Environmental, Health and Safety (EHS) Impacts

Technology Sector Evaluation: Energy

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1. Introduction

One major challenge in the world today will be to provide enough energy for human activities without exhausting the earth resources and without degrading environment. Current solutions used to produce electricity and to provide energy for transport applications as well as to mobile devices should become more efficient, less expensive and environment friendly.

Nanotechnology can provide a multitude of improvements and innovative solutions to the energy sector. The structuring of materials on the nanometre scale or using nanometre architecture allows for a reduction in the amount of material displaying specific properties required to meet a particular endpoint or use (which is one of the main challenges for this sector), as well as opening opportunities to introduce new specific properties to existing materials.

The ObservatoryNANO report on the Energy technology sector summarizes the technologies and applications involving nanotechnologies (Bertoldi & Berger, 2009) in six sub-sectors including:

- Photovoltaic
- Thermoelectricity
- Fuel cells, hydrogen production & storage
- Batteries & supercapacitors
- Fossil fuel & nuclear energy
- Energy harvesting

Although all of the sub-sectors are concerned, some applications can expect much more developments, through implementation of nanotechnologies, than other ones. Batteries, supercapacitors and low temperature fuel cells can be expected to benefit positively from nanomaterial developments, for example, improvements in the performance of catalysts and/or nanoporous membranes. Photovoltaic or thermoelectric devices have a broad spectrum of developments thanks to nano-objects like nanowires or quantum dots, as well as engineering materials on the nanoscale. As a consequence, nanotechnologies are regarded as one of the factors to recognise when assessing future developments of these application sectors.

Other fields will have less impact from nanotechnologies, for two main reasons. On the one hand, many energy sources or conversion means are based on macroscopic effects, such as wind turbines, tidal devices or mechanic energy harvesters. Harvesting or producing energy at the nanoscale will be efficient only if an additional effect of a large amount of such devices can be induced, or if it is possible to manage very low amount of energy to supply low power devices. Size reduction in most of these cases has little interest, and the main use of nanotechnologies is as mechanic reinforcement of structure materials. On the other hand, processes inducing high temperatures, like nuclear energy, fossil fuel or high temperature fuel cells, limit the use of nanotechnologies, mainly because the high temperature generally destroys the nanoscale structure of materials.

Nanotechnology exhibits a lot of interesting properties regarding energy production or harvesting, but are limited by issues such as integration, process, cost and reproducibility. Nevertheless, the economic and environmental challenges are so vital to this field that huge research and technological developments will have to find ways to save materials and energy reserves. In this context, nanotechnology remains a promising tool.

The EHS analysis of the energy sector considers nanomaterials outlined within the context of their application and provides a summary of what is known in relation to potential exposure to the material in question. The analysis further outlines some key EHS considerations and basic guidance for those developing or using the technologies outlined within the report.

For all of those nanoparticles identified as having potential EHS impact, toxicological knowledge is still emerging, although based on what is known to date a reasonable approximation of potential hazard may be made. The key common knowledge gap across all nanoparticles however is the lack of exposure measurements for the scenarios and applications in question. As the ObservatoryNANO Project progresses, it is expected that these knowledge gaps will be addressed (at least in part) and thus that later EHS reports will be able to reach more resolute conclusions on the risks posed by those nanomaterials in consideration.

2. General Considerations for the Environment, Health & Safety Impact of nanomaterials

The key benefit from nanotechnologies is the ability to exploit the specific, novel and sometimes unpredictable properties that arise from structuring matter at this scale. Over the last 10 years, nanotechnologies have received extensive investment, and have emerged as major drivers of science based innovation and industry. This has led to the development of new processes, products and materials for a wide range of applications.

In 2004 the UK's Royal Society and the Royal Academy of Engineering (RS/RAEng) published a seminal review of the "opportunities and uncertainties" presented by nanotechnologies (RS/RAEng, 2004). Whilst indicating that for many nanotechnologies, there were no foreseeable risks to health or to the environment, the report concluded that for "nanoparticles and nanotubes" there were potential risks, and that not enough was known about them. This conclusion was based on evidence gained from many years of research that exposure to particles can cause ill health within individuals or exposed populations. For example, within the occupational setting, exposure to coal dust is evidentially linked to the onset of lung diseases including pneumoconiosis and chronic obstructive pulmonary disease (COPD), and exposure to asbestos is causative of asbestosis, mesothelioma and lung cancer. In an environmental context, evidence suggests that exposure to the particulate component of atmospheric pollution may be associated with increased hospitalisation rates and cardio-vascular disease (Seaton et. al, 2009).

Publication of the RS/RAEng report led to a huge increase in research activity concerning both human health and environmental consequences (Aitken et. al., 2009a). For example, in Europe the Framework 7 NMP programme has funded more than 20 major projects, with a total budget of more that €50million. This research activity has addressed *inter alia* the toxicity and ecotoxicity of many types of nanoparticles, the kinetics of nanoparticles within biological and environmental systems, the extent to which individuals or the environment can become exposed and the level of risk which would result. These investigations have examined numerous mechanisms, end points and processes and materials, and have generated an extensive body of literature, particularly in relation to toxicology and ecotoxicology.

2.1 Establishing a knowledge on the potential hazard and exposure to nanomaterials

Scientific data compiled to date demonstrates that adverse health effects due to exposure to nanoparticles cannot be ruled out (Aitken et. Al., 2009a; 2009b; van Zijverden & Sips (eds.), 2009). However, although awareness for the importance of risk research has increased, critical information still is lacking to enable estimation of the risks posed by nanoparticles with equal certainty to those of other non-nano substances. Nevertheless, hundreds of products containing nanomaterials are currently available commercially, a situation which clearly necessitates investigation of the exposure and toxicity of these materials in the near future. Unfortunately, the research questions to be answered are so numerous that it will take years to compile the relevant data.

The potential for nanoparticles to cause damage has also been implicated within the environment, both directly via uptake into plants or organisms (including soil bacteria, eukaryotes, invertebrates and vertebrate species), and indirectly via changes in environmental variables such as pH of aquatic systems, ionic strength or dissolved organic carbon content (Aitken et. al., 2009a). Carbon nanotubes (CNT) and silver nanoparticles have been shown to cause detrimental effects in zebrafish development (Cheng et. al., 2007), and copper nanoparticles have been shown to be highly toxic to fish, daphids and algae (Griffitt et. al., 2008), and to induce stunting of exposed plant seedlings (Lee et. al., 2008).

Man and the environment can come into contact with the use of nanotechnology through a wide range of application areas. Some of these applications are produced only with the aid of nanotechnology, others contain nanomaterials. For the risk assessor, this second category is important, particularly when the applications contain non-degradable, insoluble, and freely available nanoparticles. For this category of products there are already a great many different areas of potential use, including medical applications, food, and consumer products as well as environmental and energy technology. These applications can improve the quality of life and the environment and can also lead to significantly more sustainable products, but for which it is of particular importance to understand and control potential risk.

There are already hundreds of nanotechnology applications on the market. For example, nanoparticles of titanium oxide and zinc oxide are regularly used as UV reflectors in sunscreen creams. Nanotechnology is also used to make clothing crease- and dirt-resistant, and to make electronics ever smaller, faster and more multifunctional. However, the majority of potential applications for nanotechnologies are currently still in the research and development phase and are expected to appear on the market over the coming years.

Understanding and effective management of potential risks posed by manufactured nanoparticles and nanomaterials is pivotal for responsible and sustainable development of nanotechnology. This in turn is mandatory for societal acceptance and exploiting the significant economic potential of this technology to the full.

2.2 Risk Assessment considerations for nanomaterials

In assessing the risks of non-nano chemical substances and nanomaterials alike, the following general approach is applied:

RISK = HAZARD (TOXICITY) x EXPOSURE

The intrinsic hazard (toxicity) of a nanomaterial is determined by a number of factors, such as the ability of a nanoparticle to pass through certain barriers in humans, plants or animals and cause damaging effects. The actual exposure is also determined by various factors such as the form in which the nanomaterial occurs (e.g., either bonded or as 'free' particles) he specific setting in which the nanoparticle is being manufactured applied or used (and thus likelihood of contact). Thus, a specific nanomaterial may be hazardous, but if the level of exposure is very small, the ultimate risk will always be limited. For example, a specific nanoparticle bound within ultra-high performance concrete used to construct a bridge will pose less of a potential risk to consumers (i.e. those using the bridge), than the same NP used within antimicrobial food packaging, where the potential for consumer exposure may be increased due to their close contact with the product in which the NPs are bound.

Two areas can be distinguished within risk research for nanotechnology. One area aims at risks related to exposure to nanomaterials and the second area aims at risks related to the rest of nanotechnology and its products. There is consensus that the uncertainties about these risks need to be addressed most urgently.

In 2009, the Dutch Knowledge and Information Point "Risks of Nanotechnology" (RIVM/KIR nano) recommended to focus research primarily on those questions that provide information critical to the assessment of risks to man and the environment (van Zijverden & Sips (eds.), 2009). Depending on the perspective – worker, consumer, patient, or the environment – the starting points can then be defined for controlling or limiting the risks.

From this and other literature on the topic, there may be identified several key challenges for the EHS appraisal and risk management of nanomaterials:

1. *There is a high urgency for relevant risk information:* One of the pitfalls of emerging technologies is the imbalance between technological development and attention for human health and environmental safety issues as is the case for

nanotechnology. Risk information needs to be generated and shared as quickly as possible for products on the market, underpinning the societal acceptance of further applications of this technology.

2. *Validity of known test systems is questionable, and detection of nanomaterials still problematic*. Nanomaterials create a challenge for risk research as they (might) behave differently in regular assessment and testing systems. Equipment and methods to detect nanomaterials allowing large-scale application are lacking.
3. *National, international and interdisciplinary integration is a prerequisite*. A large variety of research questions need to be addressed before uncertainties about risks for man and the environment are at the same level as for other chemical substances.

Whilst this brief introduction provides an outline of the key issues, it is impossible to outline the current knowledge on the hazard, exposure and risk assessment for nanoparticles in full. Instead the reader is directed towards the ObservatoryNANO Baseline Studies (Ross et. al., 2009) where many of the seminal studies from the last few years are identified and described.

2.3 The ObservatoryNANO Approach: Integrating EHS considerations with development of novel applications for nanotechnologies

ObservatoryNANO is concerned with mapping scientific and technological development across 10 core technology sectors, and a key task of WP5 is to undertake an appraisal of these reports and to identify potential emerging environment, health and safety issues therein, thus integrating the development of novel applications with risk research, an approach which is urgently required.

There is considerable overlap between those nanoparticles used across these 10 sectors - what differs is their use, which varies according to the application. Therefore the aspect which is specific to the technical sector in considering those novel risks which may arise from development of novel applications, is the potential for exposure. For this reason, the approach which we have adopted is to consider the potential exposure which may arise from the new applications identified.

As far as possible, we have considered the life cycle of the applications identified, whether there were possible exposures within the occupational setting, or to consumers or release to the environment. We also considered whether there was the potential for release from disposal.

Our review process involved extraction of information from each technology sector report & gathering of additional information from their lead authors. This data was then analysed, and our findings outlined within the subsequent sections of this report. In addition to a short summary of the key exposure issues identified from our analysis, our report includes three key tables as follows:

1. A table summarising all information gathered together with consideration of the potential for exposure arising throughout the lifecycle of each application
2. A table outlining those nanoparticles/nanomaterials in use within each technology sector, according to application
3. A table highlighting those applications where we consider there to be a high potential for release.

Detailed information of the type required to make strong evidence judgments about possible exposures was only very rarely available, and this is indicated in table. In none of the scenarios was actual exposure data available. However, for some applications additional information was available from the peer reviewed literature, and where this has been used this is again indicated within the table. In the majority on settings identified, due to the paucity of data assessment of whether or not exposure is plausible is based on expert judgement and information available from other similar scenarios. In this respect, these judgements should be considered provisional and where possible, effort should be placed on collecting relevant specific primary exposure data. As the ObservatoryNANO Project progresses, it is expected that these knowledge gaps will be addressed (at least in part) and thus that later EHS reports will be able to reach more resolute conclusions on the risks posed by those nanomaterials in consideration.

3. Potential EHS impacts Identified

The following table outlines and ranks the *potential* for exposure associated with the use of nanomaterials in the applications shown. In the absence of real exposure data, it is based primarily upon expert evaluation of the information provided in the technical reports. As a default we have indicated that there is a high potential for exposure in all occupational settings associated with the manufacture of nanomaterials unless adequate control measures are applied. In applications where the hazard (toxicity) of the nanomaterials is similar, those with the highest potential exposure will have the highest potential risks.

Table 1: Potential EHS Impacts Identified

ENERGY Sector										
Application & NP - Basic Info				**Exposure potential Use** (e.g. activity, exposure route, what)				**Exposure potential Disposal** (e.g. incinerated, landfilling, recycled, STP)		**Comments**
Sub sector	Application	Types of NP	Incorporation in products	Manufacturer	Professional user	Consumer	Environment	Human	Environment	
Photovoltaic	**Inorganic solar cells** CIGS Inorganic solar cells & CZTS inorganic solar cells	NPs of Copper Indium Gallium Selenide (CuInGaSe)* NPs of Copper Zinc Tin Sulfur (Cu_2ZnSnS_4)	NPs dispersed in an ink or embedded in a thin film matrix - confined into the final product	Possible release during synthesis, dispersion or incorporation into matrix. Potential contact through skin	Very low exposure potential	Very low exposure potential	Very low exposure potential	Low exposure potential (unless solar cells are broken)	Potential release in soil and surface water if not properly disposed or recycled	In the US and in Europe, many of the biggest companies that produce solar panels have decided to pre-empt the wave of regulation by voluntarily joining up and creating the first large-scale scheme to recycle
	Quantum dot solar cells	Various QD (e.g. Cadmium telluride, cadmium selenide, lead	Nanocrystals embedded in a matrix - confined into the final	Possible release during synthesis, dispersion or incorporation	Very low exposure potential	Very low exposure potential	Very low exposure potential	Low exposure potential (unless solar cells are	Potential release in soil and surface water if not	

	selenide, lead sulphide)	product	into matrix. Potential contact through skin				broken)	properly disposed or recycled	solar panels**
Nanowire solar cells	Silicon nanowires	Nanowires grown on a substrate and embedded in a matrix - confined into the final product	- Possible release during synthesis, dispersion or incorporation into matrix. Potential contact through skin -	Very low exposure potential	Very low exposure potential	Very low exposure potential	Low exposure potential (unless solar cells are broken)	Potential release in soil and surface water if not properly disposed or recycled	
Plasmon-enhanced solar cells	Metallic NPs (e.g.silver)	NP deposited at the interface of 2 thin films (embedded) - confined into the final product	Possible release during synthesis, dispersion or incorporation into matrix. Potential contact through skin and inhalation	Very low exposure potential	Very low exposure potential	Very low exposure potential	Low exposure potential (unless solar cells are broken)	Potential release in soil and surface water if not properly disposed or recycled	
Organic solar cells Dye Sensitized Solar Cells	NPs of titanium dioxide* Nanowires of zinc oxide	Nanomaterials coated with photosensitive dye molecules and embedded in a matrix (film) -confined into the final product	- Possible release during synthesis and incorporation into matrix. Potential contact through skin or inhalation	Very low exposure potential	Very low exposure potential	Very low exposure potential	Low exposure potential (unless solar cells are broken)	Potential release in soil and surface water if not properly disposed or recycled	In the US and in Europe, many of the biggest companies that produce solar panels have decided to pre-empt the wave of regulation by voluntarily joining up and

	Polymer solar cells	Carbon fullerenes*; CNT	Nanomaterials included in a matrix - confined into the final product	- Possible release during synthesis and incorporation into matrix. Potential contact through skin or inhalation	Very low exposure potential	Very low exposure potential	Very low exposure potential	Low exposure potential (unless solar cells are broken)	Potential release in soil and surface water if not properly disposed or recycled	creating the first large-scale scheme to recycle solar panels**
	Transparent electrodes/antireflection layers	CNT Graphene; zinc oxide nanostructures; Nanoporous coating of silicon dioxide;	Nanomaterials embedded into a matrix (film)	- Possible release during synthesis and incorporation into matrix. Potential contact through skin or inhalation.	Very low exposure potential	Low exposure potential - Potential release if surface is shreddered	Very low exposure potential - potential release if surface is shreddered	Low exposure potential (unless product is broken)	Potential release in soil and surface water if not properly disposed or recycled.	Applications are under development
Thermoelectricity	Thermoelectric materials for various applications such as refrigerators of electric generators	Nanowires (Zinc oxide, silicon) Nanostructured material such as superlattices of semi-conductors NPs (e.g. Bismuth Telluride	NPs or nanomaterials embedded in a host matrix material - Materials are confined into final products	- Possible release during synthesis and incorporation into matrix. Potential contact through skin or inhalation.	Very low exposure potential	Very low exposure potential	Very low exposure potential	ND	ND	Early stage of R&D
Fuel cells	**Low temperature fuel cells/** Electrodes, Electrolytes & Catalysts	(SW/MW)CNT, fullerenes,nanostructures (e.g. nanowires, nanoparticles, nanospheres) of palladium, ruthenium oxide, zirconium,	Nanomaterial deposited on the surface of the electrodes or embedded in a matrix - confined into the final product	- Possible release during synthesis, deposition or incorporation into matrix. Potential contact through skin or inhalation	Very low exposure potential	Very low exposure potential	Very low exposure potential	ND	ND	Early stage of R&D;

		platinum, silver								
Batteries	**Electrodes**	Nanomaterials such as $LiFePO_4$*, $Li_4Ti_5O_{12}$*; $LiMn_2O_4$, Nanocomposites, nanowires and nanotubes (CNT, silicon, oxides of vanadium, manganese…)	Nanomaterials coated onto the electrodes - batteries are the confined into products	- Possible release during synthesis and coating. Potential contact through skin or inhalation.	Very low exposure potential	Very low exposure potential	Very low exposure potential	Very low exposure potential.	Potential release in soil and surface water if not properly disposed or recycled.	Products follow disposal/recycling industrial procedures for batteries. According to manufacturers, some nanotechnology-based batteries are almost fully recyclable or reusable #
	Electrolytes	NPs/nanopowders of oxides (aluminium, silicon, zirconium)	NPs powders dispersed in a non-aqueous liquid or added to a solid polymer electrolyte - batteries are the confined into products	- Possible release during synthesis and dispersion. Potential contact through skin or inhalation	Very low exposure potential	Very low exposure potential	Very low exposure potential	Very low exposure potential.	Potential release in soil and surface water if not properly disposed or recycled.	Under development
Supercapacitors	**Electrodes**	(SW)CNT, graphene, NPs of manganese oxide	Nanomaterials deposited on the surface of the electrodes - supercapacitors are confined into products	- Possible release during synthesis and deposition. Potential contact through skin or inhalation.	Very low exposure potential	Very low exposure potential	Very low exposure potential	Very low exposure potential.	Potential release in soil and surface water if not properly disposed or recycled.	Under development

Fossil energy	**Catalysts for oil treatments in refining**	Nanostructured zeolites*, Metal NPs (e.g. platinum, tin), CNT	Nanostructured material used as catalyst or NPs coated onto catalyst support materials.	- No risk of release with nanostructured zeolites. High potential of release for other NPs: possible release during synthesis and coating; potential contact through skin or inhalation	- No risk of release with nanostructured zeolites. For other NPs, potential contact through skin	NA - (catalysts are removed from oil before use)	NA	NA	NA	A great variety of nanocatalysts are under development
Nuclear energy	**Strengthening materials of reactor structures**	NPs of oxides (mainly yttrium-based) Nanostructured silicon carbide	NPs dispersed (oxides) in a solid matrix or NPs compressed powders (SiC) in a solid matrix	- Possible release during synthesis, dispersion and compression. Potential contact through skin or inhalation.	Very low exposure potential	NA	ND	ND	ND	Early stage of R&D;
	Heat transfer to cooling systems	Carbon-based NPs like diamonds	Low amounts NPs added to the water circuit of the cooling system	- Possible release during synthesis and incorporation into cooling system. Potential contact through skin or inhalation.	Medium to high - Potential contact through skin	NA (not used by general population)	ND	ND	ND	Early stage of R&D;

Energy Harvesting	**Small scale** (e.g: piezoelectric, electrostatic energy or magnetic induction generators)	CNT, Nanowires of zinc oxide, gallium nitride and silicon	Nanomaterial coated onto substrate (e.g. fibers, films…)	- Possible release during synthesis and coating. Potential contact through skin or inhalation.	ND	ND	ND	ND	ND	Early stage of R&D;
	Large scale (e.g. wind, water, tidal and geothermal resources) *See also Construction sector*	CNT	Integrated in windturbine blade material	- Possible release during synthesis and incorporation into matrix. Potential contact through skin or inhalation.	Very low exposure potential	Very low exposure potential	Very low exposure potential	ND	ND	Very little R&D

NPs : Nanoparticles; QDs: quantum dots ; CNT: Carbon nanotubes; MWCNT : Multi wall carbon nanotubes ; SWCNT : single wall carbon nanotubes. ND: Not determined – NA: not applicable.
* Type of nanomaterials included in applications already available on the market
** http://www.firstsolar.com/en/recycle_program.php; PV cycling "Making the PV industry double green" at http://www.pvcycle.org/fileadmin/pvcycle_docs/documents/presentations/PVCYCLE_public%2009%202009sec.pdf
# http://www.ecolocap.com/site/en/mbt-cnt-battery.html

4.0 Conclusions

The key nanoparticles identified as carrying potential EHS impact across the Energy technology sector are outlined in table 2.

Table 2: Nanoparticles carrying potential EHS impact, according to application

	CNT	Other carbon-based nanomaterial	TiO_2	Other Oxides	Other NPs or nanomaterials
Photovolataic	•	Fullerene Graphene	•	Zinc, silicon	NPs and QDs of various semiconductors; metallic NPs; NWs of silicon
Thermoelectricity				Zinc NWs	Silicon NWs; semi-conductors; BiTe
Fuel cell	SWCNT, MWCNT	Fullerene		Zirconium, ruthenium	Platinum, silver, palladium
Batteries	•			Silicon, Vanadium, Manganese, Aluminium, Zirconium	$LiFePO_4$, $LiTi_5O_{12}$, $LiMnO_4$
Supercapacitors	SWCNT	Graphene		Manganese	
Fossil Energy	•				Zeolite, platinum, tin
Nuclear Energy		diamond		Ytrium	Silicon carbide
Harvesting	•			Zinc NWs	NWs of Gallium nitride, Silicon

NPs : Nanoparticles; NWs: Nanowires; QDs: quantum dots ; CNT: Carbon nanotubes; MWCNT : Multi wall carbon nanotubes ; SWCNT : single wall carbon nanotubes.

Consumer and environmental exposure to nanomaterials is estimated to be very improbable with applications included in the Energy sector. Indeed, nanomaterials are usually embedded in a host matrix material. Final products are generally sealed (e.g. batteries are enclosed in various devices; solar cells are embedded within solar panels…) and there is apparently no risk of release. Thus, during normal use and unless accidental destruction, there is a very low risk of exposure to the human body or to the environment especially with currently commercialized products.

Waste management of nanomaterial-based applications should follow the current legislation (Frater et al. 2006; Directive 2002/96/EC). Disposal and recycling procedures (which are not specifically dedicated to nanotechnology-based materials) are currently proposed by large companies in the photovoltaic sector.
In case of uncontrolled disposal, potential environmental contamination is conceivable (soil, wastewater or underground contamination).

Many nanomaterial-based applications of the Energy sector are still at an early stage of development. It is too early to identify which of those applications will potentially carry a high risk of exposure to nanomaterials for humans or environment. For applications already available on the market (mainly solar cells and batteries), we did not identify a high risk of potential exposure for human or environment (providing that current disposal/recycling procedures for those products are applied). Therefore, no table 3 is included in the Energy sector EHS Impact assessment.

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