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Expert Opinion

A life cycle framework for the investigation of environmentally benign nanoparticles and products

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While significant advances in our understanding of the behavior of engineered nanoparticles in the environment continue, there remains a need to engage the nanoparticle research community directly in the development and evaluation of environmentally benign nanoparticles to ensure that nanomaterial-based industries emerge as tools for sustainability rather than environmental liabilities. Current research efforts aimed at understanding the environmental implications of nanotechnology emphasize existing groups of nanoparticles and products already in commercial distribution. While this is clearly necessary, this approach fails to identify and address the many tradeoffs associated with product performance and environmental quality. We believe this to be a critical gap in the ongoing exploration of nanostructured materials and their properties and applications. We posit that a number of issues are not being holistically addressed, including resource availability and allocation, manufacturing energy requirements and embodied energy, material efficiency, environmental properties of nanomaterials and nanoproducts, and waste generation. An interdisciplinary approach to research, based on the life cycle paradigm and devoted to the identification, investigation, synthesis, testing, and analysis of groups of new, more environmentally conscious nanoparticles is needed.

1 Introduction There is growing evidence that many nanoparticles produced using current methods may have the potential for significant future environmental impacts, if the use of such materials in products continues to expand at its current rate of growth [1–6]. Such impacts arise from a variety of properties: material composition (i.e. many contain materials of limited supply and/or significant toxicity), shape (many nanoparticles possess shapes or assume shapes during fate, transport, and agglomeration with high aspect ratios), photoactivity (resulting in the generation of reactive oxygen species and/or hydroxy radicals), redox activity (such as various nano-iron crystals), and size (depending on their charge state, particles under 5 nm are capable of crossing cell walls, and can represent an inhalation hazard). This presents a conundrum: it is often just such properties that make nanoparticles desirable for research investigation and commercial development [7].

Moreover, current nanomaterial fabrication methods suggest a substantial potential for environmental and health effects that stem not from the nanomaterials themselves, but from associated energy inputs, feedstocks, and wastes. Such "collateral damages" associated with nanomaterial

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production are suggested by the high embodied energy in many nanomaterials [8–10], the feedstocks of a non-nano nature that are known to be hazardous such as organic solvents [11], and the nature of wastes produced [12].

There are currently a number of research efforts devoted to assessing the environmental impacts of nanoparticles [13, 14]. These are important aspects of environmental research in that they provide relevant information on the behavior of nanostructured materials once released into the environment that will contribute to regulatory needs. To date, these efforts have focused largely on nanoparticles that are already in production and are commercially marketed. The environmental impacts of the processes surrounding nanomaterial fabrication have received relatively little attention. Within the materials research community it is common to address the development of more environmentally benign nanofabrication processes using "single metric" drivers such as minimal water usage during manufacture, or elimination of cadmium/lead from the product. While such approaches are valuable, they often fail to capture the inherently multiobjective dimensions of nanomaterial fabrication and use. As a result, these approaches are likely to fail in identifying tradeoffs associated with product performance and environmental quality. We believe this to be a critical gap in the ongoing exploration of engineered nanoparticles, their properties and applications, and suggest that a number of issues are not being holistically addressed, including resource availability and allocation, manufacturing energy requirements and embodied energy, material efficiency, environmental properties of nanoparticles, waste generation, and end-of-life disposition.

2 Life cycle analysis Life cycle analysis (LCA) is a systems-based approach for gathering data on material and energy flows associated with products and processes. Typically each product chain is divided into four broadly defined activities (each of which can be subdivided according to the specific application): acquisition of materials; purification, manufacturing, and fabrication; commercial uses; and end-of-life disposition. The LCA approach can be superimposed on a value chain analysis of a specific material, where the environmental impacts are traced through its production, incorporation into progressively more complex products, and ultimately the disposal or end-of-life issues associated with these products. For example the value chain in the context of the fabrication of carbon nanotubes (CNTs) involves the incorporation of CNTs into flat, addressable polymer matrices, and the incorporation of the CNT/polymer matrices into video displays that have a finite useful life, culminating in disposal, reuse, or recovery.

LCA evolved from the need by industries at one or more points in the value chain to understand their manufacturing processes and market implications, but has more recently been adapted by environmental regulatory agencies and others to understand sources of waste generation and associated impacts. LCAs in general do not incorporate localized information on exposed populations, terrain, or meteorological conditions, nor do they include fine detail temporal considerations such as diurnal fluctuations in pollutant loadings, thus they are not a substitute for specific exposure and risk analyses [14]. The LCA procedure consists of four steps: scoping and definition of system boundaries, inventory of material and energy requirements, environmental impact analysis, and improvement analysis – an iterative procedure that takes place continuously as the LCA is carried out [15].

LCAs are undertaken for four principal reasons:

(i) to develop information for comparative purposes when choices among designs, processes, or materials must be made,

(ii) to quantitatively establish the nature of tradeoffs associated with various choices,

(iii) to examine a single system in order to ascertain those components, parts, or processes which are the most material or energy intensive and for which investments of resources or research might be expected to yield the greatest improvements, and

(iv) to facilitate the communication of risks and benefits to consumers and stakeholders.

LCA is a powerful tool for making holistic comparisons among possible or competing systems. Life cycle methodologies have been codified and standardized by various groups during the past several years, for example the International Standards Organization [15] has established procedures for performing detailed LCA. In addition the USEPA [16] has called for a life cycle approach to the evaluation of the benefits and costs of nanotechnology and its products.

The pace of exploration and product development in the nanotechnology area has grown exponentially during the past decade. Figure 1 summarizes the total number of published scientific articles related to nanotechnology during the nineteen year interval from 1990–2009, which now far exceeds one hundred thousand annually. In comparison research publications on the general topic of environment, health, and safety (EHS) are much smaller, but also show an increasing trend. The large majority of EHS research at

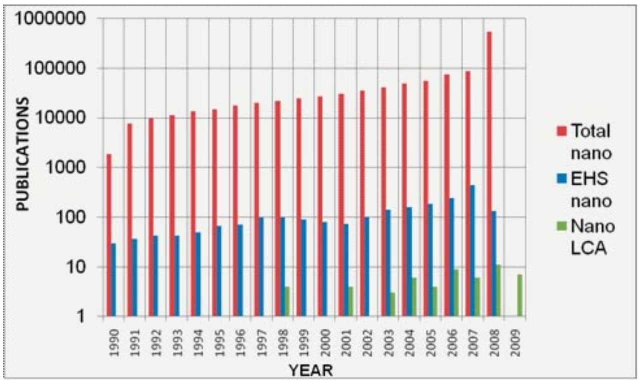

Figure 1 (online colour at: www.pss-rapid.com) Publication rates for nanotechnology.

present focuses on the toxicity, fate, transport, and transformation of nanostructured materials, particularly nanoparticles. Understanding exposure and effects of these materials is critically important information and hence such an emphasis is warranted. However, among EHS publications, those focusing on life cycle studies are considerably smaller.

3 The need for an interdisciplinary, LCA-based research program on nanostructured materials We believe a particularly strong case can be made for a focused, systematic, and iterative research approach that relies on the combination of expertise from several disciplinary perspectives. An especially important element of such a research program involves the engagement of the materals research community directly in the holistic development and evaluation of nanomaterials and products using the life cycle paradigm as a template. Table 1 summarizes the general elements of an LCA-based research program on nanostructured materials. These research needs are examined in more detail below.

3.1 Substitution of materials limited by natural abundance or geopolitical considerations The supply of many elements used in nanomaterial fabrication and nanotechnologies such as those in the area of molecular electronics is limited by natural abundance and/or accessibility due to geopolitical circumstances. Elements such as neodymium, dysprosium, tellurium, vanadium, or cerium are used in technologies ranging from catalytic converters and lasers to the magnets in computer hard drives and in electric motors and generators. Most of these are found in trace amounts and often are not present as individual metals, but are extracted from other mining ores. The energy implications associated with purifying these materials together with their limited amounts suggest there may be important environmental and strategic dimension attached to the use of these materials. The recent embargo of rare earth elements exported from China to Japan highlights the uncertainty associated with the availability of these materials and adverse political or economic consequences for supply. As in the case of materials that are known to be toxic, there may be opportunities to substitute materials of uncertain supply with more available materials.

3.2 The use of non-toxic/less toxic materials, and the bioavailability of nanoparticle components The risk presented by a nanomaterial is determined by the potential for exposure and the hazard presented by the nanomaterial. The notion of designing out either exposure (including bioavailability) or hazard in a nanomaterial has been suggested as a basis for reducing risk associated with nanomaterials [7]. However, as previously noted, the properties of a material that produce the hazard may be closely related to those that make a given material useful. Risk management based on exposure management presents a broad array of options for managing risk. From the perspective of nanomaterial design, materials and products might be conceived to have limited dispersal in the environment or be designed to self-destruct to limit persistence. Nanomaterial size, shape or surface charge might be adjusted to reduce uptake across gills, tissues in intestinal tracts, or dermal contact. In many cases, the entry of the nanoparticles into the cell through such endocytosis activity may lead to apoptosis [18]. Since the cell's membrane is composed of a bilipid layer which is only several nanometers thick, the entry of nanoparticles into the cell by endocytosis will depend upon their size as well as their charge state and functionalization with biomolecules that trigger endocytosis. There have been investigations demonstrating that coating the nanoparticles can reduce cell damage [19]. In this case, bioavailability is limited by encasing an inherently toxic material (such as a heavy metal in a quantum dot) with a more biocompatible material.

Many of the most promising nanocrystalline particles contain toxic elements, particularly cadmium, lead, selenium, tellurium, and arsenic, and to a lesser degree indium and zinc. Materials substitution can in some cases be done to obtain nanomaterials with similar functionality, but with reduced toxicity – either from exposure to the final product, or associated with materials and waste handling. For example early results of nanocrystals composed of AlP and germanium appear promising [20, 21], as do a variety of non-cadmium containing NCs [22]. We speculate that many semiconductor nanoparticles composed of less toxic and more abundant materials are potential candidates for applications as long as the surface properties can be adequately controlled.

3.3 Synthesis and fabrication of nanoparticles using lower energy or material pathways Embodied energy values of many nanoparticles are, at present, considerably greater than other high-energy, non-nano materials [8–10]. In general this is due to relatively low material efficiencies of synthesis methods, the heavy use of solvents and specialized chemicals, specialized synthesis conditions that are energy-demanding (such as high or low pressure/temperature, high purity requirements), complex processing, reprocessing, and post-processing steps, and the generation of waste products [23]. For example in the synthesis of nanocrystals via solution methods, the use of common solvents and the production of hazardous wastes are major factors in high embodied energy values. Gutowski et al. [24] have found that manufacturing methods for nanoparticles tend to be dominated by high energy-demanding, low-throughput techniques. Yet typical energy costs for low volume production of these materials is presently quite small [8]. However as demand grows it will be necessary to develop lower energy methods with higher material efficiencies and throughputs for many products.

3.4 Evaluation of life cycle characteristics of nano-based products A considerable strength of the LCA framework involves carrying nanostructured materi-

Table 1 Relation of nanostructured material and product research needs to LCA.

<table>
<tr><th></th><th></th><th colspan="4">LIFE-CYCLE STAGE</th></tr>
<tr><th></th><th></th><th>Acquisition</th><th>Purification & Manufacture</th><th>Use</th><th>End-of-life Disposition</th></tr>
<tr><td rowspan="5">RESEARCH NEED</td><td>Material abundance & acquisition</td><td>scarcity & criticality of materials</td><td>by-product & waste minimization</td><td colspan="2" rowspan="2">risk assessment for emissions inventory & characterization, including source term characterization, fate & transport, exposure and dose-response assessment</td></tr>
<tr><td>Bioavailability & Toxicity</td><td></td><td></td></tr>
<tr><td>Synthesis pathways</td><td colspan="2">energy & material intensity</td><td></td><td></td></tr>
<tr><td>Life-cycle characteristics</td><td></td><td>technology comparison</td><td>cost, functionality & efficiency</td><td>persistence, mobility, bioaccumulation</td></tr>
<tr><td>Social context</td><td>geopolitical sensitivities</td><td>worker safety</td><td>market acceptance</td><td>disposal & take-back regulations</td></tr>
</table>

als through specific product life cycles in order to ascertain the relative costs and benefits, and compare alternative products on a performance basis. Typically the results of such assessments yield a set of environmental impacts (e.g. human health, ecotoxicity, global warming, ozone depletion, etc.) that identify tradeoffs and can be input into improvement analyses in which opportunities for minimizing overall impacts are identified. A wide variety of tools is available to assist in this stage of the research framework, the end result of which identifies relevant tradeoffs of given nanostructure-product combinations [25–28].

One challenge associated with LCA of nano-based products is the difficulty in assigning functional units to describe specific products' benefits. Often, life-cycle studies for nanomaterials focus simply on the production of the material itself, and report results relative to mass of nanomaterial produced, rather than the function the material provides. Such results may be misleading, as mass-based measures may not be an appropriate basis of comparison.

An additional factor in the LCA of nano-based products is the investigation of the end-of-life disposition of products containing nanostructured materials. Many materials are manufactured under specialized conditions that result in synthesis and "self-assembly", however once present in the natural environment thermodynamic gradients may favor decomposition, although the kinetics of such reactions are largely unknown. In addition, there is a need to investigate the potential for recycling or reuse of nanocomponents. Many products have nanostructured fillers incorporated into bulk matrices, such as steel, concrete, or polymeric materials, but general experience with recycling of such composites, although limited, is not encouraging [29].

3.5 Social context for nano-based product usage While it is not known with precision the number of consumer products that contain nanomaterials, it is likely that there are at least several hundred with the number likely to grow significantly as production methods improve and costs fall. The largest consumer sectors are health and fitness, household applications, and food/beverage [30], thus there is considerable potential for exposure among populations. Yet the general level of knowledge about nanotechnology among users of these products is low, with little improvement evident over the past several years [31]. Manufacturers tend to assume normative behavior on the part of consumers, but actual usage studies are lacking. For example, technical and marketing breakthroughs in our ability to recycle certain nanocomponents contained in products may mean little if consumers are disinclined to make them available for reprocessing.

4 Challenges To be sure there are a number of challenges that must be confronted in the application of LCA methods to nanotechnological development. LCA inventory data is typically gathered in three ways: (i) in cooperation with manufacturers, who provide a source of manufacturing and process-level data on material and energy requirements, product and waste yields; (ii) through exploration of process-level or supply-chain databases built from public and private sources that report aggregated data regarding broad product categories; and (iii) through economy-wide, input–output economic analysis that aggregates census data culled from survey of broad sectors of the manufacturing industry with regard to supplier purchases and environmental emissions.

In the case of nanomaterials, each of these approaches confronts difficulties. Many manufacturers are reluctant to share process-level data on research-intensive emerging materials, fearing that competitors may be able to deduce proprietary information from public reporting of material- or process-specific inventory data. Although these concerns are somewhat alleviated by reporting aggregated results, such as in a broad database, the value of this information from technology comparison or improvement assessment is diluted. In the case of economic input–output modeling, data is necessarily backwards-looking, and will not reflect recent technology improvements or other developments that are critical to understand in a rapidly evolving field.

LCA impact analysis proceeds by assembling a material inventory of chemical quantities released to the environment throughout the supply chain. The result is typically a list of impact categories, such as global warming or human toxicity potential, that are relevant to the study. Characterization proceeds by converting each chemical quantity into an equivalent amount of substance that is represent of the impact category, such as kg of carbon dioxide (for global warming), or benzene equivalents (for cancer). In the case of nanomaterials, the use of mass-based equivalencies may be inappropriate, i.e. nanomaterials may be better characterized in terms of their principal functional property, which necessitates an understanding of the form of these materials in both the product and the environment, and their rate of release [32].

5 Concluding remarks The promise of nanotechnology for improving human health, reducing impacts on the environment, and enabling new fields of study is great. Yet, uncritical acceptance of such progress, as has been the case for many other major technological advances in the modern age, is likely to result in unforeseen, and unintended, consequences, with potential for significant harm. Unlike past technological developments, nanotechnology has come of age at a time coincident with the development of modern tools for environmental analysis and evaluation, and a better understanding of the potential for human and ecological damage of even very small quantities of materials. Life cycle analysis, too, has emerged as a powerful tool for guiding policy on many fronts. Its use as a means of informing developmental research on nanotechnology awaits acceptance and use by the interdisciplinary materials research community.

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