.H. Ceria Nanoparticles Supported on Carbon Nanotubes for the Removal of Arsenate From Water; *Mater. Lett.* **2005**, *59*, 399-403.
20. Keoliean, G.A.; Menery, D. Sustainble Development by Design—Review of Life-Cycle Design and Related Approaches; *J. Air & Waste Manage. Assoc.* **1994**, *44*, 645-668.
21. Banfield, J.F.; Zhang, H.Z. Nanoparticles and the Environment; *Rev. Miner. Geochem.* **2001**, *44*, 1-58.
22. Luther, W. *Industrial Application of Nanomaterials—Chances and Risks; Future Technologies*. Division of VDI Technologiezentrum GmbH: Dusseldorf, Germany, 2004.
23. Friedlander, S. K.; Pui, D. Y. H. *Emerging Issues in Nanoparticle Aerosol Science and Technology*; NSF Workshop Report; UCLA: Los Angeles, CA, 2003.
24. Kulmala, M. How Particles Nucleate and Grow; *Science* **2003**, *302*, 1000-1001.
25. Kulmala, M.; Vehkamaki, H.; Petajda, T.; Dal Maso, M.; Lauri, A.; Kerminen, V.M.; Birmili, W.; McMurry, P.H. Formation and Growth Rates of Ultrafine Atmospheric Particles: A Review of Observations; *J. Aero. Sci.* **2004**, *35*, 143-176.
26. Hildemann, L.M.; Markowski, G.R.; Jones, M.C.; Cass, G.R. Submicrometer Aerosol Mass Distributions of Emissions From Boilers, Fireplaces, Automobiles, Diesel Trucks, and Meat-Cooking Operations; *Aerosol. Sci. Technol.* **1991**, *14*, 138-152.
27. Maguhn, J.; Karg, E.; Kettrup, A.; Zimmermann, R. On-Line Analysis of the Size Distribution of Fine and Ultrafine Aerosol Particles in Flue and Stack gas of a Municipal Waste Incineration Plant: Effects of Dynamic Process Control Measures and Emission Reduction Devices; *Environ. Sci. Technol.* **2003**, *37*, 4761-4770.
28. Liu, Y.; Daum, P.H. The Effect of Refractive Index on Size Distributions and Light Scattering Coefficients Derived From Optical Particl ECounters; *J. Aerosol. Sci.* **2000**, *31*, 945-957.
29. Zhuang, Y.; Biswas, P. Submicrometer Particle Formation and Control in a Bench-Scale Pulverized Coal Combustor; *Energy Fuels* **2001**, *15*, 510-516.
30. Ebelt, S.; Brauer, M.; Cyrys, J.; Tuch, T.; Kreyling, W.G.; Wichmann, H.E.; Heinrich, J. Air Quality in Postunification Erfurt, East Germany: Associating Changes in Pollutant Concentrations With Changes in Emissions; *Environ. Health. Perspect.* **2001**, *109*, 325-333.
31. Lipsky, E.; Stanier, C.O.; Pandis, S.N.; Robinson, A.L. Effects of Sampling Conditions on the Size Distribution of Fine Particulate Matter Emitted From a Pilot-Scale Pulverized-Coal Combustor; *Energy Fuels* **2002**, *16*, 302-310.
32. Zhang, K.M.; Wexler, A.S. Evolution of Particle Number Distribution Near Roadways - Part i: Analysis of Aerosol Dynamics and its Implications for Engine Emission Measurement; *Atmos. Environ.* **2004**, *38*, 6643-6653.
33. Biswas, P. Measurement of High Concentration and High Temperature Aerosols. In *Aerosol Measurement: Principles, Techniques, and Applications*. Baron, P. A., Willeke, K., Eds., New York, NY: A John Wiley & Sons, Inc.,: 2001.
34. Tolocka, M.P.; Lake, D.A.; Johnston, M.V.; Wexler, A.S. Number Concentrations of Fine and Ultrafine Particles Containing Metals; *Atmos. Environ.* **2004**, *38*, 3263-3273.
35. Watson, J.G.; Zhu, T.; Chow, J.C.; Engelbrecht, J.; Fujita, E.M.; Wilson, W.E. Receptor Modeling Application Framework for Particle Source Apportionment; *Chemosphere* **2002**, *49*, 1093-1136.
36. Chow, J.C.; Watson, J.G.; Kuhns, H.; Etyemezian, V.; Lowenthal, D.H.; Crow, D.; Kohl, S.D.; Engelbrecht, J.P.; Green, M.C. Source Profiles for Industrial, Mobile, and Area Sources in the Big Bend Regional Aerosol Visibility and Observational Study; *Chemosphere* **2004**, *54*, 185-208.
37. Utsunomiya, S.; Jensen, K.A.; Keeler, G.J.; Ewing, R.C. Direct Identification of Trace Metals in Fine and Ultrafine Particles in the Detroit Urban Atmosphere; *Environ. Sci. Technol.* **2004**, *38*, 2289-2297.
38. Anderson, P.J.; Wilson, J.D.; Hiller, F.C. Particle Size Distribution of Mainstream Tobacco and Marijuana Smoke; *Am. Rev. Respir. Dis.* **1989**, *340*, 202-205.
39. Li, C. S.; Jeng, F. T.; Lin, W. H. Field Characterization of Submicron Aerosols from Indoor Combustion Sources. *J. Aerosol. Sci.* **1992**, *23(Suppl. 1)*, S547–S550.
40. Wallace, L.A.; Emmerich, S.J.; Howard-Reed, C. Source Strengths of Ultrafine and Fine Particles Due to Cooking With a Gas Stove; *Environ. Sci. Technol.* **2004**, *38*, 2304-2311.
41. Wallace, L. Real-Time Montoring of Particles, PAH, and CO in an Occupied Townhouse; *Appl. Occup. Environ. Hyg.* **2000**, *15*, 39-47.
42. Dennekamp, M.; Howarth, S.; Dick, C.A.J., Cherrie, J.W.; Donaldson, K.; Seaton, A. Ultrafine Particles and Nitrogen Oxides Generated by Gas and Electric Cooking; *Occup. Environ. Med.* **2001**, *58*, 511-516.
43. Venkataraman, C.; Habib, G.; Eiguren-Fernandez, A.; Miguel, A.H.; Friedlander, S.K. Residential Biofuels in South Asia: Carbonaceous Aerosol Emissions and Climate Impacts; *Science* **2005**, *307*, 1454-1456.
44. Tobias, H.J.; Beving, D.E.; Ziemann, P.J.; Sakurai, H.; Zuk, M.; McMurry, P.H.; Zarling, D.; Waytulonis, R.; Kittelson, D.B. Chemical Analysis of Diesel Engine Nanoparticles Using a Nano-DMA/Thermal Desorption Particle Beam Mass Spectrometer; *Environ. Sci. Technol.* **2001**, *35*, 2233-2243.
45. Sakurai, H.; Tobias, H.J.; Park, K.; Zarling, D.; Docherty, S.; Kittelson, D.B.; McMurry, P.H.; Ziemann, P.J. On-Line Measurements of Diesel Nanoparticle Composition and Volatility; *Atmos. Environ.* **2003**, *37*, 1199-1210.
46. Burtscher, H.; Kunzel, S.; Huglin, C. Characterization of Particles in Combustion Engine Exhaust; *J. Aero. Sci.* **1998**, *29*, 389-396.
47. McDonald, R.; Hu, S.H.; Martuzevicius, D.; Grinshpun, S.A. LeMasters, G.; Biswas, P; Intensive Short Term Measurements of the Ambient Aerosol in the Greater Cincinnati Airshed. *Aero. Sci. Technol.* **2004**, *38*, 70-79.
48. Rickeard, D.J.; Bateman, J.R.; Kwon, Y.K.; McAughey, J.J.; Dickens, C.J. *Exhaust Particulate Size Distribution: Vehicle and Fuel Influences in Light Duty Vehicles*; Society of Automotive Engineers: Warrendale, PA, 1996.
49. Shi, J.P.; Evans, D.E.; Khan, A.A.; Harrison, R.M. Sources and Concentration of Nanoparticles (< 10 nm Diameter) in the Urban Atmosphere; *Atmos. Environ.* **2001**, *35*, 1193-1202.
50. Harris, S.J.; Maricq, M.M. Signature Size Distributions for Diesel and Gasoline Engine Exhaust Particulate Matter; *J. Aerosol. Sci.* **2001**, *32*, 749-764.
51. Ristovski, Z.D.; Morawska, L.; Bofinger, N.D.; Hitchins, J. Submicrometer and Supermicrometer Particulate Emission From Spark Ignition Vehicles; *Environ. Sci. Technol.* **1998**, *32*, 3845-3852.
52. Faiz, A.; Weaver, C.S.; Walsh, M.P. *Air Pollution from Motor Vehicles: Standards and Technologies for Controlling Emissions*; The World Bank: Washington, DC, 1996.

53. Wehner, B.; Birmili, W.; Gnauk, T.; Wiedensohler, A. Particle Number Size Distributions in a Street Canyon and Their Transformation Into the Urban-air Background: Measurements and a Simple Model Study; *Atmos. Environ.* **2002**, *36*, 2215-2223.
54. Zhu, Y.F.; Hinds, W.C.; Kim, S.; Sioutas, C. Concentration and Size Distribution of Ultrafine Particles Near a Major Highway; *J. Air & Waste Manage. Assoc.* **2002**, *52*, 1032-1042.
55. Kim, S.; Shen, S.; Sioutas, C.; Zhu, Y.F.; Hinds, W.C. Size Distribution and Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the los Angeles Basin; *J. Air & Waste Manage. Assoc.* **2002**, *52*, 297-307.
56. Ruhle, T.; Schneider, H.; Find, J.; Herein, D.; Pfander, N.; Wild, U.; Schlogl, R.; Nachtigall, D.; Artelt, S.; Heinrich, U. Preparation and Characterisation of pt/Al2O3 Aerosol Precursors as Model pt-Emissions From Catalytic Converters; *Appl. Catal. B-Environ.* **1997**, *14,* 69-84.
57. Artelt, S.; Kock, H.; Konig, H.P.; Levsen, K.; Rosner, G. Engine Dynamometer Experiments: Platinum Emissions From Differently Aged Three-way Catalytic Converters; *Atmos. Environ.* **1999**, *33*, 3359-3567.
58. Vijay, R.; Hendershot, R.J.; Rivera-Jimenez, S.M.; Rogers, W.B.; Feist, B.J.; Snively, C.M.; Lauterbach, J. Noble Metal Free nox Storage Catalysts Using Cobalt Discovered via High-Throughput Experimentation; *Catal. Comm.* **2005**, *6*, 167-171.
59. Mathis, U.; Ristimaki, J.; Mohr, M.; Keskinen, J.; Ntziachristos, L.; Samaras, Z.; Mikkanen, P. Sampling Conditions for the Measurement of Nucleation Mode Particles in the Exhaust of a Diesel Vehicle; *Aerosol. Sci. Technol.* **2004**, *38*, 1149-1160.
60. Franck, U.; Herbarth, O.; Wehner, B.; Wiedensohler, A.; Manjarrez, M. How Do the Indoor Size Distributions of Airborne Submicron and Ultrafine Particles in the Absence of Significant Indoor Sources Depend on Outdoor Distributions?; *Indoor Air* **2003**, *13*, 174-181.
61. Aiken, J. On the Formation of Small Clear Spaces in Dusty Air *Trans. Roy. Soc. Edinburgh* **1884**, *30*, 337–368.
62. Seinfeld, J.A.; Pandis, S.N. *Atmospheric Chemistry and Physics*; John Wiley & Sons: New York, 1998.
63. Saros, M.T.; Weber, R.J.; Marti, J.J.; McMurry, P.H. Ultrafine Aerosol Measurement Using a Condensation Nucleus Counter With Pulse Height Analysis; *Aerosol. Sci. Technol.* **1996**, *25*, 200-213.
64. Chen, D.R.; Pui, D.Y.H., Hummes, D.; Fissan, H.; Quant, F.R.; Sem, G.J. Design and Evaluation of a Nanometer Aerosol Differential Mobility Analyzer (Nano-DMA); *J. Aerosol. Sci.* **1998**, *29*, 497-509.
65. Chen, D.R.; Pui, D.Y.H.A. High Efficiency, High Throughput Unipolar Aerosol Charger for Nanoparticles; *J. Nanoparticle Res.* **1999**, *1*, 115-126.
66. McMurry, P.H.; Woo, K.S. Size Distributions of 3–100-nm Urban Atlanta Aerosols: Measurement and Observations; *J. Aerosol Med. Deposition Clear. Effects Lung* **2002**, *15*, 169-178.
67. Stanier, C.O.; Khlystov, A.Y.; Pandis, S.N. Ambient Aerosol Size Distributions and Number Concentrations Measured During the Pittsburgh air Quality Study (PAQS); *Atmos. Environ.* **2004**, *38*, 3275-3284.
68. Hussein, T.; Puustinen, A.; Aalto, P.P.; Makela, J.M.; Hameri, K.; Kulmala, M. Urban Aerosol Number Size Distributions; *Atmos. Chem. Phys.* **2004**, *4*, 391-411.
69. Birmili, W.; Wiedensohler, A. The Influence of Meteorological Parameters on Ultrafine Particle Production at a Continental Site; *J. Aerosol. Sci.* **1998**, *29,* S1015-S1016.
70. Covert, D.S.; Wiedensohler, A.; Aalto, P.; Heintzenberg, J.; McMurry, P.H.; Leck, C. Aerosol Number Size Distributions From 3 to 500 nm Diameter in the Arctic Marine Boundary Layer During Summer and Autumn; *Tellus Series B-Chem. Phys. Meteorol.* **1996**, *48*, 197-212.
71. Tunved, P.; Hansson, H.C.; Kulmala, M.; Aalto, P.; Viisanen, Y.; Karlsson, H.; Kristensson, A.; Swietlicki, E.; Dal Maso, M.; Strom, J.; Komppula, M. one Year Boundary Layer Aerosol Size Distribution Data From Five Nordic Background Stations; *Atmos. Chem. Phys.* **2003**, *3*, 2183-2205.
72. Park, J.; Sakurai, H.; Vollmers, K.; McMurry, P.H. Aerosol Size Distributions Measured at the South Pole During ISCAT; *Atmos. Environ.* **2004**, *38*, 5493-5500.
73. Covert, D.S.; Kapustin, V.N.; Bates, T.S.; Quinn, P.K. Physical Properties of Marine Boundary Layer Aerosol Particles of the mid-Pacific in Relation to Sources and Meteorological Transport; *J. Geophys. Res. Atmos.* **1996**, *101*, 6919-6930.
74. Weber, R.J.; Marti, J.J.; McMurry, P.H.; Eisele, F.L.; Tanner, D.J.; Jefferson, A. Measurements of New Particle Formation and Ultrafine Particle Growth Rates at a Clean Continental Site; *J. Geophys. Res. Atmos.* **1997**, *102*, 4375-4385.
75. Wiedensohler, A.; Hansson, H.C.; Orsini, D.; Wendisch, M.; Wagner, F.; Bower, K.N.; Chourlarton, T.W.; Wells, M.; Parkin, M.; Acker, K.; Wieprecht, W.; Facchini, M.C.; Lind, J.A.; Fuzzi, S.; Arends, B.G.; Kulmala, M. Night-Time Formation and Occurrence of New Particles Associated With Orographic Clouds; *Atmos. Environ.* **1997**, *31*, 2545-2559.
76. Makela, J.M.; Aalto, P.; Jokinen, V.; Pohja, T.; Nissinen, A.; Palmroth, S.; Markkanen, T.; Seitsonen, K.; Lihavainen, H.; Kulmala, M. Observations of Ultrafine Aerosol Particle Formation and Growth in Boreal Forest; *Geophys. Res. Lett.* **1997**, *24*, 1219-1222.
77. Wiedensohler, A.; Covert, D.S.; Swietlicki, E.; Aalto, P.; Heintzenberg, J.; Leck, C. Occurrence of an Ultrafine Particle Mode Less Than 20 nm in Diameter in the Marine Boundary Layer During Arctic Summer and Autumn; *Tellus Series B-Chem. Phys. Meteorol.* **1996**, *48*, 213-222.
78. Clarke, A.D. Atmospheric Nuclei in the Pacific Midtroposphere - Their Nature, Concentration, and Evolution; *J. Geophys. Res. Atmos.* **1993**, *98*, 20633-20647.
79. Clarke, A.D.; Varner, J.L.; Eisele, F.; Mauldin, R.L.; Tanner, D.; Litchy, M. Particle Production in the Remote Marine Atmosphere: Cloud Outflow and Subsidence During ace 1; *J. Geophys. Res. Atmos.* **1998**, *103*, 16397-16409.
80. Hughes, L.S.; Cass, G.R.; Gone, J.; Ames, M.; Olmez, I. Physical and Chemical Characterization of Atmospheric Ultrafine Particles in the Los Angeles Area; *Environ. Sci. Technol.* **1998**, *32*, 1153-1161.
81. Chung, A.; Herner, J.D.; Kleeman, M.J. Detection of Alkaline Ultrafine Atmospheric Particles at Bakersfield, California; *Environ. Sci. Technol.* **2001**, *35*, 2184-2190.
82. Laakso, L.; Hussein, T.; Aarnio, P.; Komppula, M.; Hiltunen, V.; Viisanen, Y.; Kulmala, M. Diurnal and Annual Characteristics of Particle Mass and Number Concentrations in Urban, Rural and Arctic Environments in Finland; *Atmos. Environ.* **2003**, *37*, 2629-2641.
83. Koutsenogii, P.K.; Jaenicke, R. Number Concentration and Size Distribution of Atmospheric Aerosol in Siberia; *J. Aerosol. Sci.* **1994**, *25*, 377-383.
84. McGovern, F.M.; Jennings, S.G; OConnor, T.C. Aerosol and Trace Gas Measurements During the Mace Head Experiment; *Atmos. Environ.* **1996**, *30*, 3891-3902.
85. Weber, R.J.; McMurry, P.H.; Mauldin, L.; Tanner, D.J.; Eisele, F.L.; Brechtel, F.J.; Kreidenweis, S.M.; Kok, G.L.; Schillawski, R.D.; Baumgardner, D.A. Study of New Particle Formation and Growth Involving Biogenic and Trace gas Species Measured During ace 1; *J. Geophys. Res. Atmos.* **1998**, *103*, 16385-16396.
86. Eisele, F.L.; McMurry, P.H. Recent Progress in Understanding Particle Nucleation and Growth; *Philos. Trans. Royal Soc. Lond. Series B-Bio. Sci.* **1997**, *352*, 191-200.
87. O'Dowd, C.D.; Jimenez, J.L.; Bahreini, R.; Flagan, R.C.; Seinfeld, J.H.; Hameri, K.; Pirjola, L.; Kulmala, M.; Jennings, S.G.; Hoffmann, T. Marine Aerosol Formation From Biogenic Iodine Emissions; *Nature* **2002**, *417*, 632-636.
88. Jimenez, J.L.; Bahreini, R.; Cocker, D.R.; Zhuang, H.; Varutbangkul, V.; Flagan, R.C.; Seinfeld, J.H; O'Dowd, C.D.; Hoffmann, T. New particle formation from photooxidation of diiodomethane (CH_2I_2); *J. Geophys. Res. Atmos.* **2003**, *108*, 4318-4322.
89. Herner, J.D.; Aw, J.; Gao, O.; Chang, D.P.; Kleeman, M.J. Size and Composition Distribution of Airborne Particulate Matter in Northern California: i-Particulate Mass, Carbon, and Water-Soluble Ions; *J. Air & Waste Manage. Assoc.* **2005**, *55*, 30-51.
90. Fine, P.M.; Chakrabarti, B.; Krudysz, M.; Schauer, J.J.; Sioutas, C. Diurnal Variations of Individual Organic Compound Constituents of Ultrafine and Accumulation Mode Particulate Matter in the los Angeles Basin; *Environ. Sci. Technol.* **2004**, *38*, 1296-1304.
91. Schauer, J.J.; Cass, G.R. Source Apportionment of Wintertime gas-Phase and Particle-Phase Air Pollutants Using Organic Compounds as Tracers; *Environ. Sci. Technol.* **2000**, *34*, 1821-1832.
92. Cabada, J.C.; Rees, S.; Takahama, S.; Khlystov, A.; Pandis, S.N.; Davidson, C.I.; Robinson, A.L. Mass Size Distributions and Size Resolved Chemical Composition of Fine Particulate Matter at the Pittsburgh Supersite; *Atmos. Environ.* **2004**, *38*, 3127-3141.
93. Tolocka, M.P.; Lake, D.A.; Johnston, M.V.; Wexler, A.S. Ultrafine Nitrate Particle Events in Baltimore Observed by Real-Time Single Particle Mass Spectrometry; *Atmos. Environ.* **2004**, *38*, 3215-3223.
94. Yakovleva, E.; Hopke, P.K.; Wallace, L. Receptor Modeling Assessment of Particle Total Exposure Assessment Methodology Data; *Environ. Sci. Technol.* **1999**, *33*, 3645-3652.
95. Brouwer, D.H.; Gijsbers, J.H.J., Lurvink, M.W.M. Personal Exposure to Ultrafine Particles in the Workplace: Exploring Sampling Techniques and Strategies; *Annals of Occupational Hygiene* **2004**, *48*, 439-453.
96. Schmid, G.; Baumle, M.; Geerkens, M.; Helm, I.; Osemann, C.; Sawitowski, T. Current and Future Applications of Nanoclusters; *Chem. Soc. Rev.* **1999**, *28*, 179-185.
97. Dahn, C.J.; Kashani, A.; Finkelstein, J. Dust Explosibility of Metal Powders; *P/M Scie. Technol. Briefs* **2000**, *2,* 14-17.
98. Maynard, A.D.; Baron, P.A.; Foley, M.; Shvedova, A.A.; Kisin, E.R.; Castranova, V. Exposure to Carbon Nanotube Material: Aerosol Release During the Handling of Unrefined Single-Walled Carbon Nanotube Material; *J. Toxicol. Environ. Health-Part A* **2004**, *67,* 87-107.
99. Kuhlbusch, T.A.J., Neumann, S.; Fissan, H. Number Size Distribution, Mass Concentration, and Particle Composition of pm1, pm2.5, and PM10 in bag Filling Areas of Carbon Black Production; *J. Occupat. Environ. Hygiene* **2004**, *1*, 660-671.

100. Lecoanet, H.F.; Bottero, J.Y.; Wiesner, M.R. Laboratory Assessment of the Mobility of Nanomaterials in Porous Media; *Environ. Sci. Technol.* **2004**, *38*, 5164-5169.
101. Cheng, M.D.; Jenkins, C.M. Production and Dynamics of Ultrafine and Fine Particles in Contained Detonations of Aluminium Energetics; *J. Aero. Sci.* **2005**, *36*, 1-12.
102. Friedlander, S.K. *Smoke, Dust and Haze: Fundamentals of Aerosol Dynamics*; Oxford University Press: New York, 2000.
103. Hinds, W.C. *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*; John Wiley & Sons: New York, 1999.
104. Stokes, G.G. *Trans. Cambridge Phil. Soc.* **1851**, *9*, 8-106.
105. Cunningham, E. *Proc. Roy. Soc.* **1910**, *81 A*, 357.
106. Biswas, P.; Flagan, R.C. High Velocity Inertial Impactors; *Environ. Sci. Technol.* **1984**, *18*, 611-616.
107. Hillamo, R.E.; Kauppinen, E.I. On the Performance of the Berner low-Pressure Impactor; *Aerosol. Sci. Technol.* **1991**, *14*, 33-47.
108. Lee, P.; Chen, D.R.; Pui, D.Y.H. Experimental Study of a Nanoparticle Virtual Impactor; *J. Nanopart. Res.* **2003**, *5*, 269-280.
109. Biswas, P.; Flagan, R.C. the Particle Trap Impactor; *J. Aerosol. Sci.* **1988**, *19*, 113-121.
110. Wu, C.Y.; Biswas, P., Donnelly, A. Aerosol Science & Engineering. Available at http://aerosol.ees.ufl.edu and http://www.aerosols.wastl.edu/aagrl/Courses/CYCOCRESP/.
111. Tsai, C.J.; Chen, D.R.; Chein, H.M.; Chen, S.C.; Roth, J.L.; Hsu, Y.D.; Li, W.L.; Biswas, P. Theoretical and Experimental Study of an Axial Flow Cyclone for Fine Particle Removal in Vacuum Conditions; *J. Aerosol. Sci.* **2004**, *35*, 1105-1118.
112. Shrimpton, J.S.; Crane, R.I. Small Electrocyclone Performance; *Chem. Eng. Technol.* **2001**, *24*, 951-955.
113. Baron, P.A.; Willeke, K. *Aerosol Measurement*. New York, NY: John Wiley & Sons, Inc., Chapter 31: 2001.
114. Fisk, W.J.; Faulkner, D.; Palonen, J.; Seppanen, O. Performance and Cost of Particle Air Filtration Technologies; *Indoor Air* **2002**, *12*, 223-234.
115. Lee, J.K.; Kim, S.C.; Shin, J.H.; Lee, J.E.; Ku, J.H.; Shin, H.S. Performance Evaluation of Electrostatically Augmented Air Filters Coupled With a Corona Precharger; *Aerosol. Sci. Technol.* **2001**, *35*, 785-791.
116. Lee, M.; Otani, Y.; Namiki, N.; Emi, H. Prediction of Collection Efficiency of High-Performance Electret Filters; *J. Chem. Eng. Japan* **2002**, *35*, 57-62.
117. Oh, Y.W.; Jeon, K.J.; Jung, A.I.; Jung, Y.W.A. Simulation Study on the Collection of Submicron Particles in a Unipolar Charged Fiber; *Aerosol. Sci. Technol.* **2002**, *36*, 573-582.
118. Alonso, M.; Alguacil, F.J. Filtration of Unipolarly Charged Aerosol Nanoparticles With an Initially Discharged Dielectric Screen; *J. Colloid Inter. Sci.* **1999**, *216*, 71-76.
119. Waldman, L.; Schmitt, K. H. Thermophoresis and Diffusophoresis of Aerosols. In: *Aerosol Science*. Davies, C. N., Ed. Academic Press: New York, 1966.
120. Yang, G.X.; Zhuang, H.R.; Biswas, P. Characterization and Sinterability of Nanophase Titania Particles Processed in Flame Reactors; *Nanostruct. Mater.* **1996**, *7*, 675-689.
121. McMillin, B.K.; Biswas, P.; Zachariah, M.R. in Situ Characterization of Vapor Phase Growth of Iron Oxide-Silica Nanocomposites. 1. 2-d Planar Laser-Induced Fluorescence and mie Imaging; *J. Mater. Res.* **1996**, *11*, 1552-1561.
122. Zachariah, M.R.; Aquino, M.I.; Shull, R.D.; Steel, E.B. Formation of Superparamagnetic Nanocomposites From Vapor-Phase Condensation in a Flame; *Nanostruct. Mater.* **1995**, *5*, 383-392.
123. Mueller, R.; Jossen, R.; Kammler, H.K.; Pratsinis, S.E. Growth of Zirconia Particles Made by Flame Spray Pyrolysis; *Aiche J.* **2004**, *50*, 3085-3094.
124. Kim, H.W.; Choi, M. in Situ Line Measurement of Mean Aggregate Size and Fractal Dimension Along the Flame Axis by Planar Laser Light Scattering; *J. Aerosol. Sci.* **2003**, *34*, 1633-1645.
125. Sahle-Demessie, E.; Gonzalez, M.; Wang, Z.M.; Biswas, P. Synthesizing Alcohols and Ketones by Photoinduced Catalytic Partial Oxidation of Hydrocarbons in TiO2 Film Reactors Prepared by Three Different Method; *Ind. Eng. Chem. Res.* **1999**, *38*, 3276-3284.
126. Fuchs, N.A. On the Stationary Charge Distribution on Aerosol Particles in a Bipolar Ionic Atmosphere; *Geofis. Pura. Appl.* **1963**, *56*, 185-193.
127. Adachi, M.; Kousaka, Y.; Okuyama, K. Unipolar and Bipolar Diffusion Charging of Ultrafine Aerosol Particles; *J. Aerosol. Sci.* **1985**, *16*, 109-124.
128. Adachi, M.; Okuyama, K.; Kousaka, Y.; Kozuru, H.; Pui, D.Y.H. Bipolar Diffusion Charging of Aerosol Particles Under High Particle/ion Concentration Ratios; *Aerosol. Sci. Technol.* **1989**, *11*, 144-156.
129. Zhuang, Y.; Kim, Y.J.; Lee, T.G.; Biswas, P. Experimental and Theoretical Studies of Ultra-Fine Particle Behavior in Electrostatic Precipitators; *J. Electrostat.* **2000**, *48*, 245-260.
130. Alonso, M.; Hernandez-Sierra, A.; Alguacil, F.J. Electrical Charging of Aerosol Nanoparticles and Some Practical Applications; *Revista De Metalurgia* **2003**, *39*, 41-57.
131. Kulkarni, P.; Namiki, N.; Otani, Y.; Biswas, P. Charging of Particles in Unipolar Coronas Irradiated by in-Situ Soft x-Rays: Enhancement of Capture Efficiency of Ultrafine Particles; *J. Aero. Sci.* **2002**, *33*, 1279-1296.
132. Watanabe, T.; Tochikubo, F.; Koizumi, Y.; Tsuchida, T.; Hautanen, J.; Kauppinen, E.I. Submicron Particle Agglomeration by an Electrostatic Agglomerator; *J. Electrostat.* **1995**, *34*, 367-383.
133. Ylatalo, S.I.; Hautanen, J. Electrostatic Precipitator Penetration Function for Pulverized Coal Combustion; *Aerosol. Sci. Technol.* **1998**, *29*, 17-30.
134. Ahearn, D.G.; Crow, S.A; Simmons, R.B.; Price, D.L.; Mishra, S.K.; Pierson, D.L. Fungal Colonization of Air Filters and Insulation in a Multi-Story Office Building: Production of Volatile Organics; *Curr. Microbiol.* **1997**, *35*, 305-308.
135. Taylor, P.E.; Flagan, R.C.; Miguel, A.G.; Valenta, R.; Glovsky, M.M. Birch Pollen Rupture and the Release of Aerosols of Respirable Allergens; *Clin. Exper. Allergy* **2004**, *34*, 1591-1596.
136. de la Mora, J.F. Diffusion Broadening in Converging Differential Mobility Analyzers; *J. Aerosol. Sci.* **2002**, *33*, 411-437.
137. Sgro, L.A.; de la Mora, J.F.A. Simple Turbulent Mixing cnc for Charged Particle Detection Down to 1.2 nm; *Aerosol. Sci. Technol.* **2004**, *38*, 1-11.
138. Kim, C.S.; Okuyama, K.; de la Mora, J.F. Performance Evaluation of an Improved Particle Size Magnifier (psm) for Single Nanoparticle Detection; *Aerosol. Sci. Technol.* **2003**, *37*, 791-803.
139. Kumar, P.; Chen, D.; Dudukovic, M.; Biswas, P. A high throughput DMA for measuring nanoparticle size distributions during synthesis of iron oxide in flame reactors. *Aerosol Sci. Technol.*, 2005 (submitted).
140. Kymalainen, M.; Janka, K.; Keskinen, J.; Moisio, M.; Backman, R.; Hupa, M. Measurement of Time-Dependent Fume Release Rate During Black Liquor Pyrolysis; *J. Pulp Paper Sci.* **1996**, *22*, J17-J23.
141. Keskinen, J.; Pietarinen, K.; Lehtimaki, M. Electrical Low-Pressure Impactor; *J. Aerosol. Sci.* **1992**, *23*, 353-360.
142. Hurd, A.J.; Ho, P. in Situ Light-Scattering Study of Particles Synthesized in a rf Silane Ammonia Glow-Discharge; *J. Aerosol. Sci.* **1991**, *22*, 617-635.
143. Knosche, C.; Friedrich, H.; Stintz, M. Determination of Particle Size Distribution and Electrokinetic Properties With the AcoustoSizer in Comparison With Other Methods; *Part. Part. Sys. Char.* **1997**, *14*, 175-180.
144. Noble, C.A.; Prather, K.A. Real-Time Single Particle Mass Spectrometry: a Historical Review of a Quarter Century of the Chemical Analysis of Aerosols; *Mass Spectrom. Rev.* **2000**, *19*, 248-274.
145. Middlebrook, A.M.; Murphy, D.M.; Lee, S.H.; Thomson, D.S.; Prather, K.A.; Wenzel, R.J.; Liu, D.Y.; Phares, D.J.; Rhoads, K.P.; Wexler, A.S.; Johnston, M.V.; Jimenez, J.L.; Jayne, J.T.; Worsnop, D.R.; Yourshaw, I.; Seinfeld, J.H.; Flagan, R.C. A Comparison of Particle Mass Spectrometers During the 1999 Atlanta Supersite Project; *J. Geophys. Res. Atmos.* **2003**, 108, No. 8424.
146. de la Mora, J.F.; Riescochueca, P. Aerodynamic Focusing of Particles in a Carrier Gas; *J. Fluid Mech.* **1988**, *195*, 1-21.
147. Rao, N.P.; Navascues, J. Fernadez de la Mora, J. Aerodynamic Focusing of Particles in Viscous Jets; *J. Aerosol. Sci.* **1993**, *24*, 879-892.
148. Schreiner, J.; Voigt, C.; Mauersberger, K.; McMurry, P.; Ziemann, P. Aerodynamic Lens System for Producing Particle Beams at Stratospheric Pressures; *Aerosol. Sci. Technol.* **1998,** *29*, 50-56.
149. de la Mora, .J.F. Drastic Improvement of the Resolution of Aerosol Size Spectrometers via Aerosynamic Focusing: The Case of Variable-Pressure Impactors; *Chem. Eng. Comm.* **1996,** *151*, 101-124.
150. Mahadevan, R.; Lee, D.; Sakurai, H.; Zachariah, M.R. Measurement of Condensed-Phase Reaction Kinetics in the Aerosol Phase Using Single Particle Mass Spectrometry; *J. Phys. Chem. A* **2002**, *106,* 11083-11092.
151. Azaroff, L. V. *Elements of X-Ray Crystallography;* McGraw Hill: New York, 1968.
152. Xu, C.Y.; Zhang, P.X.; Yan, L. Blue Shift of Raman Peak From Coated TiO2 Nanoparticles; *J. Raman Spect.* **2001**, *32*, 862-865.
153. Almquist, C.; Biswas, P. Role of Synthesis Method and Particle Size of Nanostructured Titanium Dioxide on its Photoactivity; *J. Catal.* **2002**, *212*, 145-156.
154. Wang, Z. M.; Yang, G.; Biswas, P.; Bresser, W.; Boolchand, P. Processing of Iron-Doped Titania Powders in Flame Aerosol Reactors; *Powder Technol.* **2001**, *114*, 197-204.
155. Dionysiou, D.D. Environmental Applications and Implications of Nanotechnology and Nanomaterials; *J. Environ. Eng.-Asce* **2004**, *130*, 723-724.
156. Anastas, P.T.; Zimmerman, J.B. Design through the 12 principles of green engineering; *Environ. Sci. Technol.* **2003**, *37*, 94a-101a.
157. CEBC. *NSF Engineering Research Center for Environmentally Beneficial Catalysis*. Available at http://www.cebc.ku.edu/research/strategicplan.shtml (accessed 2004).
158. Socolof, M.L.; Overly, J.G.; Kincaid, L.E.; Geibig, J.R. *Desktop Computer Displays: A Life-Cycle Assessment: Vol I and II*. Design for the Environment Computer Display Project; Washington, DC, 2001.

159. Bekyarova, E.; Davis, M.; Burch, T.; Itkis, M.E.; Zhao, B.; Sunshine, S.; Haddon, R.C. Chemically Functionalized Single-Walled Carbon Nanotubes as Ammonia Sensors; *J. Phys. Chem. B* **2004**, *108*, 19717-19720.
160. Kong, J.; Franklin, N.R.; Zhou, C.W.; Chapline, M.G.; Peng, S.; Cho, K.J.; Dai, H.J. Nanotube Molecular Wires as Chemical Sensors; *Science* **2000**, *287*, 622-625.
161. Cui, Y.; Wei, Q.Q.; Park, H.K.; Lieber, C.M. Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species; *Science* **2001**, *293*, 1289-1292.
162. Kennedy, M.K.; Kruis, F.E.; Fissan, H.; Mehta, B.R. Fully Automated, gas Sensing, and Electronic Parameter Measurement Setup for Miniaturized Nanoparticle gas Sensors; *Rev. Sci. Inst.* **2003**, *74*, 4908-4915.
163. Fan, Z.Y.; Wang, D.W.; Chang, P.C.; Tseng, W.Y.; Lu, J.G. zno Nanowire Field-Effect Transistor and Oxygen Sensing Property; *Appl. Phys. Lett.* **2004**, *85*, 5923-5925.
164. Linak, W.P.; Wendt, J.O.L. Toxic Metal Emissions From Incineration - Mechanisms and Control; *Prog. Energy Combust. Sci.* **1993**, *19*, 145-185.
165. Uberoi, M.; Shadman, F. Sorbents for Removal of Lead Compounds From Hot Flue Gases; *AIChE J.* **1990**, *36*, 307.
166. Uberoi, M.; Punjak, W.A.; Shadman, F. the Kinetics and Mechanism of Alkali Removal From Flue-Gases by Solid Sorbents; *Prog. Energy Combust. Sci.* **1990**, *16*, 205-211.
167. Scotto, M.V.; Uberoi, M.; Peterson, T.W.; Shadman, F.; Wendt, J.O.L. Metal Capture by Sorbents in Combustion Processes; *Fuel Process. Technol.* **1994**, *39*, 357-372.
168. Owens, T.M.; Biswas, P. Vapor Phase Sorbent Precursors for Toxic Metal Emissions Control From Combustors; *Indust. Eng. Chem. Res.* **1996**, *35*, 792-798.
169. Owens, T.M.; Biswas, P. Reactions Between Vapor Phase Lead Compounds and in Situ Generated Silica Particles at Various Lead-Silicon Feed Ratios: Applications to Toxic Metal Capture in Combustors; *J. Air & Waste Manage. Assoc.* **1996**, *46*, 530-538.
170. Wu, C.Y.; Lee, T. G.; Tyree, G.; Arar, E.; Biswas, P. Capture of Mercury in Combustion Systems by In Situ Generated Titania Particles With uv Irradiation; *Environ. Engr. Sci.* **1998**, *15*, 137-148.
171. Biswas, P.; Zachariah, M.R. In Situ Immobilization of Lead Species in Combustion Environments by Injection of gas Phase Silica Sorbent Precursors; *Environ. Sci. Technol.* **1997**, *31*, 2455-2463.
172. Linak, W.P.; Srivastava, R.K.; Wendt, J.O.L. Sorbent Capture of Nickel, Lead, and Cadmium in a Laboratory Swirl Flame Incinerator; *Combust. Flame* **1995**, *100*, 241.
173. Senior, C.; Bustard, C.J.; Durham, B.; Baldrey, K.; Michaud, D. Characterization of fly ash From Full-Scale Demonstration of Sorbent Injection for Mercury Control on Coal-Fired Power Plants; *Fuel Process. Technol.* **2004**, *85*, 601-612.
174. Flagan, R. C.; Seinfeld, J. H. *Fundamentals of Air Pollution Engineering;* Prentice Hall: Englewood Cliffs, NJ, 1988.
175. Uberoi, M.; Shadman, F. Simultaneous Condensation and Reaction of Metal Compound Vapors in Porous Solids; *Ind. Eng. Chem. Res.* **1991**, *30*, 624-631.
176. Chun, P.; Hall, M.J. Sorbent Capture of Lead and Barium in a Bench-Scale Incinerator Combusting Simulated Waste Lubricating Oil; *Combust. Sci. Technol.* **1996**, *116*, 517-539.
177. Davis, S.B.; Wendt, J.O.L. Quantitative Analysis of High Temperature Toxic Metal Sorption Rates Using Aerosol Fractionation; *Aero. Sci. Technol.* **2000**, *33*, 536-543.
178. Ho, T.C.; Chuang, T.C.; Chelluri, S.; Lee, Y.; Hopper, J.R. Simultaneous Capture of Metal, Sulfur and Chlorine by Sorbents During Fluidized Bed Incineration; *Waste Manage.* **2001**, *21*, 435-441.
179. Iida, K.; Pierman, J.; Tolaymat, T.; Townsend, T.; Wu, C.Y. Control of Chromated Copper Arsenate Wood Incineration air Emissions and ash Leaching Using Sorbent Technology; *J. Environ. Eng.-Asce* **2004**, *130*, 184-192.
180. Linak, W.P.; Miller, C.A.; Wood, J.P.; Shinagawa, T.; Yoo, J. I.; Santoianni, D.A.; King, C.J.; Wendt, J.O.L., Seo, Y.C. High Temperature Interactions Between Residual oil ash and Dispersed Kaolinite Powders; *Aerosol. Sci. Technol.* **2004**, *38*, 900-913.
181. Wu, C.Y.; Biswas, P. an Equilibrium Analysis to Determine the Speciation of Metals in an Incinerator; *Combust. Flame* **1993**, *93*, 31-40.
182. Wu, C.Y.; Barton, T.A. Thermodynamic Equilibrium Analysis to Determine the Potential Sorbent Materials for the Control of Arsenic Emissions From Combustion Sources; *Environ. Eng. Sci.* **2001**, *18*, 177-190.
183. Brown, T.D.; Smith, D.N.; Hargis, R.A; O'Dowd, W. J. Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate. *J. Air & Waste Manage. Assoc.* **1999**, *49*, 628-640.
184. Kwon, S.; Vidic, R.D. Evaluation of two Sulfur Impregnation Methods on Activated Carbon and Bentonite for the Production of Elemental Mercury Sorbents; *Environ. Eng. Sci.* **2000**, *17*, 303-313.
185. Huang, H.S.; Wu, J.A.M., Livengood, C.D. Development of dry Control Technology for Emissions of Mercury in Flue Gas; *Hazard. Waste Hazard. Mater.* **1996**, *13*, 107-119.
186. Crocker, C.R.; Benson, S.A.; Holmes, M.; Zhuang, Y.; Pavlish, J.H.; Galbreath, K.C. Comparison of Sorbents and Furnace Additives for Mercury Control in Low Rank Fuel Combustion Systems. *Abstracts of Papers of the American Chemical Society 227*. U1089-U1089 126—Fuel Part 1, March 28, 2004.
187. O'Dowd, W.J.; Hargis, R.A.; Granite, E.J.; Pennline, H.W. Recent Advances in Mercury Removal Technology at the National Energy Technology Laboratory; *Fuel Process. Technol.* **2004**, *85*, 533-548.
188. Pitoniak, E.; Wu, C.Y.; Londeree, D.; Mazyck, D.; Bonzongo, J.C.; Powers, K.; Sigmund, W. Nanostructured Silica-Gel Doped With TiO2 for Mercury Vapor Control; *J. Nanopart. Res.* **2003**, *5*, 281-292.
189. Rodriguez, S.; Almquist, C.; Lee, T.G.; Furuuchi, M.; Hedrick, E.; Biswas, P.A. Mechanistic Model for Mercury Capture With in Situ-Generated Titania Particles: Role of Water Vapor; *J. Air & Waste Manage. Assoc.* **2004**, *54*, 149-156.
190. Biswas, P.; Yang, G.; Zachariah, M.R. In Situ Processing of Ferroelectric Materials From Lead Waste Streams by Injection of Gas Phase Titanium Precursors: Laser Induced Fluorescence and x-ray Diffraction Measurements; *Combust. Sci. Technol.* **1998**, *134*, 183-200.
191. Zimmer, A.T.; Biswas, P. Mechanistic Understanding of Aerosol Emissions From a Brazing Operation; *Am. Ind. Hyg. Assoc. J.* **2000**, *16*, 351-361.
192. Zimmer, A. T. Personal Communication: Use of Welding Exhaust for Wastewater Remediation, 2004.
193. National Research Council. *Innovation in Ground Water and Soil Cleanup: From Concept to Commercialization*; National Research Council: Washington, DC, 1997.
194. Waychunas, G. A. *Structure, Aggregation and Characterization of Nanoparticles*. The Mineralogical Society of America: Washington, DC, 2001.
195. Obare, S.O.; Meyer, G.J. Nanostructured Materials for Environmental Remediation of Organic Contaminants in Water; *J. Environ. Sci. Health Part a-Toxic/Hazard. Substances Environ. Eng.* **2004**, *39*, 2549-2582.
196. Elliott, D.W.; Zhang, W.X. Field Assessment of Nanoscale Biometallic Particles for Groundwater Treatment; *Environ. Sci. Technol.* **2001**, *35*, 4922-4926.
197. Kulkarni, P.; Sureshkumar, R.; Biswas, P. Multiscale Simulation of Irreversible Deposition in Presence of Double Layer Interactions; *J. Colloid Interface Sci.* **2003**, *260*, 36-48.
198. Kulkarni, P.; Biswas, P. Morphology of Nanostructured Films for Environmental Applications: Simulation of Simultaneous Sintering and Growth; *J. Nanopart. Res.* **2003**, *5*, 259-268.
199. Ponder, S.M.; Darab, J.G.; Mallouk, T.E. Remediation of cr(vi) and pb(ii) Aqueous Solutions Using Supported, Nanoscale Zero-Valent Iron; *Environ. Sci. Technol.* **2000**, *34*, 2564-2569.
200. Kwon, S.; Vidic, R.; Borguet, E. The Effect of Surface Chemical Functional Groups on the Adsorption and Desorption of a Polar Molecule, Acetone, From a Model Carbonaceous Surface, Graphite; *Surface Sci.* **2003**, *522*, 17-26.
201. Oliveira, L.C.A., Petkowicz, D.I.; Smaniotto, A.; Pergher, S.B.C. Magnetic Zeolites: a new Adsorbent for Removal of Metallic Contaminants From Water; *Water Res.* **2004**, *38*, 3699-3704.
202. Meyer, D.E.; Wood, K.; Bachas, L.G.; Bhattacharyya, D. Degradation of Chlorinated Organics by Membrane-Immobilized Nanosized Metals; *Environ. Prog.* **2004**, *23*, 232-242.
203. Yang, G.X.; Biswas, P.; Boolchand, P.; Sabata, A. Deposition of Multifunctional Titania Ceramic Films by Aerosol Routes; *J. Am. Ceramic Soc.* **1999**, *82*, 2573-2579.
204. Almquist, C.B.; Sahle-Demessie, E.; Enriquez, J.; Biswas, P. the Photocatalytic Oxidation of low Concentration MTBE on Titanium Dioxide From Groundwater in a Falling Film Reactor; *Environ. Prog.* **2003**, *22*, 14-23.
205. Namiki, N.; Cho, K.; Fraundorf, P.; Biswas, P. Tubular Reactor Synthesis of Doped Nanostructured Titanium Dioxide and its Enhanced Activation by Coronas and Soft X-ray. *Ind. Eng. Chem. Res.*, in press.
206. Long, R.Q.; Yang, R.T. Carbon Nanotubes as Superior Sorbent for Dioxin Removal; *J. Am. Chem. Soc.* **2001**, *123*, 2058-2059.
207. Liu, G.H.; Wang, J.L.; Zhu, Y.F.; Zhang, X.R. Application of Multiwalled Carbon Nanotubes as a Solid-Phase Extraction Sorbent for Chlorobenzenes; *Anal. Lett.* **2004**, *37*, 3085-3104.
208. Zhang, Q.W.; Kusaka, Y.; Sato, K.; Nakakuki, K.; Kohyama, N.; Donaldson, K. Differences in the Extent of Inflammation Caused by Intratracheal Exposure to Three Ultrafine Metals: Role of Free Radicals; *J. Toxicol. Environ. Health-Part a-Curr. Iss.* **1998**, *53*, 423-438.
209. Adams, R.D.; Captain, B.; Hall, M.B.; Smith, J. L.,. Jr.;; Webster, C.E. High Nuclearity Iridium-Platinum Clusters: Synthesis, Structures, Bonding, and Reactivity. *J. Amer. Chem. Soc.* **2005**, *127*, 1007-1014.
210. Haruta, M. Gold as a Novel Catalyst in the 21st Century: Preparation, Working, Mechanism and Applications; *Gold Bull.* **2004**, *37*, 27-36.

211. Schlogl, R.; Abd Hamid, S.B. Nanocatalysis: Mature Science Revisited or Something Really New?; *Angewandte Chemie-International Edition* **2004**, *43*, 1628-1637.
212. Kamat, P.V.; Meisel, D. Nanoscience Opportunities in Environmental Remediation; *Comptes Rendus Chimie* **2003**, *6*, 999-1007.
213. Fujishima, A.; Rao, T.N.; Tryk, D.A. Titanium Dioxide Photocatalysis; *J. Photochem. Photobio. C: Photochem. Rev.* **2000**, *1*, 1-21.
214. Gerischer, H. Photocatalysis in Aqueous-Solution With Small Tio2 Particles and the Dependence of the Quantum Yield on Particle-Size and Light-Intensity; *Electrochimica Acta* **1995**, *40*, 1277-1281.
215. Carp, O.; Huisman, C.L.; Reller, A. Photoinduced Reactivity of Titanium Dioxide; *Prog. Solid State Chem.* **2004**, *32*, 33-177.
216. Weber, A.P.; Seipenbusch, M.; Kasper, G. Size Effects in the Catalytic Activity of Unsupported Metallic Nanoparticles; *J. Nanopart. Res.* **2003**, *5*, 293-298.
217. Wegner, R.; Pratsinis, S.E. Flame Synthesis of Nanoparticles; *Chimica Oggi-Chemistry Today* **2004**, *22*, 27-29.
218. DOE. *Basic Research Needs for the Hydrogen Economy: Report of the Basic Energy Science Workshop on Hydrogen Production, Storage and Use*; Office of Science, US Department of Energy: Washington, DC, 2003.
219. Dresselhaus, M.S.; Thomas, I.L. Alternative Energy Technologies; *Nature* **2001**, *414*, 332-337.
220. U.S. Department of Energy. *Targets for On-Board Hydrogen Storage Systems, Office of Energy Efficient and Renewable Energy, U.S. Department of Energy*. Available at http://www.eere.energy.gov/hydrogenand fuelcells/pdfs/freedomcar_targets_explanations.pdf (accessed 2005).
221. Sukhatme, S. P. Solar Energy, 2nd ed.; New Dehli, India: McGraw Hill, 1996.
222. Bak, T.; Nowetny, J.; Rekas, M.; Sorrell, C.C. Review Article: Photo-Electrochemical Hydrogen Generation From Water Using Solar Energy. Material-Related Aspects; *Intl. J. Hydrogen Energy* **2002**, *27*, 991-1022.
223. Fujishima, A.; Honda, K. Electrochemical Photocatalysis of Water at a Semiconductor Electrode; *Nature* **1972**, *238*, 37-38.
224. Choi, W.Y.; Termin, A.; Hoffmann, M.R. The Role of Metal-ion Dopants in Quantum-Sized Tio2—Correlation Between Photoreactivity and Charge-Carrier Recombination Dynamics; *J. Phys. Chem.* **1994**, *98*, 13669-13679.
225. Karn, R.K.; Srivastava, O.N. On the Synthesis and Photochemical Studies of Nanostructured TiO2 and TiO2 Admired vo2 Photoelectrodes in Regard to Hydrogen Production Through Photoelectrolysis; *Int. J. Hydrogen Energy* **1999**, *24*, 965-971.
226. Wei, S.H.; Zunger, A. Band-Gap Narrowing in Ordered and Disordered Semiconductor Alloys; *Appl. Phys. Lett.* **1990**, *56*, 662-664.
227. Zhao, G.L.; Kozuka, H.; Lin, H.; Takahashi, M.; Yoko, T. Preparation and Photoelectrochemical Properties of ti1-XVxO2 Solid Solution Thin Film Photoelectrodes With Gradient Bandgap; *Thin Solid Films* **1999**, *340*, 125-131.
228. Gratzel, M. the Artificial Leaf; *Bio-Mimetic Photocatalysis* **1999**, *3*, 3-17.
229. Khan, S.U.M., Al-Shahry, M.; Ingler, W.B. Efficient Photochemical Water Splitting by a Chemically Modified n-TiO2 2; *Science* **2002**, *297*, 2243-2245.
230. Kaiser, I.; Ernst, K.; Fischer, C.H.; Konenkamp, R.; Rost, C.; Sieber, I.; Lux-Steiner, M.C. the eta-Solar Cell With CuInS2: a Photovoltaic Cell Concept Using an Extremely Thin Absorber (eta); *Solar Energy Mater. Solar Cells* **2001**, *67*, 89-96.
231. Yu, G.; Gao, J.; Hummelen, J.C.; Wudl, F.; Heeger, A.J. Polymer Photovoltaic Cells - Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions; *Science* **1995**, *270*, 1789-1791.
232. Barbec, C.J. Polymeric Photovoltaic Devices; *Mater. Today* **2000**, *3*, 5-8.
233. Armor, J.N. Review: The Multiple Roles for Catalysis in the Production of H2; *Appl. Catal. A: General* **1999**, *176*, 159-176.
234. Fu, Q.; Kudriavtseva, S.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Gold-Ceria Catalysts for low-Temperature Water-Gas Shift Reaction; *Chem. Eng. J.* **2003**, *93*, 41-53.
235. Hilaire, S.; Wang, X.; Luo, T.; Gorte, R.J.; Wagner, J.A. Comparative Study of Water-gas-Shift Reaction Over Ceria Supported Metallic Catalysts; *Appl. Catal. a-Gen.* **2001**, *215*, 271-278.
236. Park, J.W.; Jeong, J.H.; Yoon, W.L.; Kim, C.S.; Lee, D.K.; Park, Y.K.; Rhee, Y.W. Selective Oxidation of co in Hydrogen-Rich Stream Over cu-ce Catalyst Promoted With Transition Metals; *Int. J. Hydrodgen Energy* **2005**, *30*, 209-220.
237. Hagh, B.F. Optimization of Autothermal Reactor for Maximum Hydrogen Production; *Int. J. Hydrodgen Energy* **2003**, *28*, 1369-1377.
238. Cheekatamarla, P.K.; Lane, A.M. *Efficient Bimetallic Catalysts for the Autothermal Reforming of Diesel Fuel*. AIChE Spring National Meeting: New Orleans, LA, 2004.
239. Wang, W.; Stagg-Williams, S.M.; Noronha, F.B.; Mattos, L.V.; Passos, F.B. Partial Oxidation and Combined Reforming of Methane on ce-Promoted Catalysts; *Abstracts Pap. Am. Chem. Soc.* **2004**, *227*, U1077-U1077.
240. Chen, M.S.; Goodman, D.W. The Structure of Catalytically Active Gold on Titania; *Science* **2004**, *306*, 252-255.
241. Schlapbach, L.; Zuttel, A. Hydrogen-Storage Materials for Mobile Applications; *Nature* **2001**, *414*, 353-358.
242. SNL (Sandia National Laboratory). Available at: http://hydpark.ca.sandia.gov/DBFrame.html (accessed 2005).
243. Zaluska, A.; Zaluski, L.; Strom-Olsen, J.O. Nanocrystalline Magnesium for Hydrogen Storage; *J. Alloys Compounds* **1999**, *288*, 217-225.
244. Zaluska, A.; Zaluski, L.; Strom-Olsen, J.O. Structure, Catalysis and Atomic Reactions on the Nano-Scale: a Systematic Approach to Metal Hydrides for Hydrogen Storage; *Appl. Phys. a-Mater. Sci. Process.* **2001**, *72*, 157-165.
245. Liang, J.J. Theoretical Insight on Tailoring Energetics of mg Hydrogen Absorption/Desorption Through Nano-Engineering; *Appl. Phys. a-Mater. Sci. Process.* **2005**, *80*, 173-178.
246. Liang, G.; Huot, J.; Boily, S.; Van Neste, A.; Schulz, R. Hydrogen Storage Properties of the Mechanically Milled MgH2-v Nanocomposite; *J. Alloys Compounds* **1999**, *291*, 295-299.
247. Bogdanovic, B.; Schwickardi, M. ti-Doped Alkali Metal Aluminum Hydrides as Potential Novel Reversible Hydroge Storage Materials; *J. Alloys Comp.* **1997**, *253*, 1-9.
248. Oelerich, W.; Klassen, T.; Bormann, R. Metal Oxides as Catalysts for Improved Hydrogen Sorption in Nanocrystalline mg-Based Materials; *J. Alloys Comp.* **2001**, *315*, 237-242.
249. Higuchi, K.; Yamamoto, K.; Kajioka, H.; Toiyama, K.; Honda, M.; Orimo, S.; Fujii, H. Remarkable Hydrogen Storage Properties in Three-Layered pd/mg/pd Thin Films; *J. Alloys Comp.* **2002**, *330*, 526-530.
250. Yukawa, H.; Nakatsuka, K.; Morinaga, M. Design of Hydrogen Storage Alloys in View of Chemical Bond Between Atoms; *Solar Energy Mater. Solar Cells* **2000**, *62*, 75-80.
251. Nijkamp, M.G.; Raaymakers, J. E. M. J.; van Dillen, A.J.; de Jong, K.P. Hydrogen Storage Using Physisorption - Materials Demands; *Appl. Phys. a-Mater. Sci. Process.* **2001**, *72*, 619-623.
252. Simonyan, V.V.; Johnson, J.K. Hydrogen Storage in Carbon Nanotubes and Graphitic Nanofibers; *J. Alloys Comp.* **2002**, *330*, 659-665.
253. Zuttel, A.; Orimo, S. Hydrogen in Nanostructured, Carbon-Related, and Metallic Materials. *Mrs Bulletin*, **2002**, *27*, 705–711.
254. Dagani, R. Tempest in a Tiny Tube; *Chem. Eng. News* **2002**, *80*, 25-28.
255. Zuttel, A.; Nutzenadel, C.; Sudan, P.; Mauron, P.; Emmenegger, C.; Rentsch, S.; Schlapbach, L.; Weidenkaff, A.; Kiyobayashi, T. Hydrogen Sorption by Carbon Nanotubes and Other Carbon Nanostructures; *J. Alloys Comp.* **2002**, *330*, 676-682.
256. DOE. *National Hydrogen Vision and Roadmap*. Available at: http://www.eere.energy.gov/hydrogenandfuelcells/ (accessed 2005).
257. Wilson, M.S.; Valerio, J.A.; Gottesfeld, S. Low Platinum Loading Electrodes for Polymer Electrolyte Fuel-Cells Fabricated Using Thermoplastic Ionomers; *Electrochim. Acta* **1995**, *40*, 355-363.
258. Uchida, M.; Fukuoka, Y.; Sugawara, Y.; Ohara, H.; Ohta, A. Improved Preparation Process of Very-low-Platinum-Loading Electrodes for Polymer Electrolyte Fuel Cells; *J. Electrochem. Soc.* **1998**, *145*, 3708-3713.
259. Starz, K.A.; Auer, A.; Lehmann, T.; Zuber, R. Characterization of Platinum-Based Electrocatalysts for Mobile PEMFC Applications; *J. Power Sources* **1999**, *84*, 167-172.
260. Brankovic, S.R.; Wang, J.X.; Adzic, R.R.A. Novel low pt Loading, High co Tolerance Fuel Cell Electrocatalyst; *Electrochem. Solid-State Lett.* 4:A217–A220, 2001.
261. Lattner, J.R.; Harold, M.P. Comparison of Conventional and Membrane Reactor Fuel Processors for Hydrocarbon-Based pem Fuel Cell Systems; *Int. J. Hydrodgen Energy* **2004**, *29*, 393-417.
262. Yamazaki, Y.; Jang, M.Y.; Taniyama, T. Proton Conductivity of Zirconium Tricarboxybutylphosphonate/pbi Nanocomposite Membrane; *Sci. Technol. Adv. Mater.* **2004**, *5*, 455-459.
263. Tullo, A.H. Fuel Cells Rally; *Chem. Eng. News* **2005**, *83,* 18-20.
264. McNicol, B.D.; Rand, D.A.J., Williams, K.R. Direct Methanol-Air Fuel Cells for Road Transportation; *J. Power Sources* **1999**, *83*, 15-31.
265. Yu, H.B.; Kim, J.H.; Lee, H.I.; Scibioh, M.A.; Lee, J.; Han, J.; Yoon, S.P.; Ha, H.Y. Development of Nanophase CeO2-pt/c Cathode Catalyst for Direct Methanol Fuel Cell; *J. Power Sources* **2005**, *140*, 59-65.
266. Steele, B.C.H. Appraisal of ce1-y NospacegdyqqO2-y/2 Electrolytes for it-SOFC Operation at 500 Degrees c; *Solid State Ionics* **2000**, *129*, 95-110.
267. Xia, C.R.; Chen, F.L.; Liu, M.L. Reduced-Temperature Solid Oxide Fuel Cells Fabricated by Screen Printing; *Electrochem. Solid State Lett.* **2001**, *4*, A52-A54.
268. Casado-Rivera, E.; Gal, Z.; Angelo, A.C.D.; Lind, C; DiSalvo, F.J.; Abruna, H.D. Electrocatalytic Oxidation of Formic Acid at an Ordered Intermetallic PtBi surface; *Chemphyschem* **2003**, *4*, 193-199.
269. Prinn, R.G.; Huang, J.; Weiss, R.F.; Cunnold, D.M.; Fraser, P.J.; Simmonds, P.G.; McCulloch, A.; Harth, C.; Salameh, P. O'Doherty, S.; Wang, R; H. J.; Porter, L.; Miller, B. R. Evidence for Substantial Variations of Atmospheric Hydroxyl Radicals in the Past Two Decades. *Science* **2001**, *292*, 1882-1888.
270. Tromp, T.K.; Shia, R.L.; Allen, M.; Eiler, J.M.; Yung, Y.L. Potential Environmental Impact of a Hydrogen Economy on the Stratosphere; *Science* **2003**, *300*, 1740-1742.

271. Novelli, P.C.; Lang, P.M.; Masarie, K.A.; Hurst, D.F.; Myers, R.; Elkins, J.W. Molecular Hydrogen in the Troposphere: Global Distribution and Budget; *J. Geophys. Res. Atmos.* **1999**, *104*, 30427-30444.
272. Hoehler, T.M.; Bebout, B.M.; Des Marais, D.J. the Role of Microbial Mats in the Production of Reduced Gases on the Early Earth; *Nature* **2001**, *412*, 324-327.
273. Tarascon, J.M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries; *Nature* **2001**, *414*, 359-367.
274. Le, D.B.; Passerini, S.; Guo, J.; Ressler, J.; Owens, B.B.; Smyrl, W.H. High Surface Area V2O5 Aerogel Intercalation Electrodes; *J. Electrochem. Soc.* **1996**, *143*, 2099-2104.
275. Dong, W.; Rolison, D.R.; Dunn, B. Electrochemical Properties of High Surface Area Vanadium Oxide Aerogels; *Electrochem. Solid State Lett.* **2000**, *3*, 457-459.
276. Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J.M. Nano-Sized Transition-Metaloxides as Negative-Electrode Materials for Lithium-Ion Batteries; *Nature* **2000**, *407*, 496-499.
277. Croce, F.; Appetecchi, G.B.; Persi, L.; Scrosati, B. Nanocomposite Polymer Electrolytes for Lithium Batteries; *Nature* **1998**, *394*, 456-458.
278. Seaton, A.; Macnee, W.; Donaldson, K.; Godden, D. Particulate Air-Pollution and Acute Health-Effects; *Lancet* **1995**, *345*, 176-178.
279. Seaton, A. Particles in the air: the Enigma of Urban air Pollution; *J. Royal Soc. Med.* **1996**, *89*, 604-607.
280. Liao, D.P.; Creason, J.; Shy, C.; Williams, R.; Watts, R.; Zweidinger, R. Daily Variation of Particulate Air Pollution and Poor Cardiac Autonomic Control in the Elderly; *Environ. Health. Perspect.* **1999**, *107*, 521-525.
281. Gold, D.R.; Litonjua, A.; Schwartz, J.; Lovett, E.; Larson, A.; Nearing, B.; Allen, G.; Verrier, M.; Cherry, R.; Verrier, R. Ambient Pollution and Heart Rate Variability; *Circulation* **2000**, *101*, 1267-1273.
282. Samet, J.M.; Dominici, F.; Curriero, F.C.; Coursac, I.; Zeger, S.L. Fine Particulate Air Pollution and Mortality in 20 US Cities, 1987–1994; *N. Engl. J. Med.* **2000**, *343*, 1742-1749.
283. Pekkanen, J.; Timonen, K.L.; Ruuskanen, J.; Reponen, A.; Mirme, A. Effects of Ultrafine and Fine Particles in Urban Air on Peak Expiratory Flow Among Children With Asthmatic Symptoms; *Environ. Res.* **1997**, *74*, 24-33.
284. Peters, A.; Dockery, D.W.; Muller, J.E.; Mittleman, M.A. Increased Particulate Air Pollution and the Triggering of Myocardial Infarction; *Circulation* **2001**, *103*, 2810-2815.
285. Penttinen, P.; Timonen, K.L.; Tiittanen, P.; Mirme, A.; Ruuskanen, J.; Pekkanen, J. Ultrafine Particles in Urban Air and Respiratory Health Among Adult Asthmatics; *Eur. Respir. J.* **2001**, *17*, 428-435.
286. Ibald-Mulli, A.; Wichmann, H.E.; Kreyling, W.; Peters, A. Epidemiological Evidence on Health Effects of Ultrafine Particles; *J. Aerosol Med. Deposition Clear. Effects Lung* **2002**, *15*, 189-201.
287. Pekkanen, J.; Peters, A.; Hoek, G.; Tiittanen, P.; Brunekreef, B.; de Hartog, J.; Heinrich, J.; Ibald-Mulli, A.; Kreyling, W.G.; Lanki, T.; Timonen, K.L.; Vanninen, E. Particulate air Pollution and Risk of st-Segment Depression During Repeated Submaximal Exercise Tests Among Subjects With Coronary Heart Disease - the Exposure and Risk Assessment for Fine and Ultrafine Particles in Ambient air (ULTRA) Study; *Circulation* **2002**, *106*, 933-938.
288. de Hartog, J.J.; Hoek, G.; Peters, A.; Timonen, K.L.; Ibald-Mulli, A.; Brunekreef, B.; Heinrich, J.; Tiittanen, P.; van Wijnen, J.H.; Kreyling, W.; Kulmala, M.; Pekkanen, J. Effects of Fine and Ultrafine Particles on Cardiorespiratory Symptoms in Elderly Subjects With Coronary Heart Disease - the ULTRA Study; *Am. J. Epidemiol.* **2003**, *157*, 613-623.
289. Peters, A.; Wichmann, H.E.; Tuch, T.; Heinrich, J.; Heyder, J. Respiratory Effects Are Associated With the Number of Ultrafine Particles; *American J. Respir. Crit. Care Med.* **1997**, *155*, 1376-1383.
290. Wiesner, M.R. Environmental Implications of Nanotechnologies; *Env. Eng.* **2003**, *39*, 8-11.
291. Hussain, N.; Jaitley, V.; Florence, A.T. Recent Advances in the Understanding of Uptake of Microparticulates Across the Gastrointestinal Lymphatics; *Adv. Drug Deliv. Rev.* **2001**, *50*, 107-142.
292. Samet, J.M. What Properties of Particulate Matter Are Responsible for Health Effects?; *Inhalat. Toxicol.* **2000**, *12*, 19-21.
293. Schlesinger, R.B. Properties of Ambient pm Responsible for Human Health Effects: Coherence Between Epidemiology and Toxicology; *Inhalat. Toxicol.* **2000**, *12*, 23-25.
294. Dreher, K.L.; Jaskot, R.H.; Lehmann, J.R.; Richards, J.H.; McGee, J.K.; Ghio, A.J.; Costa, D.L. Soluble Transition Metals Mediate Residual Oil Fly Ash Induced Acute Lung Injury; *J. Toxicol. Environ. Health* **1997**, *50*, 285-305.
295. Elder, A.C.P., Gelein, R.; Finkelstein, J.N.; Cox, C.; Oberdorster, G. Pulmonary Inflammatory Response to Inhaled Ultrafine Particles is Modified by Age, Ozone Exposure, and Bacterial Toxin; *Inhalat.Toxicol.* **2000**, *12*, 227-246.
296. von Klot, S.; Wolke, G.; Tuch, T.; Heinrich, J.; Dockery, D.W.; Schwartz, J.; Kreyling, W.G.; Wichmann, H.E.; Peters, A. Increased Asthma Medication Use in Association With Ambient Fine and Ultrafine Particles; *Eur. Respir. J.* **2002**, *20*, 691-702.
297. Jaques, P.A.; Kim, C.S. Measurement of Total Lung Deposition of Inhaled Ultrafine Particles in Healthy Men and Women; *Inhalat. Toxicol.* **2000**, *12*, 715-731.
298. Oberdörster, G. Pulmonary Effects of Inhaled Ultrafine Particles; *Internat. Arch. Occupat. Environ. Health* **2001**, *74*, 1-8.
299. Oberdörster, G.; Ferin, J.; Lehnert, B.E. Correlation Between Particle-Size, in-Vivo Particle Persistence, and Lung Injury; *Environ. Health. Perspect.* **1994**, *102*, 173-179.
300. Donaldson, K.; Stone, V.; Clouter, A.; Renwick, L.; MacNee, W. Ultrafine particles; *Occup. Environ. Med.*, **2001**, *58*, 211–216.
301. Cheng, Y.S.; Smith, S.M.; Yeh, H.C.; Kim, D.B.; Cheng, K.H.; Swift, D.L. Deposition of Ultrafine Aerosols and Thoron Progeny in Replicas of Nasal Airways of Young-Children; *Aerosol. Sci. Technol.* **1995**, *23*, 541-552.
302. Cheng, Y.S.; Yeh, H.C.; Guilmette, R.A.; Simpson, S.Q.; Cheng, K.H.; Swift, D.L. Nasal Deposition of Ultrafine Particles in Human Volunteers and Its Relationship to Airway Geometry; *Aerosol. Sci. Technol.* **1996**, *25*, 274-291.
303. Cheng, K.H.; Cheng, Y.S.; Yeh, H.C.; Guilmette, R.A.; Simpson, S.Q.; Yang, Y.H.; Swift, D.L. in Vivo Measurements of Nasal Airway Dimensions and Ultrafine Aerosol Deposition in the Human Nasal and Oral Airways; *J. Aerosol. Sci.* **1996**, *27*, 785-801.
304. Cohen, B.S.; Sussman, R.G.; Lippmann, M. Ultrafine Particle Deposition in a Human Tracheobronchial Cast; *Aerosol. Sci. Technol.* **1990**, *12*, 1082-1091.
305. Smith, S.; Cheng, U.S.; Yeh, H.C. Deposition of Ultrafine Particles in Human Tracheobronchial Airways of Adults and Children; *Aero. Sci. Technol.* **2001**, *35*, 697-709.
306. Cohen, B.S.; Xiong, J.Q.; Asgharian, B.; Ayres, L. Deposition of Inhaled Charged Ultrafine Particles in a Simple Tracheal Model; *J. Aero. Sci.* **1995**, *26*, 1149-1160.
307. Cohen, B.S.; Xiong, J.Q.; Fang, C.P.; Li, W. Deposition of Charged Particles on Lung Airways; *Health Phys.* **1998**, *74*, 554-560.
308. McDonald, R.; Biswas, P.A. Methodology to Establish the Morphology of Ambient Aerosols; *J. Air & Waste Manage. Assoc.* **2004**, *54*, 1069-1078.
309. ICRP(International Commission on Radiological Protection). *ICRP Publications 71: Age Dependant Doses to Members of the Public from Intake of Radionuclides: Part 4 Inhalation Dose Coefficients, 71*; *Annals of the ICRP*; Elsevier: New York, 1996.
310. ICRP(International Commission on Radiological Protection). *ICRP Publications 89: Basic Anatomical and Physiological Data for Use in radiological Protection: Reference Values*; Elsevier: New York, 2003.
311. NCRP (National Council on Radiation Protection and Measurement). *Deposition, Retention and Dosimetry of Inhaled Radioactive Substances; NCRP Report No. 125*; NCRP: Bethesda, MD, 1997.
312. Broday, D.M. Deposition of Ultrafine Particles at Carinal Ridges of the Upper Bronchial Airways; *Aero. Sci. Technol.* **2004**, *38*, 991-1000.
313. Oberdorster, G.; Finkelstein, J.N.; Johnson, C.; Gelein, R.; Cox, C.; Baggs, R.; Elder, A.C.P. *Acute Pulmonary Effects of Ultrafine Particles in Rats and Mice;* Health Effects Institute: Boston, MA, 2000.
314. Oberdorster, G.; Sharp, Z.; Atudorei, V.; Elder, A.; Gelein, R.; Lunts, A.; Kreyling, W.; Cox, C. Extrapulmonary Translocation of Ultrafine Carbon Particles Following Whole-Body Inhalation Exposure of Rats; *J. Toxicol. Environ. Health-Part A* **2002**, *65*, 1531-1543.
315. Berry, J.P.; Arnoux, B.; Stanislas, G.; Galle, P.; Chretien, J.A. Microanalytic Study of Particles Transport Across the Alveoli: Role of Blood Platelets; *Biomedicine* **1977**, *27*, 354-357.
316. Nemmar, A.; Hoet, P.H.M., Vanquickenborne, B.; Dinsdale, D.; Thomeer, M.; Howylaerts, M.F.; Vanbilleon, H.; Mortelmans, L.; Nemery, B. Passage of Inhaled Particles Into the Blood Circulation in Humans; *Circulation* **2002**, *105*, 411.
317. Silva, V.M. Ultrafine Particle (UFP) Effects on Experimental Thrombosis: The Ear Vein Model; *Toxicologist.* **2004**, *78(S-1)*, 17.
318. Kreyling, W.G.; Semmler, M.; Erbe, F.; Mayer, P.; Takenaka, S.; Schulz, H.; Oberdorster, G.; Ziesenis, A. Translocation of Ultrafine Insoluble Iridium Particles From Lung Epithelium to Extrapulmonary Organs is Size Dependent but Very low; *J. Toxicol. Environ. Health-Part A* **2002**, *65*, 1513-1530.
319. Semmler, M.; Seitz, J.; Erbe, F.; Mayer, P.; Heyder, J.; Oberdorster, G.; Kreyling, W.G. Long-Term Clearance Kinetics of Inhaled Ultrafine Insoluble Iridium Particles From the rat Lung, Including Transient Translocation Into Secondary Organs; *Inhalation Toxicol.* **2004**, *16*, 453-459.
320. Nemmar, A.; Vanbilloen, H.; Hoylaerts, M.F.; Hoet, P.H.M., Verbruggen, A.; Nemery, B. Passage of Intratracheally Instilled Ultrafine Particles From the Lung Into the Systemic Circulation in Hamster; *Am. J. Respir. Crit. Care Med.* **2001**, *164*, 1665-1668.
321. Yeates, D.B.; Mauderly, J.L. Inhaled Environmental/Occupational Irritants and Allergens: Mechanisms of Cardiovascular and Systemic Responses; *Environ. Health. Perspect.* **2001**, *109*, 479-481.
322. Nemmar, A.; Hoylaerts, M.F.; Hoet, P.H.M., Vermylen, J.; Nemery, B. Size Effect of Intratracheally Instilled Particles on Pulmonary Inflammation and Vascular Thrombosis; *Toxicol. Appl. Pharmacol.* **2003**, *186*, 38-45.

323. Oberdörster, G.; Sharp, Z.; Atudorei, V.; Elder, A.; Gelein, R.; Kreyling, W.; Cox, C. Translocation of Inhaled Ultrafine Particles to the Brain; *Inhalation Toxicol.* **2004**, *16*, 437-445.
324. Tjalve, H.; Henriksson, I. Uptake of Metals in the Brain via Olfactory Pathways; *Neurotoxicol.* **1999**, *20*, 181-195.
325. Bodian, D.; Howe, H. A. The Rate of Progression of Poliomyelitis Virus in Nerves; *Bull. Johns Hopkins Hosp.* **1941**, *LXIX*, 79-85.
326. De Lorenzo, A.J.D. The Olfactory Neuron and the Blood-Brain Barrier. In: *Taste and Smell in Vertebrates*. Wolstenholme, G. E. W., Knight, J., Eds. CIBA Foundation Symposium Series: Churchill, London, 1970.
327. Hunter, D.D.; Dey, R.D. Identification and Neuropeptide Content of Trigeminal Neurons Innervating the Rat Nasal Epithelium; *Neuroscience* **1998**, *83*, 591-599.
328. Warheit, D.B.; Seidel, W.C.; Carakostas, M.C.; Hartsky, M.A. Attenuation of Perfluoropolymer Fume Pulmonary Toxicity: Effect of Filters, Combustion Method and Aerosol Age. *Exp. Mol. Pathol.* **1990**, *52*, 309–329.
329. Fernandez-Urrusuno, R.; Fattal, E.; Feger, J.; Couvreur, P.; Therond, P. Evaluation of Hepatic Antioxidant Systems After Intravenous Administration of Polymeric Nanoparticles; *Biomaterials* **1997**, *18*, 511-517.
330. Luster, M. *Challenges in the Design of Toxicity Studies of Nanoscale Materials.* Proceedings of Developmental Approaches for Evaluation of Toxicological Interactions of Nanoscale Materials: Gainesville, FL, 2004.
331. Ferin, J.; Oberdorster, G.; Penney, D.P. Pulmonary Retention of Ultrafine and Fine Particles in Rats; *Am. J. Respir. Cell Mol. Biol.* **1992**, *6*, 535-542.
332. Donaldson, K.; Stone, V.; Gilmour, P.S.; Brown, D.M.; MacNee, W. Ultrafine Particles: Mechanisms of Lung Injury; *Philos. Trans. Royal Soc. Lond. Series a-Math. Phys. Eng. Sci.***2000**, *358*, 2741-2748.
333. Donaldson, K.; Beswick, P.H.; Gilmour, P.S. Free Radical Activity Associated with the Surface of Particles: A Unifying Factor in Determining Biological Activity?; *Toxicol. Lett.* **1996**, *88*, 293-298.
334. Heinrich, U.; Muhle, H.; Hoymann, H.G.; Mermelstein, R. Pulmonary-Function Changes in Rats After Chronic and Subchronic Inhalation Exposure to Various Particulate Matter; *Exper. Pathol.* **1989**, *37*, 248-252.
335. Lee, K.P.; Kelly, D.P.; Schneider, P.W.; Trochimowicz, H.J. Inhalation Toxicity Study on Rats Exposed to Titanium Tetrachloride Atmosphere Hydrolysis Products for Two Years; *Toxicol. Appl. Pharmacol.* **1986**, *83*, 30-45.
336. Oberdorster, G.; Yu, C.P. Commentary—Lung Dosimetry—Considerations for Noninhalation Studies; *Exper. Lung Res.* **1999**, *25*, 1-6.
337. Bermudez, E.; Mangum, J.B.; Wong, B.A.; Asgharian, B.; Hext, P.M.; Warheit, D.B.; Everitt, J.I. Pulmonary Responses of Mice, Rats, and Hamsters to Subchronic Inhalation of Ultrafine Titanium Dioxide Particles; *Toxic. Sci.* **2004**, *77*, 347-357.
338. Lademann, J.; Weigmann, H.J.; Rickmeyer, C.; Barthelmes, H.; Schaefer, H.; Mueller, G.; Sterry, W. Penetration of Titanium Dioxide Microparticles in a Sunscreen Formulation Into the Horny Layer and the Follicular Orifice; *Skin Pharmacol. Appl. Skin Physiol.* **1999**, *12*, 247-256.
339. Pflucker, F.; Wendel, V.; Hohenberg, H.; Gartner, E.; Will, T.; Pfeiffer, S.; Wepf, R.; Gers-Barlag, H. The Human Stratum Corneum Layer: an Effective Barrier Against Dermal Uptake of Different Forms of Topically Applied Micronised Titanium Dioxide; *Skin Pharmacol. Appl. Skin Physiol.* **2001**, *14*, 92-97.
340. Schulz, J.; Hohenberg, H.; Pflucker, F.; Gartner, E.; Will, T.; Pfeiffer, S.; Wepf, R.; Wendel, V.; Gers-Barlag, H.; Wittern, K.P. Distribution of Sunscreens on Skin; *Adv. Drug Deliv. Rev.* **2002**, *54*, S157-S163.
341. Arts, J.H.E., Spoor, S.M.; Muijser, H. Short-Term Inhalation Exposure of Healthy and Compromised Rats and Mice to Fine and Ultrafine Carbon Particles; *Inhal. Toxicol.* **2000**, *12*, 261-266.
342. Gilmour, P.S.; Ziesenis, A.; Morrison, E.R.; Vickers, M.A.; Drost, E.M.; Ford, I.; Karg, E.; Mossa, C.; Schroeppel, A.; Ferron, G.A.; Heyder, J.; Greaves, M.; MacNee, W.; Donaldson, K. Pulmonary and Systemic Effects of Short-Term Inhalation Exposure to Ultrafine Carbon Black Particles; *Toxicol. Appl. Pharmacol.* **2004**, *195*, 35-44.
343. Warheit, D.B.; Laurence, B.R.; Reed, K.L.; Roach, D.H.; Reynolds, G.A.M., Webb, T.R. Comparative Pulmonary Toxicity Assessment of Single-Wall Carbon Nanotubes in Rats; *Toxicol. Sci.* **2004**, *77*, 117-125.
344. Lam, C.W.; James, J.T.; McCluskey, R.; Hunter, R.L. Pulmonary Toxicity of Single-Wall Carbon Nanotubes in Mice 7 and 90 Days After Intratracheal Instillation; *Toxicol. Sci.* **2004**, *77*, 126-134.
345. Shvedova, A.; Kisin, V.; Murray, A.; Schwegler-Berry, D.; Gandelsman, V.; Baron, P.; Maynard, A.; Gunther, M.; Castranova, V. Exposure of Human Bronchial Epithelial Cells to Carbon Nanotubes Caused Oxidative Stress and Cytotoxicity; *Free Radicals and Oxidative stress: Chemistry, Biochemistry, and Pathophysiological Implications; Proceedings of the Society of Free Radical Research Meeting,* June 26–29, Ioannia, Greece.
346. Shvedova, A.A.; Castranova, V.; Kisin, E.R.; Schwegler-Berry, D.; Murray, A.R.; Gandelsman, V.Z.; Maynard, A.; Baron, P. Exposure to Carbon Nanotube Material: Assessment of Nanotube Cytotoxicity Using Human Keratinocyte Cells; *J. Toxicol. Environ. Health-Part A* **2003**, *66*, 1909-1926.
347. Sayes, C.M.; Fortner, J.D.; Guo, W.; Lyon, D.; Boyd, A.M.; Ausman, K.D.; Tao, Y.J.; Sitharaman, B.; Wilson, L.J.; Hughes, J.B.; West, J.L.; Colvin, V.L. the Differential Cytotoxicity of Water-Soluble Fullerenes; *Nano Lett.* **2004**, *4*, 1881-1887.
348. Icso, J.; Szollosova, M.; Sorahan, T. Lung-Cancer Among Iron-ore Miners in East Slovakia—A Case-Control Study; *Occup. Environ. Med.* **1994**, *51*, 642-643.
349. Lubianova, I.P. Effects of Iron-Containing Welding Smoke on Pathological Changes in the Body; *Med. Tr. Prom. Ekol.* **1998**, *9*, 27-37.
350. Weinberg, E.D. Iron Withholding: A Defense Against Viral Infections; *Biometals* **1996**, *9*, 393-399.
351. Simonart, T.; Van Vooren, J.P.; Parent, D.; Heenen, M.; Boelaert, J.R. Role of Iron in Dermatology; *Dermatology* **2000**, *200*, 156-159.
352. Kovalenko, I.B. Eczema and Mycoses of the Feet Among Ferrous Metallurgy Workers; *Vestn. Deratol. Venerol.* **1986**, *11*, 50-55.
353. Ghio, A.J.; Stonehuerner, J.; Pritchard, R.J.; Piantadosi, C.A.; Quigley, D.R.; Dreher, K.L.; Costa, D.L. Humic-Like Substances in air Pollution Particulates Correlate With Concentrations of Transition Metals and Oxidant Generation; *Inhalation Toxicol.* **1996**, *8*, 479-494.
354. Smith, K.R.; Aust, A.E. Mobilization of Iron From Urban Particulates Leads to Generation of Reactive Oxygen Species in Vitro and Induction of Ferritin Synthesis in Human Lung Epithelial Cells; *Chem. Res. Toxicol.* **1997**, *10*, 828-834.
355. van Maanen, J.M.S., Borm, P.J.A., Knaapen, A.; van Herwijnen, M.; Schilderman, P. A. E. L.; Smith, K.R.; Aust, A.E.; Tomatis, M.; Fubini, B. In Vitro Effects of Coal Fly Ashes: Hydroxyl Radical Generation, Iron Release, and dna Damage and Toxicity in Rat Lung Epithelial Cells; *Inhalation Toxicol.* **1999**, *11*, 1123-1141.
356. Zhang, Q.W.; Kusaka, Y.; Zhu, X.Q.; Sato, K.; Mo, Y.Q.; Kluz, T.; Donaldson, K. Comparative Toxicity of Standard Nickel and Ultrafine Nickel in Lung After Intratracheal Instillation; *J. Occupat. Health* **2003**, *45*, 23-30.
357. Amdur, M.O.; Chen, L.C.; Guty, J.; Lam, H.F.; Miller, P.D. Speciation and Pulmonary Effects of Acidic Sox Formed on the Surface of Ultrafine Zinc Oxide Aerosols; *Atmos. Environ.* **1988**, *22*, 557-560.
358. Amdur, M.O.; Chen, L.C. Furnace-Generated Acid Aerosols: Speciation and Pulmonary Effects; *Environ. Health Perspect.* **1989**, *79*, 147-150.
359. Chen, L.C.; Peoples, S.M.; Amdur, M.O. Pulmonary Effects of Sulfur-Oxides on the Surface of Copper-Oxide Aerosol; *Am. Ind. Hygiene Assoc. J.* **1991**, *52*, 187-191.
360. NCI (National Cancer Institute). *Cancer Nanotechnology*; NIH Publication No. 04–5489; Bethesda, MD, 2004.
361. Ginger, D.; Mirkin, C.A.; Cao, C.Y. Beyond Molecular Fluorophores: Next Generation Biosensing With Gold Nanoparticles; *Biophotonics Int.* **2003**, *10*, 48-51.
362. Lee, K.B.; Park, S.; Mirkin, C.A. Multicomponent Magnetic Nanorods for Biomolecular Separations; *Angewandte Chemie-International Edition* **2004**, *43*, 3048-3050.
363. Chan, W.C.W., Nie, S.M. Quantum dot Bioconjugates for Ultrasensitive Nonisotopic Detection; *Science* **1998**, *281*, 2016-2018.
364. Brasuel, M.G.; Miller, T.J.; Kopelman, R.; Philbert, M.A. Liquid Polymer Nano-PEBBLEs for cl- Analysis and Biological Applications; *Analyst* **2003**, *128*, 1262-1267.
365. Monson, E.; Brasuel, M.; Philbert, M. A.; Kopelman, R. Nanosensors for In Vitro Bioanalysis. In *Biomedical Photonics Handbook*; Vo-Dinh, T., Ed.; CRC Press: Boca Raton, FL, 2003.
366. Jakab, G.J.; Risby, T.H.; Hemenway, D.R. *Use of Physical Chemistry and In Vivo Exposure to Investigate the Toxicity of Formaldehyde Bound to Carbonaceous Particles in the Murine Lung*; Boston: Health Effects Institute, 1992, Report no. 53.
367. Lecoanet, H.F.; Wiesner, M.R. Velocity Effects on Fullerene and Oxide Nanoparticle Deposition in Porous Media; *Environ. Sci. Technol.* **2004**, *38*, 4377-4382.
368. Xu, X.H.N., Brownlow, W.J.; Kyriacou, S.V.; Wan, Q.; Viola, J.J. Real-Time Probing of Membrane Transport in Living Microbial Cells Using Single Nanoparticle Optics and Living Cell Imaging; *Biochemistry* **2004**, *43*, 10400-10413.
369. Oberdörster, E. Manufactured Nanomaterials (Fullerenes, c-60) Induce Oxidative Stress in the Brain of Juvenile Largemouth Bass; *Environ. Health. Perspect.* **2004**, *112*, 1058-1062.
370. EPA, *U. S. Air Quality Criteria for Particulate Matter; EPA 600/P-99/002aF-bF*; U.S. Environmental Protection Agency: Washington, DC, 2004.
371. Keywood, M.D.; Ayers, G.P.; Gras, J.L.; Gillett, R.W.; Cohen, D.D. Relationships Between Size Segregated Mass Concentration Data and Ultrafine Particle Number Concentrations in Urban Areas; *Atmos. Environ.* **1999**, *33*, 2907-2913.
372. Woo, K.S.; Chen, D.R.; Pui, D.Y.H., McMurry, P.H. Measurement of Atlanta Aerosol Size Distributions: Observations of Ultrafine Particle Events; *Aero. Sci. Technol.* **2001**, *34*, 75-87.

373. Moudgil, B.; Powers, K.; Roberts, S. Developing Experimental Approaches for Evaluation of Toxicological Interactions of Nanoscale Materials. Available at: http://www.nanotoxicology.ufl.edu/index.html (accessed 2005).
374. Oberdorster, G. Dosimetry Issues and Challenges in Characterizing the Fate of Nanoscale Materials in the Body. Available at: http://www.nanotoxicology.ufl.edu/Oberdorster.htm (accessed 2005).
375. Teague, C. Nanotechnology Development and Potential Toxicological Issues. Available at: http://www.nanotoxicology.ufl.edu/Teague.htm (accessed 2005).
376. Knight, G.; Bigu, J.; Morgan, P.; Stewart, D.B. Size Distribution of Airborne Dust in Mines. In *Aerosols in the Mining and Industrial Work Environments*. Marple, V.A., Liu, B.Y.H., Eds. Ann Arbor Science: Ann Arbor, MI, 1983.
377. Rendall, R.E.G.; Phillips, J.I.; Renton, K.A. Death Following Exposure to Fine Particulate Nickel from a Metal Arc Process. *Ann. Occupat. Hygiene* **1994**, *38*, 921–930.
378. Hewett, P. The Particle-Size Distribution, Density, and Specific Surface-Area of Welding Fumes From Smaw and Gmaw Mild-Steel and Stainless-Steel Consumables; *Am. Ind. Hygiene Assoc. J.* **1995**, *56,* 128-135.
379. Hameri, K.; Aalto, P.; Kulmala, M.; Sammaljarvi, E.; Spring, E.; Pihkala, P. Formation of Respirable Particles During Ski Waxing; *J. Aerosol. Sci.* **1996**, *27,* 339-344.
380. Camata, R.P.; Hirasawa, M.; Okuyama, K.; Takeuchi, K. Observation of Aerosol Formation During Laser Ablation Using a Low-Pressure Differential Mobility Analyzer; *J. Aerosol. Sci.* **2000**, *31,* 391-401.
381. Zimmer, A.T.; Biswas, P. Characterization of Aerosols Resulting From arc Welding Processes; *J. Aerosol. Sci.* **2001**, *32,* 993-1008.
382. Zimmer, A.T.; Baron, P.A.; Biswas, P. The Influence of Operating Parameters on Number-Weighted Aerosol Size Distribution Generated From a Gas Metal Arc Welding Process; *J. Aerosol. Sci.* **2002**, *33,* 519-531.
383. Zimmer, A.T.; Maynard, A.D. Investigation of the Aerosols Produced by a High-Speed, Hand-Held Grinder Using Various Substrates; *Ann. Occupat. Hygiene* **2002**, *46,* 663-672.
384. Wheatley, A.D.; Sadhra, S. Occupational Exposure to Diesel Exhaust Fumes; *Ann. Occupat. Hygiene* **2004**, *48,* 369-376.
385. Cheng, M.D.; Jenkins, C.M. *Characterization of Ariborne Ultrafine and Nanometer Particles During Energetic Materials Synthesis and Testing*. Fall Materials Research Society Meeting: Boston, MA, 2003.
386. Cunningham, E.A.; Jablonski, W.; Todd, J.J. Electron Microscopy Studies of Silica Fume Emissions From a Silicon Smelter in Southern Tasmania, Australia; *Am. Ind. Hygiene Assoc. J.* **1996**, *57,* 1024-1034.
387. Zimmer, A.T. the Influence of Metallurgy on the Formation of Welding Aerosols; *J. Environ. Monitoring* **2002**, *4,* 628-632.

About the Authors

Pratim Biswas is the Stifel and Quinette Jens Professor of the Environmental Engineering Science Program, Department of Chemical Engineering, at Washington University in St. Louis. Chang-Yu Wu is an associate professor in the Department of Environmental Engineering Sciences at the University of Florida. Address correspondence to: Pratim Biswas, Environmental Engineering Science Program, Department of Chemical Engineering, Washington University in St. Louis, St. Louis, MO, 63130; e-mail: pratim.biswas@wustl.edu.