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nanomanufacturing**

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## Table of Contents

<b>1 Description of Task.....</b>	<b>3</b>
<b>2 Description of Work &amp; Main Achievements.....</b>	<b>3</b>
2.1 Introduction.....	3
2.2 Environmental reliefs potentials of nanotechnology .....	5
2.3 Evaluation of nanomaterial based products and applications in LCA-studies.....	6
2.4 Evaluation of specific manufactured nanoparticles .....	12
2.5 Analysis of other ,green‘ and ‘safer‘ approaches.....	18
2.5.1 Green chemistry .....	18
2.5.2 Green Engineering .....	19
2.5.3 Sustainability check for nanoproducts - German Oeko-Institut.....	20
2.5.4 5 Principles of ,Design for Safer Nanotechnology‘ .....	21
2.5.5 German Advisory Council on the Environment.....	22
2.5.6 German NanoKommission .....	23
2.5.7 Switzerland, Federal Office of Public Health FOPH and Federal Office for the Environment FOEN.....	25
2.5.8 LICARA nanoSCAN.....	26
2.5.9 Criticality of raw materials.....	27
2.6 Sustainable nanotechnologies – 12 design principles for ‘Green nano‘ .....	28
<b>3 Deviations from the Workplan .....</b>	<b>33</b>
<b>4 Performance of the Partners .....</b>	<b>33</b>
<b>5 Conclusions.....</b>	<b>33</b>
<b>6 List of Figures .....</b>	<b>36</b>
<b>7 List of Tables .....</b>	<b>36</b>
<b>8 References.....</b>	<b>37</b>

## 1 Description of Task

The development of nanomaterials especially of the next generation of functionalized nanomaterials is still in an early phase of development.

Task 4.6 has the objective to develop criteria and guiding principles for green design of nanomanufacturing and nanomaterials.

## 2 Description of Work & Main Achievements

### 2.1 Introduction

The main goal of the project is the development of the SUN Decision Support System (SUNDS) with the integration of nano-EHS data and methods for practical use by industries and regulators. For this tool information and data are needed from toxicological and risk analysis and LCA. This tool is an approach of the design and production phases of new nanotechnological based innovation (see Figure 1).

On the other side the development of nanomaterials especially of next generation nanomaterials is still in an early phase of development. In this situation, we face the Collingridge dilemma between broad design options and the narrow availability of reliable knowledge about expectable impacts (Collingridge 1980). On the one side there is high uncertainty and lack of knowledge at an early stage of the product cycle of nanomaterials since possible impacts only to a certain extend are based on the character of the technology and product itself. This limitation of knowledge is in the same order of magnitude in view of intended (opportunities) as well as unintended effects (threads). In the following phases of product life cycle intended as well as unintended impacts are to a growing extend based on product use, its circumstances and intentions, which are still unknown in earlier phases. On the other side the knowledge about possible impact is higher when the products and processes are established, but measures to control and change product shape and product use are more difficult because of already invested capital and entrenched habits (called path dependencies).

Inasmuch as nano-based products and processes are for the most part still in an early phase of development, there still exists, at least in principle, a large degree of freedom of measures to influence research efforts and process and product development towards a more green and sustainable design. Focusing on the character of the technology, product or process, there are great possibilities and opportunities to realize intended options and to minimize unexpected side-effects and costs. Some approaches and tools for this kind of analysis and orientation in different development phases are represented in Figure 1.

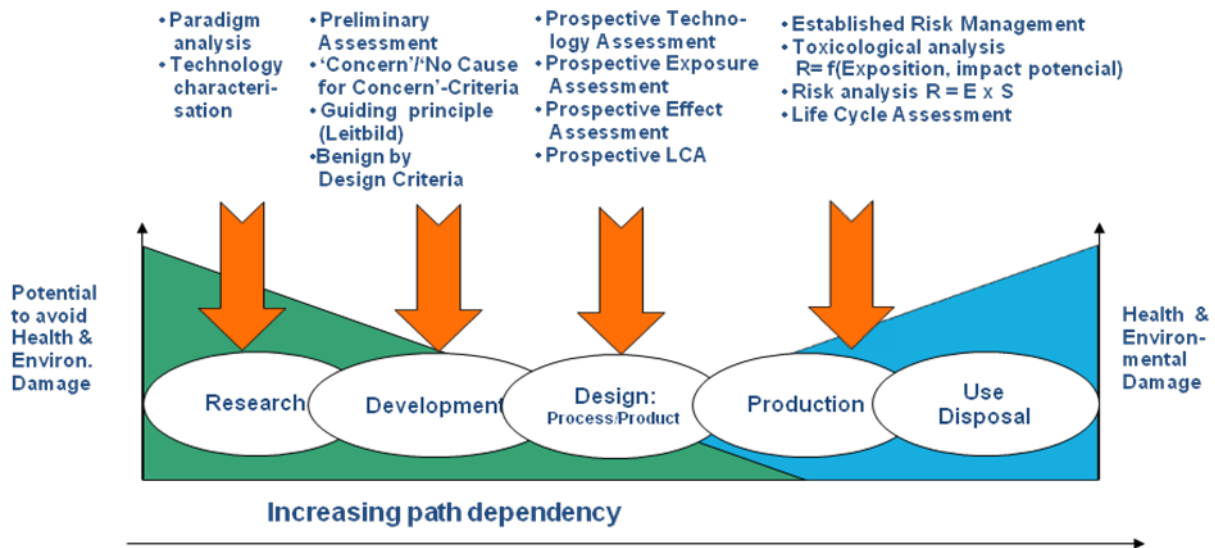


Figure 1: Approaches to technology assessment and engineering design according to the phases of innovation (in accordance with Steinfeldt et al. 2007)

The illustration demonstrates that throughout the entire process – from basic and applied research through development, use, and disposal phases – appropriate precautionary options can and must be designed. In each of the phases, various players are (collectively) involved and responsible. The development of precautionary options and the integration of resource aspects should already begin in the basic research phase. The results should subsequently lead to different research and development efforts in the area of applied research. The design phase of production processes and products is, to a certain extent, already predetermined inasmuch as their foundation is established in the initial research and development phase. Yet there is still a relatively high degree of freedom in process and product design, which can be decisive for aspects such as the “intrinsic safety” of the technology, processes, and products, as well as the impact of later phases (Steinfeldt et al. 2007). Design options are more limited, but to a large extent still possible.

Options for a more sustainable design become significantly smaller in the production phase and beyond. But in some cases, for instance facing hazardous substances, it is still possible to implement additional measures by means of product safety sheets, in view of hazardous substances categories that regulate the handling of processes and products, and through the enforcement of disposal regulations.

Moreover, each of the subsequent phases has its own players capable of influencing development. Each has a share in the development and corresponding opportunities to influence the development and thus contributes decisively to the potential impacts of the technologies, processes, and products being developed.

In view of the enormous knowledge problems of prospective technology assessments, the importance of concurrent approaches to specific developments of nanomaterials, - products and - processes must be emphasized. In early phases, the focus lays on what is already known, the technology, the materials and, if already in view, the products and processes that are based on them. In this situation, criteria and guiding principles for the shaping of green resp. sustainable nanomanufacturing processes and nanomaterials are needed.

An analysis to environmental reliefs potentials of nanotechnology, an evaluation of specific manufactured nanoparticles, of nanomaterial based products and applications in LCA-studies, and a literature search and analysis to different ‘green’ and ‘safer’ approaches serves as a basis for the development of criteria and principles for safer and green nanotechnology.

## 2.2 Environmental reliefs potentials of nanotechnology

Environmental relief potentials are defined here not only to include environmental engineering in the narrower sense (end-of-pipe technologies), but also and specifically process, production, and product-integrated environmental protection measures – thus not least regarding the “input side” into technosphere on the path towards a sustainable economy. This is about reduction and modification of quantities (resource und energy efficiency) and qualities properties (consistency) of the material and energy flows entering the techno sphere.

The analysis of new and existing nanotech products and processes in respect of environmental protection/pollution reveals a large and varied number of existing and potential areas of application (figures 2 and 3); however, it must be noted that their environmental relevance has so far only been qualitatively represented. Quantitative investigations of anticipated or still to be realized environmental benefits arising from specific nanotechnological products and processes, as well as further-ranging environmental innovations such as product and production-integrated environmental protection or energy-related solutions have so far been an exception.

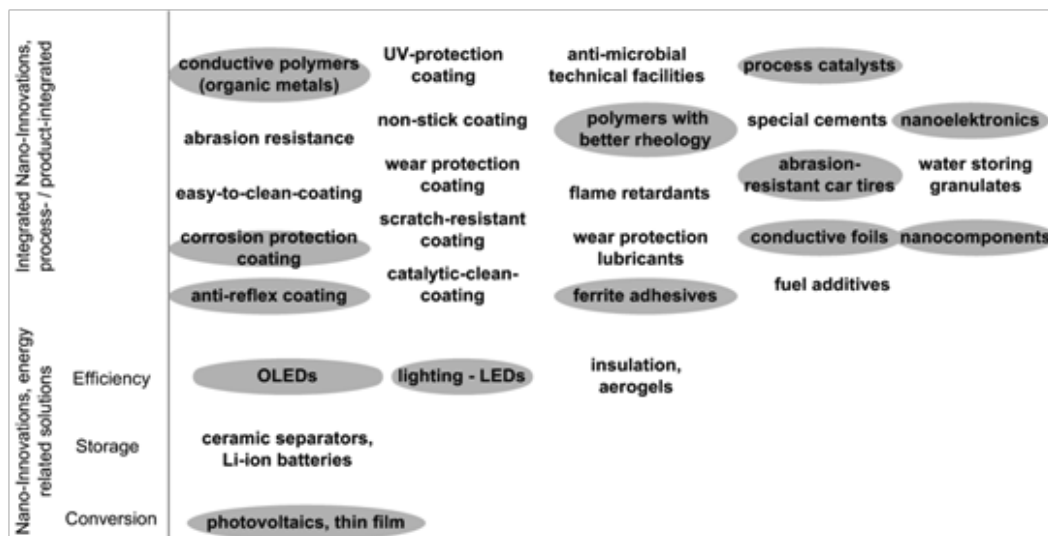
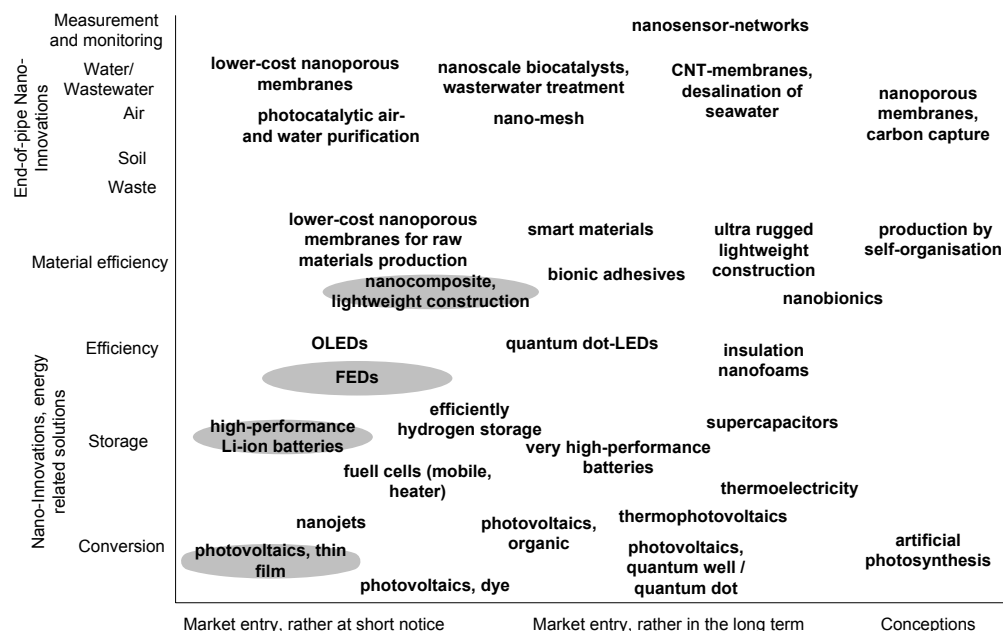


Figure 2: Nanotechnology-based products / applications on the market (Steinfeldt 2010)



**Figure 3: Anticipated nanotechnology-based applications (Steinfeldt 2010)**

In addition to the potential applications in the area of end-of-pipe technologies, such as membranes (catalysis already extends beyond the purification of exhaust gases in many areas well into the area of integration), the following illustrations reveal that the most predominant and especially far-reaching potentials for nano-based environmental innovations are in the areas of integrated innovation and energy. In many application fields high potentials for the realization of environmental benefits are expected. Those applications for which separate case studies already exist and thus quantitative data about potential environmental benefits is available are marked with a light-grey background.

### ***2.3 Evaluation of nanomaterial based products and applications in LCA-studies***

In recent years nanomaterial based products and applications studies were more and more examined in LCA-studies. A summary of the hereby identified life cycle aspects and environmental benefits is provided in Table 1.

**Table 1: Overview of studies about life cycle aspects of nanotechnology-based applications**

Nano-Product	Approach	Tech Benefits	Environmental Benefits	References
Anti-reflex glass for solar applications as compared with traditional glass	No assessment, only indication of the environmental benefit	Increased solar transmission	6% higher energy efficiency	(Bine 2002)
Clay-polypropylene nanocomposite in light-duty vehicle body panels as compared with steel and aluminium	Economic Input-Output Life Cycle Assessment (EIO-LCA)	Reduced weight	Overall reduced environmental impact; large energy savings	(Lloyd and Lave 2003)
Nanoscale platinum-group metal (PGM) particles in automotive catalysts	Eco-profile following LCA methodology	Reduced platinum-group metal (PGM) loading levels by 50%	Overall reduced environmental impact (10-40%)	(Steinfeldt et al. 2003)
Photovoltaic, dye photovoltaic cells as compared with multicrystalline silicon solar cells	Eco-profile following LCA methodology	Dye photovoltaic cells with better energy payback time, but smaller efficiency		(Steinfeldt et al. 2003)
Nanoscale platinum-group metal (PGM) particles in automotive catalysts	EIO-LCA	Reduced platinum-group metal (PGM) loading levels by 95%	Overall reduced environmental impact	(Lloyd et al. 2005)
Ultradur® High Speed plastic as compared with conventional Ultradur	BASF Eco-Efficiency-Analysis	Significantly improved flowability, reduction of working time and energy consumption of	Reduced environmental impact (1,5% - 9%), only ozone depletion higher	(BASF AG 2005, Steinfeldt et al. 2010a)

Car tire with nanoscaled SiO <sub>2</sub> and Carbon black	No Assessment, only indication of the environmental benefit	injection moulding process Increased road resistance	Up to 10% lower fuel consumption	(UBA 2006)
Nanocoatings as compared with conventional coatings	Eco-profile following LCA methodology	Necessary coating thickness smaller while maintaining functionality	5 – 8% higher resource efficiency, 65% lower emissions of volatile organic compound	(Steinfeldt et al. 2007)
Styrene synthesis, CNT catalyst as compared with iron oxide-based catalysts	Eco-profile following LCA methodology	Change of type of reaction, reduction of the reaction temperature, change of reaction medium Higher lifetime	Ca. 50% reduced energy consumption of the synthesis process	(Steinfeldt et al. 2007)
White LED and quantum dots as compared with incandescent lamps and compact fluorescents	Eco-profile following LCA methodology		Compared to lamp higher energy efficiency, compared to fluorescent lamp only with light efficiency higher 65 lm/W	(Steinfeldt et al. 2007)
Organic LED displays and nanotube field emitter displays as compared with CRT, liquid-crystal, and plasma screens	Eco-profile following LCA methodology	Increased energy efficiency, higher display resolution, reduced display thickness	Higher energy and resource efficiency; reduced material input by OLEDs, twice as high energy efficiency in the use phase	(Steinfeldt et al. 2007)
Ferrite adhesives as compared with conventional adhesives	Eco-profile following LCA methodology	Energy efficiently adhesives hardening by use of magnetic characteristics	12% (-40%) higher energy efficiency, dependent of size of adhered	(Wigger 2007)
Polypropylene nanocomposite in packaging film, agricultural film, automotive panel as compared with conventional films	Environmental and cost assessment	Reduced weight, increased elasticity and strength of PP	For agricultural film lower impact for five out of seven environmental categories (35%); for packaging film and automotive panel very smaller or none benefit	(Roes et al. 2007)
Nano-delivery system as compared with conventional mikro-delivery system (vitamin E)	Screening LCA	Higher penetration and conversion rates	Potential for efficiency enhancement ca. 34%	(Novartis International AG et al. 2007)
Comparison of different PVD coating TiN, TiAlN, Ti+TiAlN	LCA		TiN has the smallest environmental	(Bauer et al. 2008)

FED screen with CNT compared with conventional screen technologies	Simplified LCA	Increased energy efficiency	impact Overall reduced environmental impact	(Bauer et al. 2008)
Carbon nanofiber polymer composites compared with steel for equal stiffness design (body panel of automobile)	LCA, SimaPro	Material substitution of steel	Energy savings from substitution dependent on polymer type, weight reduction and CNF content rate	(Khanna and Bakshi 2009)
Nanotechnology-based disposable packaging (nano-PET bottle) as compared with conventional packaging	Environmental Assessment, in particular CO <sub>2</sub> -emissions	Improved barrier characteristics in particular against oxygen	Nano- PET bottle opposite to aluminium 1/3 and to glass of 60% fewer greenhouse gases	(Möller et al. 2009)
Glass coating with easy to clean effects compared with conventional glass surface	LCA, SimaPro	Easy to clean surface	Reduced environmental impact only when realizable decrease cleaning agent consumption	(Klade et al. 2009)
Nano-coating for wooden surfaces compared with conventional coatings	LCA, SimaPro		Overall reduced environmental impact except global warming impact is worse	(Klade et al. 2009)
Nickel nanoparticle deposition compared with conventional nickel phosphorus electroplating for facilitating diffusion brazing of arrayed microfluidics-assisted diffusion brazing	LCA, SimaPro software	Reduced usage of nickel and lower diffusion bonding energy requirements	Ca. 10 - 15% reduced environmental impact	(Haapala et al. 2009)
Carbon nanotubes	Systematic analysis of the laser vaporization processes energy consumption	Use in a number of applications such as lithium ion batteries, fuel cells, and conductive wiring	Energy would be lower if a larger amount of material is purified at once	(Ganter, et al. 2009)
Nanofluid solar hot water technology compared with conventional solar technology	Environmental and economic analysis	Improved efficiency	Ca. 6% reduced embodied energy content and carbon dioxide emissions	(Otanicar and Golden 2009)
Manufacture of nanotechnology based solderable surface finishes on printed circuit boards	Eco-profile following LCA methodology, Umberto software,	Necessary layer thickness smaller with same functionality	In relation to qualitatively comparable procedures depending upon	(Steinfeldt et al. 2010a)



as compared with conventional surface finishes	qualitative preliminary risk assessment		environmental impact category around factors from 4 to 390 better	
Nanotechnology-based (MWCNT) conductive foils as compared with conventional foils	Eco-profile following LCA methodology, Umberto software, qualitative preliminary risk assessment	Necessary foils thickness smaller with same functionality	12,5% - 20% reduced environmental impact	(Steinfeldt et al. 2010a)
Nanotechnology-based hybrid system city bus (Li-ion-batteries) as compared with conventional diesel city bus	Prospective Eco-profile following LCA methodology, Umberto software	Reduction of fuel consumption by the hybrid system	Ca. 20% reduced environmental impact by the future scenario	(Steinfeldt et al. 2010a)
Car air filter with nanofibre coating as compared with conventional car air filter	Environmental assessment, Umberto software	Reduction of air resistance and the associated fan power	8% reduced energy consumption of fan, regarding the overall system environmental benefit very small	(Martens et al. 2010)
Next generation CNT composite materials as carrier tray for electronics components compared with conventional out polycarbonate	Prospective Eco-profile following LCA methodology, Umberto software, qualitative preliminary risk assessment	New material smooth and non dusty	Increase of possible production efficiency of electronics components (e.g. 1%) produces an enhancement of environmental impacts (also 1%)	(Steinfeldt et al. 2010b)
Electrodeposited Ni-MWCNT composite films for metal substrates for wind power plant compared with conventional material	Prospective Eco-profile following LCA methodology, Umberto software, qualitative preliminary risk assessment	Lower friction coefficients under dry conditions, i.e. superior solid lubrication	Increase of possible energy production efficiency of wind power plant of 0,25% produces an enhancement of environmental impacts between 3,7-11%	(Steinfeldt et al. 2010b)
Quantum dot photovoltaics (QDPV) compared with conventional PV	LCA, SimaPro software	Higher energy efficiency	Reduced environmental impact (CO <sub>2</sub> , SO <sub>x</sub> , NO <sub>x</sub> emissions), but higher heavy metal emissions	(Sengül and Theis 2011)
Future nanocrystalline silicon based multi-junction PV compared with conventional PV	Life-cycle energy payback analysis (EPBT)	Great potential for increasing the efficiency of photon-to-electricity conversion	Assumptions to the PECVD process have large influence of EPBT	(Kim and Fthenakis 2011)
Nanocrystalline	LCA, SimaPro, in		Greenhouse gas	(Meulen and

materials in thin-film silicon solar cells compared with conventional solar cells Silver nanoparticles in socks compared with conventional socks	particular cumulative energy demand and greenhouse gas emissions Screening-level LCA, SimaPro	Enhanced biocidal treatment	emissions of nano-crystalline silicon PV higher than amorphous modules Silver socks have overall higher environmental impacts, nanoscale silver content and production process have largest influence on the impacts	Alsema 2011)  (Meyer et al. 2011)
Nanosilver T-shirts compared with conventional T-shirts	Prospective LCA	Enhanced biocidal treatment	Lower washing frequencies can compensate the increased climate footprint of Nanosilver T-shirt production	(Walser et al. 2011)
Microfibrillated celluloses for composites, coatings, and films	Comparison of different types and production techniques	Higher toughness values, unique structural, functional and optical properties	Lower energy input, renewable, bio-degradable, do not contain harmful chemicals	(Spence et al. 2011)
Cellulose nanowhiskers	Environmental aspects and related impacts of two cellulose nanowhiskers product systems are evaluated	Reinforce the mechanical properties of different polymers	EC systems require less energy and water, emitted less pollutants, and contributed less to climate change, human toxicity, and eutrophication	(Figueirêdo et al. 2012)
Starch nanocrystals (SNC) as nano-fillers in polymeric matrix	LCA	Higher barrier properties and higher biodegradability than NCC	Cumulative impact variation is -37 % for Scenario 2: reduced water consumption	(LeCorre et al. 2012)
Carbon nanotube field emission displays	Cradle-to-grave LCA	Image quality and viewing angles comparable to a cathode ray tube, thinner structure, CNT-FED-to-LCD lifespan ratio of 4.5:1	More efficient power consumption during use, 50% less energy than comparable equipment	(Upadhyayula et al. 2013)
Nano insulation materials made of hollow silica nanospheres	Synthesis, characterization, and life cycle assessment	Great flexibility in modifying their properties	Recycling of chemicals, up-scaling production, and use of environmentally friendly materials greatly affect the	(Gao et al. 2013)

			process environmental footprint	
Titanium dioxide nanotubes	Mathematical modeling approach for direct energy consumptions in the electrochemical anodization process	Outstanding charge transport and carrier lifetime		(Li et al. 2013)
TiO <sub>2</sub> in polyethersulfone membrane	Cradle to gate LCA	Microfiltration and ultrafiltration, enhance membrane flux		(Zuin et al. 2013)
Carbon nanotube-enabled chemical gas sensor	Cradle-to-Gate LCA coupled with an impact–benefit ratio	Significant human health benefits	SWNTs impacts are minimal compared with those associated with other material and processing stages	(Gilbertson et al. 2014)
multi-walled carbon nanotubes, Ag	LCA case studies		Can decrease the GWP as compared to conventional	(Kralisch et al. 2014)
Zero valent iron nanoparticles	LCA of the nZVI synthesis green method	Ground water treatment and soil remediation		(Martins et al. 2014)
Nano insulation materials made of hollow silica nanospheres	Synthesis, characterization, and life cycle assessment	Great flexibility in modifying their properties	Recycling of chemicals, up-scaling production, and use of environmentally friendly materials greatly affect the process environmental footprint	(Gao et al. 2014)
Nano insulation material based on hollow silica nanospheres	Cradle-to-gate LCA	Reduce energy demands in buildings without altering wall thickness	Halved energy consumption in the ethanol recycling results to -12% CED and - 17% CC impact	(Schlanbusch et al. 2014)
Nanosilver in medical applications	Cradle-to-grave LCA of a nanosilver-enabled medical bandage using TRACI 2.1	Bactericidal properties		(Pourzahedi and Eckelman 2014)
Nanosilver in T-Shirts	LCA comparing different antibacterial T-shirts	Prevent undesirable odours	20–30% lower impacts in key categories	(Manda et al. 2015)
Nano-silica polymers in power capacitors	Modified existing	Size reduction or	Reduce environmental	(Alaviitala and Mattila

	production technology representing a prototype using nanomaterials	increased functionality	impacts by c.a. 20%, mainly metal depletion, land transformation and ecotoxicity	2015)
Paints containing manufactured nanomaterials (MNM) mainly Ag and TiO <sub>2</sub>	LCA comparison of facade coatings with and without MNM		25 % SiO <sub>2</sub> , 30–100 % Ag, 10 % TiO <sub>2</sub> less than without nano	(Hischier et al. 2015)
Cellulose nanomaterials	LCRA of selected applications		renewable material, can replace petroleum-based materials	(Shatkin and Kim 2015)

The accomplished studies mainly focused on cradle-to-gate assessments. Cradle-to-gate is an assessment only of a partial product life cycle from manufacture to the factory gate. The use phase and the end of life phase (recycling, disposal) are omitted (Meyer et al. 2009). For these phases, which are very important with respect to emissions into the environment, almost no data exists.

The results of the LCA comparisons make clear that nanotech applications neither intrinsically nor exclusively can be associated with a high potential for a large degree of environmental relief. Nevertheless, for selected application contexts high potentials for significant environmental relief can be identified using the methods of prospective LCA based on a comparable functionality of the analyzed solutions. In some of the studies the uncertainties combined with the prospective approach are quite high. Often only possible capabilities of applications based on nanomaterials are compared in scenarios with appropriate assumptions. The represented environmental benefits of nanomaterial based applications must be judged with caution against the background of various data gaps and methodical problems.

## 2.4 Evaluation of specific manufactured nanoparticles

The largest groups of manufactured nanoparticles for industrial applications comprise inorganic nanoparticles (e.g. TiO<sub>2</sub>, ZnO, SiO<sub>2</sub>, Ag), carbon-based nanomaterials (carbon nanofiber, multi wall carbon nanotubes (MWCNT), single wall carbon nanotubes (SWCNT)), nanocellulose, and quantum dots (semiconductor nanoparticles with a specific size (e.g. CdSe, CdS, GaN). Besides qualitative environmental assessments of the different manufacturing methods (Steinfeldt et al. 2007, Sengül et al. 2008), quantified material and energy flows data exist only for a very small number of manufacturing processes and/or for individual nano-materials. A summary of published studies is shown in Table 2. Particularly remarkable is that the majority of the studies investigated the production of carbon-based nanomaterials.

**Table 2: Overview of studies of published LCAs of the manufacture of nanoparticles and nanocomponents (based on Meyer et al (2009) and own data)**

Nanoparticle and/or nanocomponent	Assessed impact(s)	References
Carbon nanotubes	Substance Flow Analysis (SFA)	(Lekas 2005)
Metal nanoparticle production (TiO <sub>2</sub> , ZrO <sub>2</sub> )	Cradle-to-gate energy assessment, global warming potential	(Osterwalder et al. 2006)
Nanoclay production	Cradle-to-gate assessment, energy use, global warming potential, ozone layer depletion, abiotic depletion,	(Roes et al. 2007)

Several nanomaterial syntheses	photo-chemical oxidant formation, acidification, eutrophication, cost E-factor Analysis	(Eckelman et al. 2008)
Carbon nanoparticle production	Cradle-to-gate energy assessment	(Kushnir and Sandén 2008)
Carbon nanotube production	Cradle-to-gate assessment with SimaPro software, energy use, global warming potential, ...	(Singh et al. 2008)
Single-walled carbon nanotube (SWCNT) production	Cradle-to-gate assessment with SimaPro software, energy use, global warming potential, ...	(Healy et al. 2008)
Carbon nanofiber production	Energy use, global warming potential, ozone layer depletion, radiation, ecotoxicity, acidification, eutrophication, land use	(Khanna et al. 2008)
Nanoscale semiconductor	Cradle-to-gate assessment, energy use, global warming potential	(Krishnan et al. 2008)
Single-walled carbon nanotube (SWCNT) synthesis process	Stochastic multiattribute analysis	(Canis et al. 2010)
Nanoscaled polyanilin production	Cradle-to-gate assessment with Umberto software, energy use energy use, global warming potential, ...	(Steinfeldt et al. 2010a)
Multi-walled carbon nanotube (MWCNT) production	Cradle-to-gate assessment with Umberto software, energy use, global warming potential, ...	(Steinfeldt et al. 2010a)
Nanoscaled Titanium dioxide	Cradle-to-gate assessment, Ecoindicator 99 methodology, energy use, exergy	(Grubb and Bakshi 2010)
Fullerene (C60, C70)	Cradle-to-gate assessment with SimaPro, energy use, material intensity	(Anctil et al. 2011)
Nanocellulose	Cradle-to-gate LCA of four comparable lab scale nanocellulose fabrication routes	(Li, et al. 2013)
Zinc oxide	Cradle-to-gate environmental analysis was for six different methods of ZnO nanoparticles synthesis	(Pompermayer et al. 2013)
Graphene	Prospective cradle-to-gate assessment, energy use, water use, toxicity, ecotoxicity	(Arvidsson et al. 2014)
Alumina nanofluid	Combined life cycle assessment and Risk Assessment evaluated by means of qualitative risk assessment	(Barberio et al. 2014)
Nanosilver	Comparative cradle-to-gate assessment, TRACI impact categories	(Pourzahedi and Eckelman 2015)
Nanocellulose	Comparative cradle-to-gate assessment environmental of three production routes	(Arvidsson, et al. 2015)
TiO2	Cradle-to-gate assessment with SimaPro, IMPACT 2002+ and EATOS calculations	(Pini et al. 2014)

Lekas evaluated carbon nanotubes (CNT) in a substance flow analysis throughout the economy from cradle to grave. The goal of the study was to gather production and use

information of carbon nanotubes (current production, raw material inputs and quantities, end-use applications and destination of materials) from literature and nanotube companies (Lekas 2005).

Osterwalder and coworkers performed cradle-to-gate assessments of titanium dioxide (TiO<sub>2</sub>) and zirconia dioxide (ZrO<sub>2</sub>) nanoparticle production (Osterwalder et al. 2006). The goal of the study was to compare the energy requirements and greenhouse gas emissions of the classical milling process with those of a novel flame synthesis technique using organic precursors. The functional unit of the study was 1 kg of manufactured material.

Roes and co-workers evaluated the use of nanocomponents in packaging films, agricultural films, and automotive panels (Roes et al. 2007). The goal of the prospective assessment was to determine if the use of nanoclay additives in polymers (polypropylene, polyethylene, glass fibre-reinforced polypropylene) is more environmentally advantageous than conventional materials. Specific material and energy flows of the nanoclay production have been collected. The manufacturing of nanoclay includes several processes, e.g. raw clay (Ca-bentonite) extraction, separation, spray drying, organic modification, filtering, and heating.

Eckelman and co-workers performed an E-factor analysis of several nanomaterial syntheses (Eckelman et al. 2008). The E-factor is an approach to measure environmental impact and sustainability that has been commonly employed by chemists. The E-factor (or waste-to-product ratio) includes all chemicals involved in production. Energy and water inputs are generally not included in E-factor calculations, nor are products of combustion, such as water vapour or carbon dioxide. Unfortunately, these results are not comparable with the other studies.

Kushnir and Sanden modeled the requirements of future production systems of carbon nanoparticle and also used a cradle-to-gate perspective, including all energy flows up to the production and purification of carbon nanoparticles (Kushnir and Sanden 2008). All calculations were applied for a functional unit of 1 kg of nanoparticles. Several production systems (fluidized bed chemical vapour deposition (CVD), floating catalyst CVD, HiPco, pyrolysis, electric arc, laser ablation, and solar furnace) were investigated and possible efficiency improvements discussed. Carbon nanoparticles were identified as highly energy-intensive materials, in the order of 2 to 100 times more energy intensive than e.g. aluminium, given a thermal to electric conversion efficiency of 0.35.

Singh and co-workers performed environmental impact assessments for two future continuous processes for the production of carbon nanotubes (CNT) (Singh et al. 2008). The high-pressure carbon monoxide disproportionation in a plug-flow reactor (CNT-PFR) and the cobalt-molybdenum fluidized bed catalytic reactor (CNT-FBR) were selected for the conceptual design. The CNT-PFR reactor contains catalytic particles formed in situ by thermal decomposition of iron carbonyl. The CNT-FBR process employs the synergistic effect between the cobalt and molybdenum giving high selectivity to carbon nanotubes from CO disproportionation.

Healy and co-workers have performed life cycle assessment of three more established SWNT manufacturing processes: arc ablation (arc), chemical vapour deposition (CVD), and high pressure carbon monoxide (HiPco) (Healy et al. 2008). Each method consists of process steps that include catalyst preparation, synthesis, purification, inspection, and packaging. In any case, the inspection and packaging steps contribute minimally to the overall environmental loads of the processes. Although the technical attributes of the SWNT products that are generated via each process may not always be fully comparable, the study provides a baseline for the environmental footprint of each process. All calculations are made with a functional unit of 1 g of SWNT.

Khanna and co-workers (Khanna et al. 2008) have performed a cradle-to-gate assessment of carbon nanofiber (CNF) production. The goal of the assessment was to

determine the non-renewable energy requirements and environmental impacts associated with the production of 1 kg of CNFs. Life cycle energy requirements for CNFs from a range of feedstock materials are found to be 13 to 50 times higher than those of primary aluminium on an equal mass basis.

Krishnan and co-workers presented a cradle-to-gate assessment, developed a library of material and energy requirements, and published the global warming potential of nanoscale semiconductor manufacturing (Krishnan et al. 2008). The goal of the study was to identify potential process improvements. The functional unit selected was 1 silicon wafer with 300-mm in diameter that can be used to produce 442 processor chips. The total energy required for the process was 14,100 MJ/wafer including 2,500 MJ/wafer that accounts for the manufacture of fabrication equipment. The greenhouse gas potential was 13 kg CO<sub>2</sub> eq/wafer.

Canis and co-workers (Canis et al. 2010) discussed a product development problem of selecting the most advantageous technology for manufacturing SWCNT. Four different synthesis processes were investigated: High Pressure Carbon Monoxide (HiPCO), arc discharge (Arc), chemical vapor deposition (CVD), and laser vaporization (Laser). The case study is an example of a method based on stochastic multicriteria decision analysis (MCDA)-for situations where knowledge of the amounts is lacking and uncertainty about criteria scores is significant. Unfortunately, the results are not comparable with the other studies.

Steinfeldt and co-workers performed several in-depth life cycle assessments of processes and products, including cradle-to-gate assessments of the production of nanoscaled polyaniline and of the production of multi-walled carbon nanotube (MWCNT) (Steinfeldt et al. 2010a). With the cooperation of producers, it was possible to develop detailed models of the manufacturing processes for nanoscaled polyaniline and MWCNT, and to generate specific life cycle assessment data.

Grubb and Bakshi (2010) performed a life cycle assessment of the hydrochloride nanomanufacturing process for TiO<sub>2</sub> nanoparticles in comparison with conventional bulk titanium dioxide. The functional unit of the study was 1 kg of manufactured material. This work also included an exergy analysis to account for material resource consumption in the process.

Anctil and co-workers (Anctil et al. 2011) have performed a cradle-to-gate energy assessment of manufacturing of fullerenes and modified derivatives. The inventory is based on the functional unit of 1 kg of product (either C<sub>60</sub> or C<sub>70</sub>). Four several synthesis methods were investigated. The embodied energy of 1 kg C<sub>60</sub> after synthesis and separation is very different (pyrolysis with tetralin 12.7 GJ/kg C<sub>60</sub>; pyrolysis with toluene 17.0 GJ/kg C<sub>60</sub>; plasma Arc 88.6 GJ/kg C<sub>60</sub>, and plasma radio frequency (RF) 106.9 GJ/kg C<sub>60</sub>).

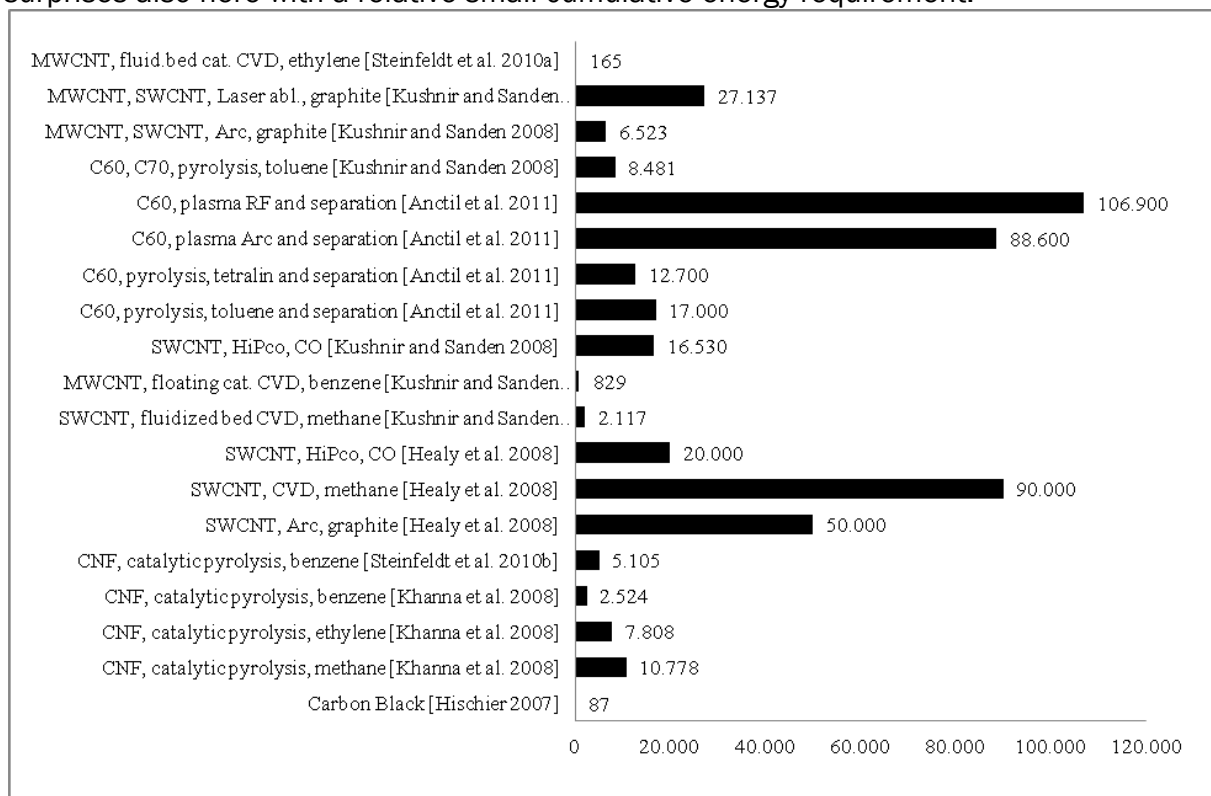
Arvidsson and co-workers (Arvidsson et al. 2014) have performed prospective life cycle assessment of two Graphene manufacturing processes: ultrasonication and chemical reduction. The embodied energy of 1 kg graphene in solution is different with 470 MJ/kg by ultrasonication and with 1100 MJ/kg by chemical reduction.

Arvidsson and co-workers (Arvidsson et al. 2015) have assessed the cradle-to-gate environmental impacts of three production routes for cellulose fibrils (CNF) made from wood pulp. The results show that CNF produced with carboxymethylation route has the highest environmental impacts.

The data above can provide some insight regarding the potential burdens that must be addressed if the large-scale use of these types of nanoparticles and nanocomponents is to continue. For this purpose the data from the studies is expressed in a common mass-based unit. Accordingly, energy demand is presented in MJ-Equivalents/kg material and global warming potential is expressed as kg CO<sub>2</sub>-Equivalent/kg product. Energy

consumption during the product life cycle is very important because it relates to the consumption of fossil fuels and the generation of greenhouse gases. Therefore, it is desirable to design manufacturing processes that minimize the use of energy. The data for energy consumption of the materials discussed above is shown in Figure 4 and 5. Additionally into the comparison data of conventional materials is included.

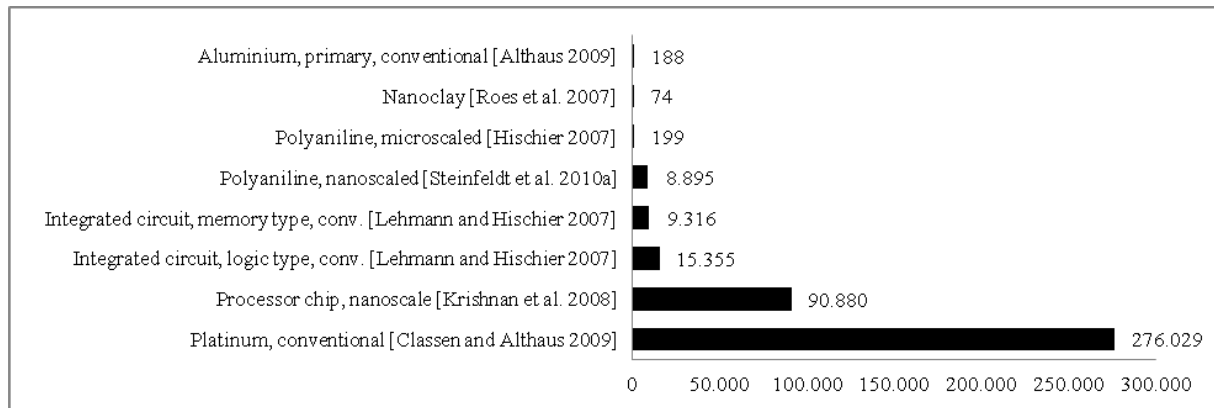
The represented cumulative energy requirements for various carbon nanoparticle manufacturing processes differ very strongly from each other. The various processes for the production of SWCNT (excluding equipment fabrication) are by far the most energy intensive processes as compared with the production of other carbon nanoparticles. A cause for the very large differences between the examined studies lies in the different process conditions (temperature, pressure) of the manufacturing processes. Furthermore large differences are found in the assumptions of reactions and purification yields. The relative small reference value appears remarkable for the mass production of carbon black by means of flame synthesis. The production of MWCNT based on catalyst CVD surprises also here with a relative small cumulative energy requirement.



**Figure 4: Comparison of the cumulative energy requirements for various carbon nanoparticle manufacturing processes [MJ-Equivalent/kg material]**

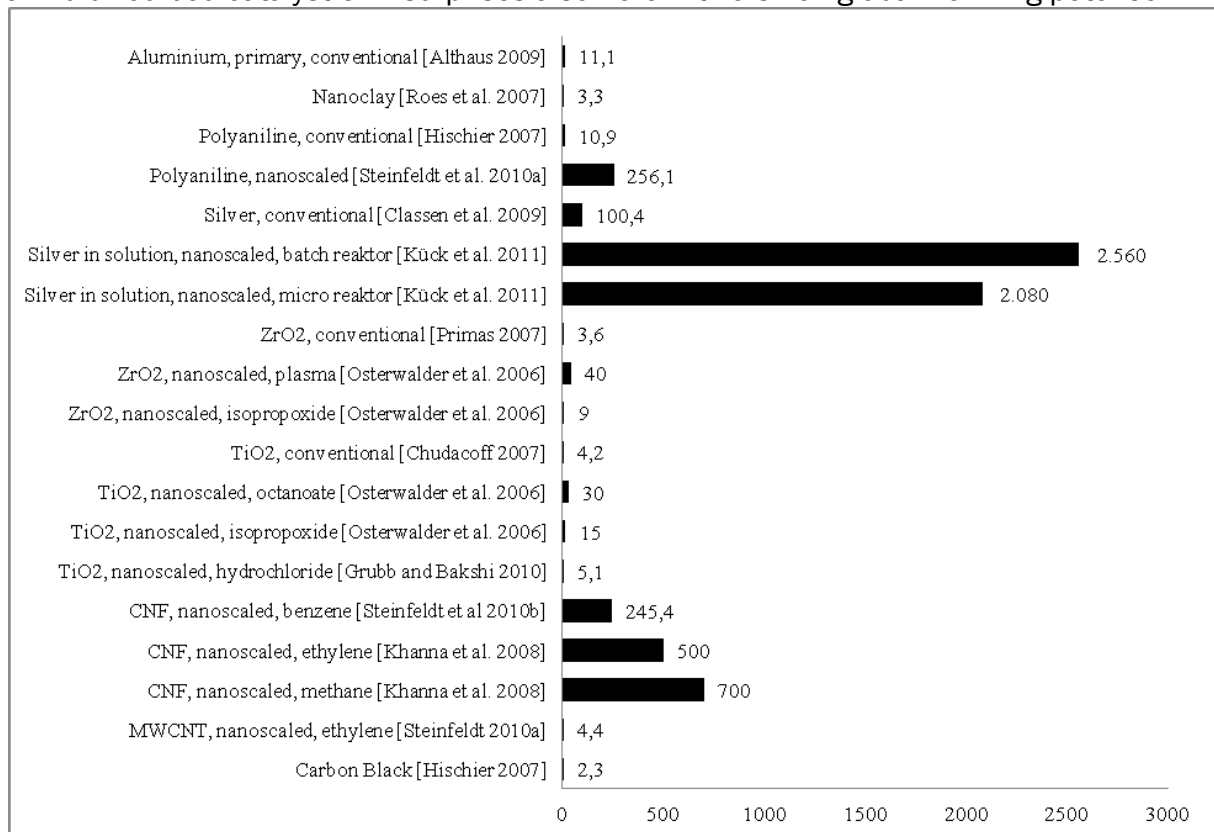
The comparison of the cumulative energy requirements for the production of other conventional and nanoscaled materials and components make clear that the production of nanosemiconductors is also a very energy intensive process. Only the extraction of the precious metal platinum as example is still more complex. The production of nanoscaled polyaniline is likewise very energy-intensive.





**Figure 5: Comparison of the cumulative energy requirements for the production of various conventional and nanoscaled materials and components [MJ-Equivalent/kg product] (in parts own calculation)**

A comparison of the global warming potential for the production of various conventional and nanoscaled materials is shown in Figure 6. The production of silver nanoparticles has the largest impact when compared to the other materials. However, the production of carbon nanofiber and nanoscaled polyaniline demonstrates also a high global warming potential. The reason for the larger global warming potentials for silver nanoparticle, CNF and polyaniline manufacturing is the much larger energy requirements when compared to other nanoparticle production. Also the cleaning agents in the manufacturing processes have a large influence of the global warming potentials. The production of MWCNT based on fluidized bed catalyst CVD surprises also here with a small global warming potential.



**Figure 6: Comparison of the global warming potential for the production of various conventional and nanoscaled materials [CO2-Equivalent/kg product] (in parts own calculation)**

This represented results place no comprehensive life cycle assessments, the results do offer useful insight when considering the environmental impact of various nanomaterials and nanotechnology-based applications (see the overview of applications in Table 1). It is commonly pointed out that the nanocomponent is only a fraction of the total product

(often only 1,2 or 4 per cent) implying that only a small fraction of the environmental impact of a nanoproduct can be attributed to the nanocomponent and its manufacture. The high specific energy demand for the production of nanoparticle relates itself then in nanoproduct.

## **2.5 Analysis of other ,green‘ and ‘safer‘ approaches**

A literature search serves as a basis for the development of criteria and principles for safer and green nanotechnology.

### **2.5.1 Green chemistry**

Green chemistry consists of chemicals and chemical processes designed to reduce or eliminate negative environmental impacts. The use and production of these chemicals may involve reduced waste products, non-toxic components, and improved efficiency. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations. The 12 Principles of Green Chemistry, originally published by Paul Anastas and John Warner (1998), provide a road map for chemists to implement green chemistry.

#### **Twelve Principles of Green Chemistry**

1. **Prevention**  
It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy**  
Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Syntheses**  
Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals**  
Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries**  
The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency**  
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks**  
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives**  
Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**  
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation**  
Chemical products should be designed so that at the end of their function they

break down into innocuous degradation products and do not persist in the environment.

**11. Real-time analysis for Pollution Prevention**

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

**12. Inherently Safer Chemistry for Accident Prevention**

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

### 2.5.2 Green Engineering

In adaption of the 12 Principles of Green Chemistry Anastas and Zimmermann (Anastas et al 2000, Anastas and Zimmermann 2003) developed the following 12 Principles of Green Engineering. These principles provide a road map for engineers to implement green engineering.

#### Twelve 12 Principles of Green Engineering

**1. Inherent rather than circumstantial**

The inherent nature of the selected material should be taken into consideration to ensure that it is as benign as possible (i.e. non-toxic, and/or minimal energy and materials inputs required to complete the process).

**2. Prevention instead of treatment**

Materials and processes that generate minimal waste should be used, which can avoid costs and risks associated with substances that would otherwise have to be handled, treated and disposed of.

**3. Design for separation**

Products should be designed with physical and chemical properties that permit self-separation processes, to reduce waste and save in disassembly and reassembly time and costs.

**4. Maximize mass, energy, space and time efficiency**

Products should be designed for maximum efficiency, using real-time monitoring to ensure the actual process is performing in accordance with the required design conditions.

**5. Output-pulled versus input-pushed**

The amount of materials or energy used should be minimised, by applying Le Châtelier's Principle<sup>1</sup> to continually remove products or 'outputs' so that the output is then 'pulled' through the system.

**6. Conserve Complexity**

Complexity in products should be minimized to create more favourable properties for reuse and recycling.

**7. Durability rather than immortality**

Products should be designed to have a targeted lifetime, to avoid environmental problems such as waste to landfill, persistence and bioaccumulation.

**8. Meet need, minimize excess**

Technologies should be innovated that target specific demands of the user to minimize waste and cost.

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<sup>1</sup> Le Châtelier's Principle states that when a stress (such as temperature or pressure) is applied to a system at equilibrium, the system readjusts to relieve or offset the applied stress. This principle can be applied in an 'input-pushed' process, where the addition of more inputs (stresses) leads to the generation of more outputs.

**9. Minimize material diversity**

Products should be designed with less material diversity to create more options for recyclability and reuse.

**10. Integrate local material and energy flows**

Products, processes and systems should be designed to use local materials and energy resources to minimize inefficiencies and consumption associated with transportation.

**11. Design for commercial 'afterlife'**

Products, processes and systems should be designed so their components can be reused or reconfigured to maintain their value and useability for new products (sometimes referred to as 'design for modularity').

**12. Renewable rather than depleting**

Renewable materials should be used so that the source can be replenished and provide virtually infinite service with minimal, if any, waste.

**2.5.3 Sustainability check for nanoproducts - German Oeko-Institut**

The German Oeko-Institut has been developed a Sustainability check for nanoproducts (Möller et al 2012; Öko-Institut 2011). This tool is aimed at enabling companies to carry out data-driven self-assessment of their nanoproducts' sustainability during the development stage and when placing products on the market.

In terms of methodology, the Nano-Sustainability Check is based on PROSA (Product Sustainability Assessment), a tool for strategic analysis and assessment of product portfolios, products and services which has been developed by the Öko-Institut. PROSA takes into account the entire life cycle and analyses and assesses the environmental, economic and social opportunities and risks of future development paths.

The aspects investigated within the Nano Sustainability Check are represented in the form of 14 key performance indicators. The focus is on aspects of environmental and climate protection, which are – as far as possible – considered from a quantitative point of view. In addition, questions relating to the fields of occupational safety and health are examined, as well as benefit and socio-economic aspects. The results of the individual key performance indicators are combined into a single representation. To this purpose, the "SWOT analysis" originally derived from business administration is taken up and adapted for the purposes of the Nano-Sustainability Check. The strength / weakness analysis refers to the intrinsic properties and potentials of the product, for example in terms of the product carbon footprint, user benefits and life-cycle costs. Complementarily, the opportunity / threat analysis takes into account external conditions such as employment effects, societal benefits and risk perception (Möller et al 2012).

As an example the results of the individual key indicators for a investigated product X-SEED (material scenario) are summarised in the following SWOT matrix.

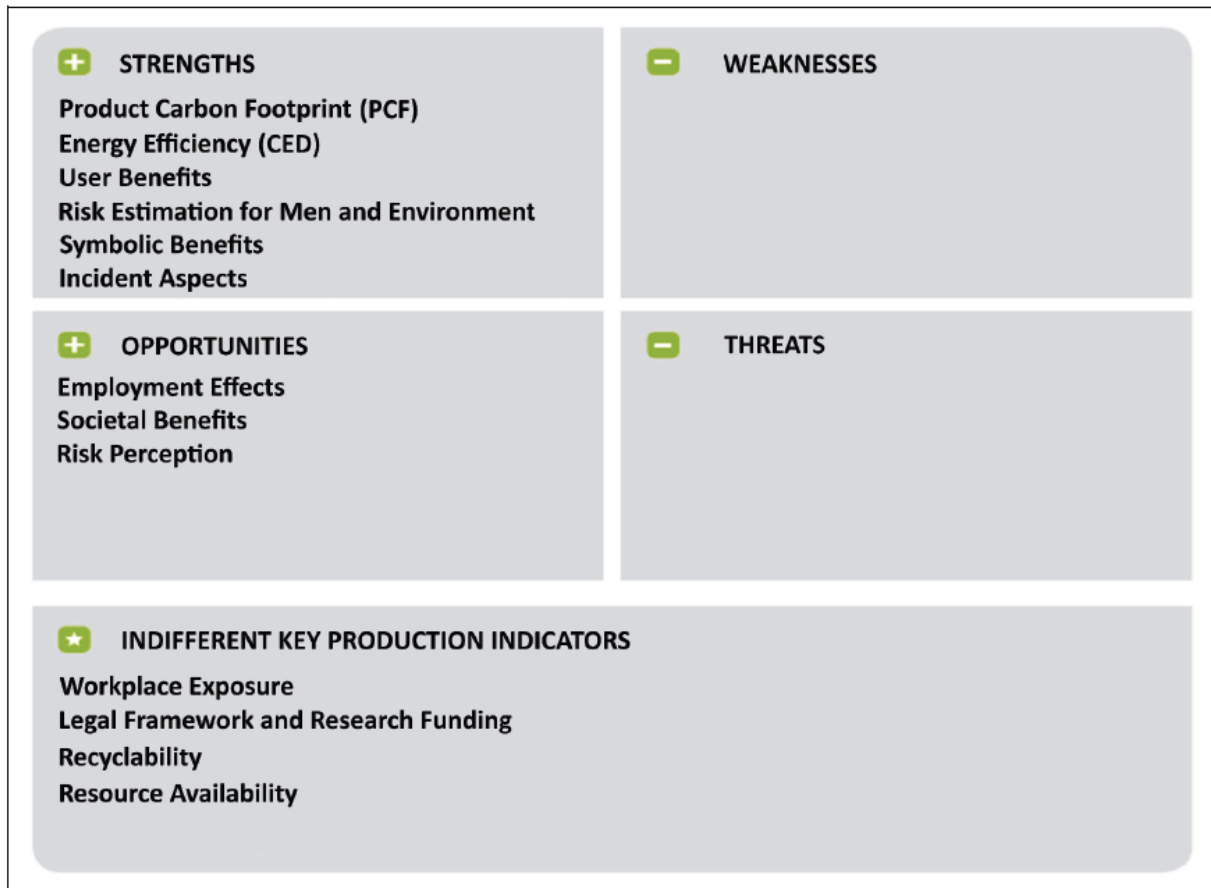


Figure 7: SWOT matrix summarising the results of the key indicators for the case example of “X-SEED” (material scenario) (Öko-Institut 2011).

Of particular interest is the indicator of incident aspects for the development of criteria for the precautionary design and for improved recyclability of engineered nanomaterials. The evaluation of the indicator hazardous incident is orientated on the structure of the Swiss precautionary matrix with an excel tool.

#### 2.5.4 5 Principles of ‘Design for Safer Nanotechnology’

Morose (2010) propose five design principles for product designers to use during the design stage for products that contain nanoparticles. By using these design principles, the health risk of the nanoparticle may be mitigated by potentially lowering the hazard and/or the exposure potential of the nanoparticle.

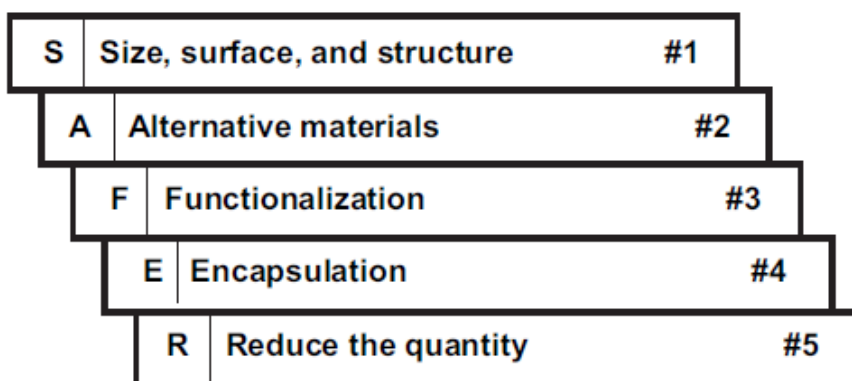


Figure 8: The five principles of safer nanotechnology.

The health and safety risk of the nanoparticle may be reduced by lowering the hazard

and/or the exposure potential of the nanoparticle. The ultimate goal of the principles for safer nanotechnology would be to move all nanoparticles incorporated into products to the low risk zone. A risk mitigation matrix is shown in Fig. 8 to illustrate this approach.

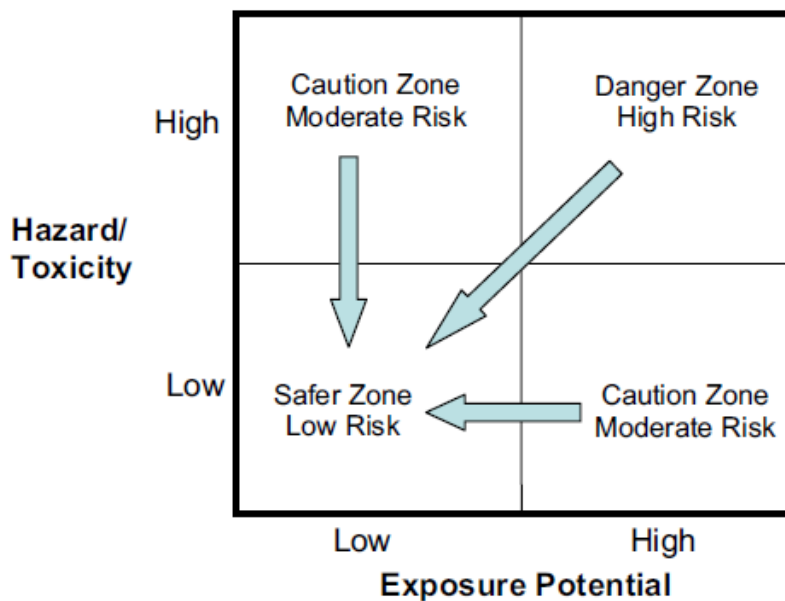


Figure 9: Nanotechnology risk mitigation matrix.

### 2.5.5 German Advisory Council on the Environment

The German Advisory Council on the Environment (SRU) has investigated the application of the precautionary principle to a new technology by the example of nanomaterials (SRU 2011). In this study the opportunities and risks of nanomaterials are mirrored against the requirements of the precautionary principle. Possible options are outlined in general terms, and specific recommendations for the application of the precautionary principle to nanomaterials are set.

Regulatory decisions on the basis of the precautionary principle should follow an analytical and a normative process. The German Advisory Council on the Environment has developed following model for the identification of precautionary action by the state (see figure).

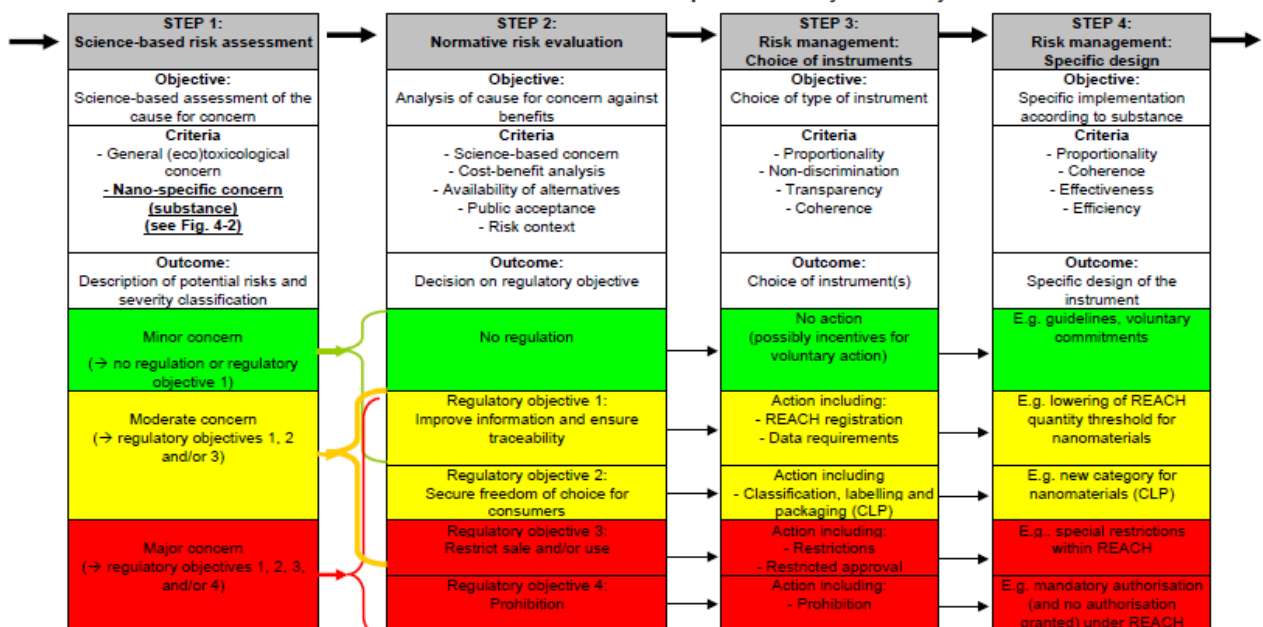


Figure 10: Model for the identification of of precautionary action by the state SRU (2011b, 12).

For the early stage of the development of new nanomaterials the SRU proposes a decision tree and criteria for preliminary science-based risk assessment (see Fig.). The criteria relate to easily determined material properties (size, solubility, persistence and surface reactivity) so that initial risk analysis can be carried out.

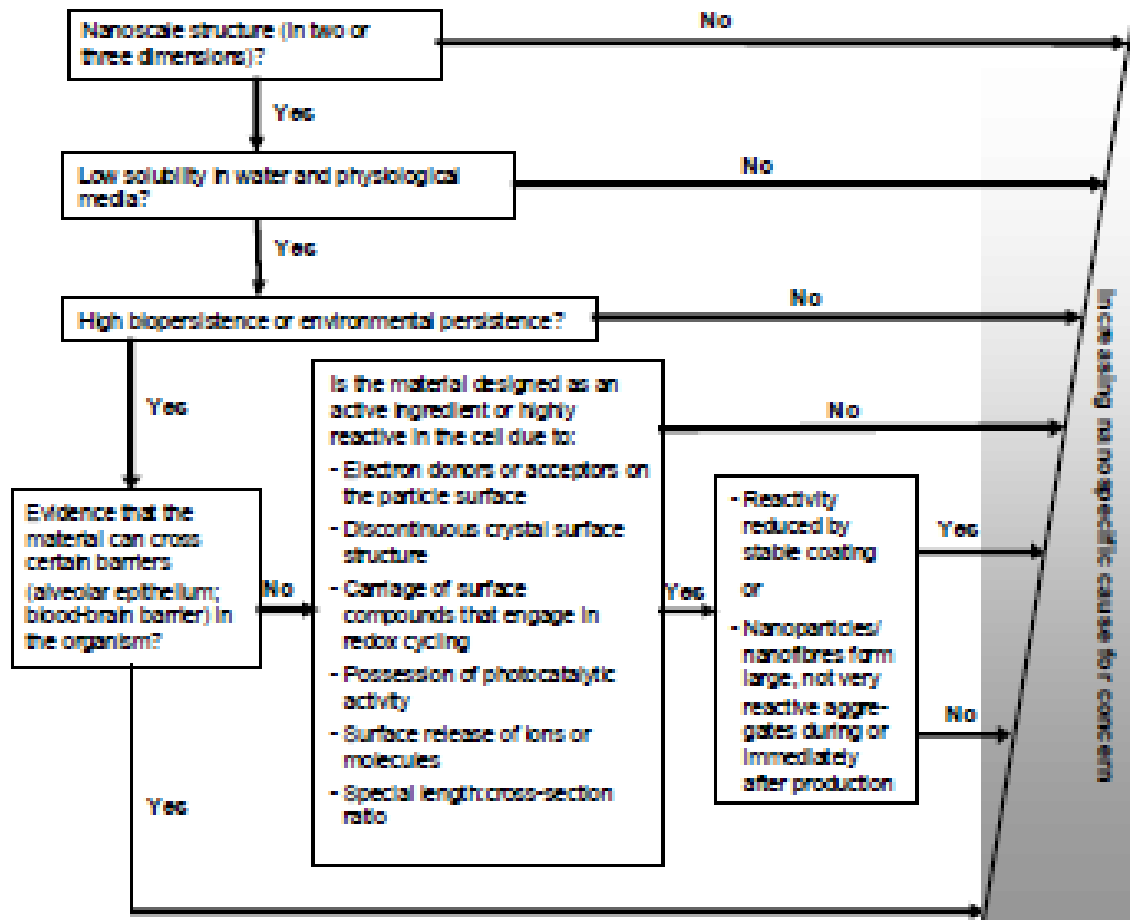


Figure 11: Decision tree for risk categorisation of nanoparticles and nanofibres SRU (2011b, 16).

This decision tree could serve as a good basis for the development of guiding principles. Unfortunately it is a lack of an operationalization of the described criteria.

### 2.5.6 German NanoKommission

The 'German NanoKommission' has recently developed such an approach for a 'preliminary assessment' of engineered nanomaterials (NanoKommission 2009). Among the list of criteria suggesting 'relief' are those that indicate the loss of nano functionalities by solubility or degradability. The list of criteria suggesting high 'concern' covers i) criteria indicating high exposure because of e. g. purposeful release and/or persistence, ii) criteria indicating possible problematic effects because of reactivity and/or problematic morphology, and iii) criteria indicating problems in risk management like lack of traceability.

The following list of criteria (NanoKommission 2009, 44) indicating concern or no cause for concern below is the result of intense discussion between the German stakeholders from the business sector, federal authorities, NGOs (environmental and consumer associations) and the scientific sector. The criteria should be understood as references to expected hazards.

**No cause for concern-Criteria**

- Loss of nano-properties as a result of:
  - Good solubility (in water, body fluids ...), if this causes the loss of nano-properties
  - Rapid degradability (biological, photocatalytic ...) in non-toxic degradation products
  - Fixed, permanent bonding in matrices (stability of matrix, type of bond, end-of-life behavior)
  - Presence of firmly bound aggregates (determined by conditions of production)
  - Agglomeration behavior: formation of stable, large agglomerates, (e.g. size, stability ...)
  - Nanostructured modifications on surfaces, and nanostructures that do not release particles and are not reactive (e.g. nanopores, lotus effect ...)

**Concern-Criteria**

- Indications of expected high level of exposure:
  - Production volume and/or quantity used for the field of application (probability of exposure)
  - High level of mobility in nanoform
    - in organisms (alveolar macrophage mobility, persistence in water, fat and body fluids, transport through cell membranes, blood-brain barrier, placenta, consideration of the special case of drug delivery systems)
    - in the environment (long-range transport, persistence in water and fat, solubility in fat and water, bioavailability, dustiness)
    - mobilization potential ("piggyback", infiltration, sorption, complex formation)
  - Targeted release (e.g. groundwater remediation, agricultural applications, consumer-oriented applications, interior applications...)
  - Persistence of nano-properties
  - Bioaccumulation
- Indications of potentially problematic effects:
  - High level of reactivity (catalytic / chemical / biological)
  - Problematic morphology (stable, long tubes or fibers, aspect ratio, fullerenes, crystal structure, porosity)
  - Indications of problematic interactions (e.g. piggyback)
  - Indications of problematic transformations (ageing, changes to surface properties, porosity) or metabolites (e.g. changes to or loss of coating)
- Indications of risk management problems:
  - poor verifiability
  - unclear fate

The second dialogue phase of the German NanoKommission (NanoKommission 2010a) guidelines has been developed for collecting data and comparing benefit and risk aspects of nanoproducts.

Issue Group 2's Guidelines consist of the following components: a product profile characterising the product to be assessed, a list of criteria enabling systematic identification of benefit and risk aspects selected by the Issue Group as being representative and generally applicable, and guidance relating to procedures for assessing a product and presenting the results (NanoKommission 2010b, 4). The Guidelines support the collection and presentation of data with a view to providing also an initial assessment of nanoproducts only. The majority of the criteria for benefit and



risk aspects of a product are unfortunately not quantifiable.

### 2.5.7 Switzerland, Federal Office of Public Health FOPH and Federal Office for the Environment FOEN

In the context of the Swiss Action Plan Synthetic Nanomaterials a precautionary matrix for products and applications has been developed (BAG/BAFU 2011a and b). The matrix should help businesses to assess the need for nanospecific measures (precautionary need) for synthetic nanomaterials and their applications for employees, consumers and the environment.

The precautionary matrix which is publicly available in the form of an Excel tool boosts the self-responsibility of industry and trade thus enabling them to identify the risk potential and the precautionary need for human health and the environment throughout the entire life cycle of nanomaterials (see Figure 12).

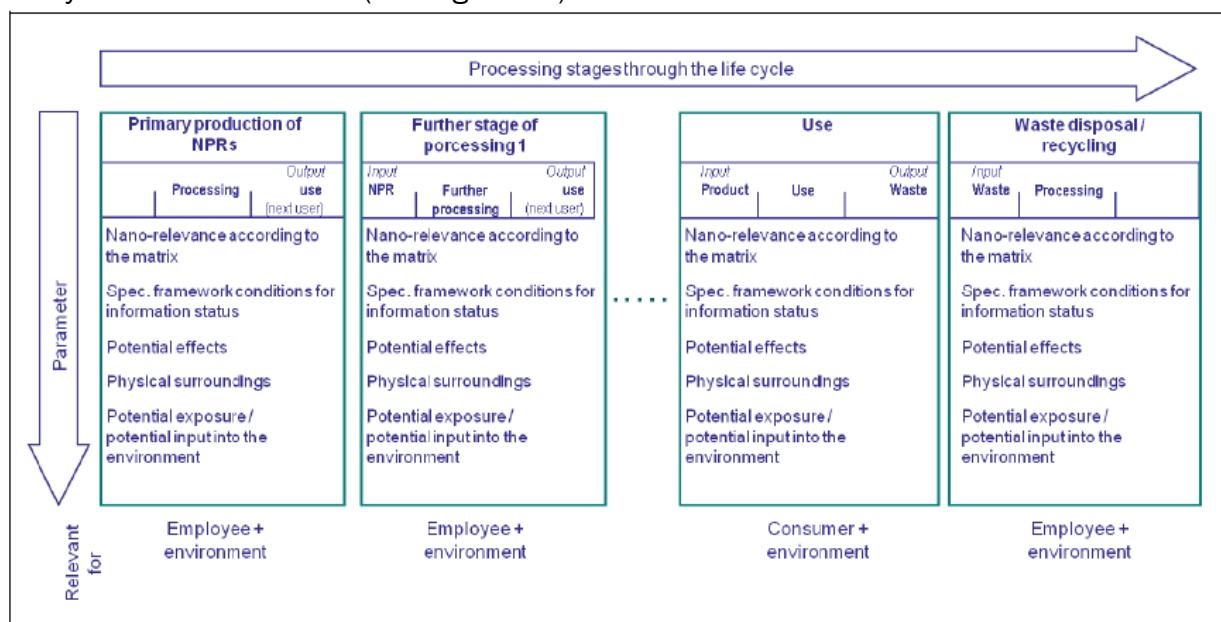


Figure 12: Processing stages as part of the entire life cycle BAG/BAFU (2011b 10)

The precautionary matrix is based on a limited number of evaluation parameters (size, reactivity and stability, release potential, amount of particles). The precautionary matrix is made up of modules for the evaluation parameters. These parameters are used to estimate the precautionary need for employees, consumers and the environment at each defined step in the life cycle.

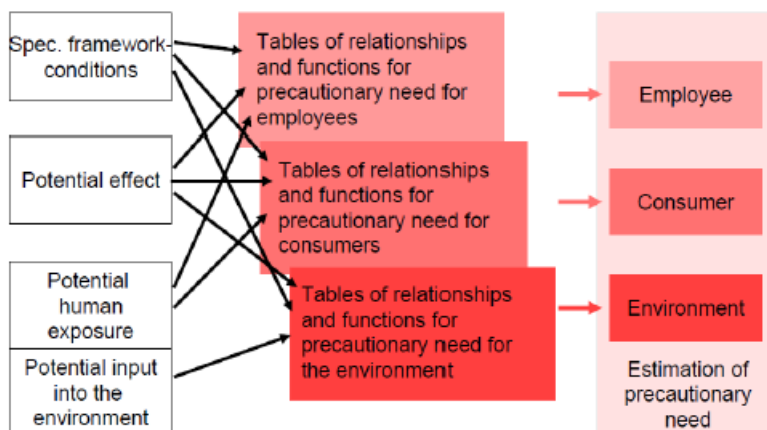


Figure 13: Parameters for estimating the precautionary need BAG/BAFU (2011b 15).

The Special on the matrix is that calculations of ‘Precautionary need’ are performed with an excel tool. As result of the evaluation of the precautionary matrix the user get a general classification of the nanospecific need for action.

Table 3: Classification of the precautionary need BAG/BAFU (2011b 30).

Score	Classification	Importance
0 - 20	A	The nanospecific need for action can be rated as low even without further clarification.
>20	B	Nanospecific action is needed. Existing measures should be reviewed, further clarification undertaken and, if necessary, measures to reduce the risk associated with manufacturing, use and disposal implemented in the interests of precaution.

### 2.5.8 LICARA nanoSCAN

LICARA is the acronym for an EU FP7 project named ‘Life Cycle Assessment and Risk Assessment of Nanoproducs’. The three research institutes – TNO, Empa, and RAS – and the participated private sector companies (NCB, SNT, Freso, Nanothinx and AGPYME) have developed the LICARA concept. The LICARA guidelines and their accompanying tool – known as LICARA nanoSCAN – can be used to assess the benefits and risks of engineered nanoparticles, nanomaterials, and nanoproducs. (Som et al. 2014) Both the LICARA guidelines and the LICARA nanoSCAN tool are structured in modules: the guidelines in seven ‘steps’ and the tool in seven ‘boxes’. For this tool small and medium-sized enterprises have to answer different relevant questions and to evaluate the results in a semi-quantitative way.

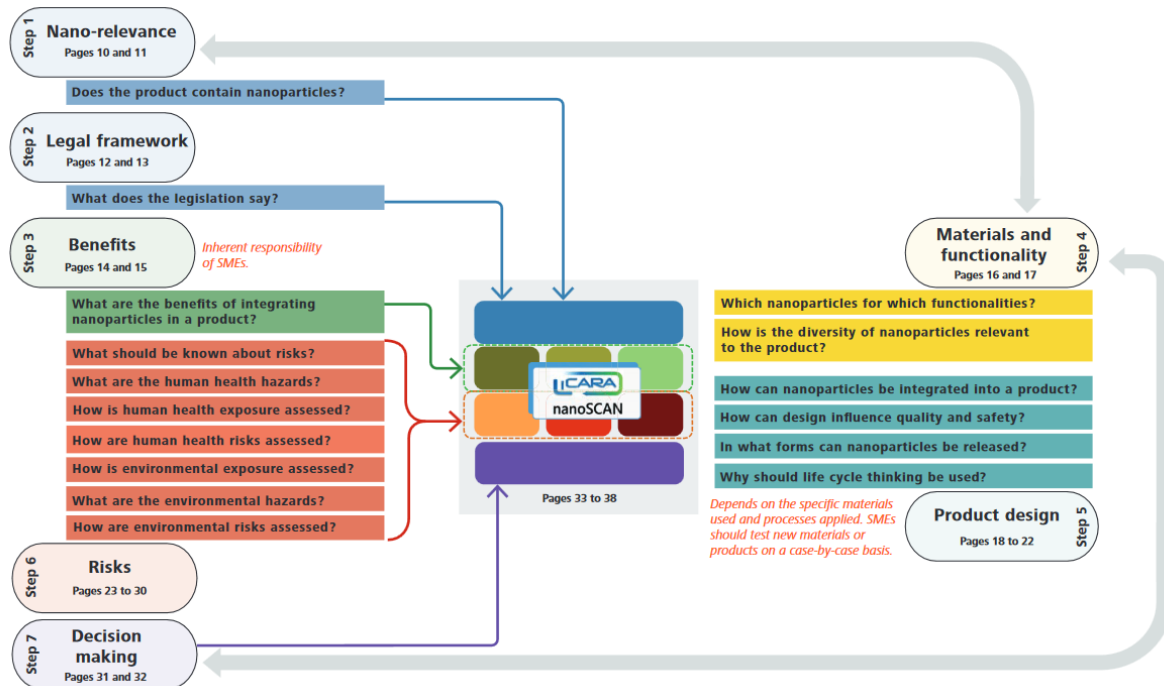


Figure 14: LICARA concept, and the interfaces between the guidelines and the tool (Som et al. 2014 4).

The LICARA nanoSCAN tool will also integrate in SUNDS.

### 2.5.9 Criticality of raw materials

In recent years, the aspects of criticality of materials are explored around the world in scientific studies (National Research Council 2008, European Commission 2010a and b, OECD 2010, Buchert et al 2009, Erdmann et al 2011).

The broad concept of the raw material criticality includes both the supply risks on the one hand and the vulnerability of a system (e.g. companies, industry, economy, global) to a potential supply disruption on the other.

The EU-study analyses a selection of 41 minerals and metals with a relative concept of criticality. This means that raw material is a critical raw material if risks of supply shortage and their impacts on the economy are higher compared with mostly of the other raw materials. Two types of risks are examined:

- a) the "supply risk" taking into account the political-economic stability of the producing countries, the level of concentration of production, the potential for substitution and the recycling rate; and
- b) the "environmental country risk" assessing the risks that measures might be taken by countries with weak environmental performance in order to protect the environment and, in doing so, endanger the supply of raw materials to the EU (European Commission 2010a 5).

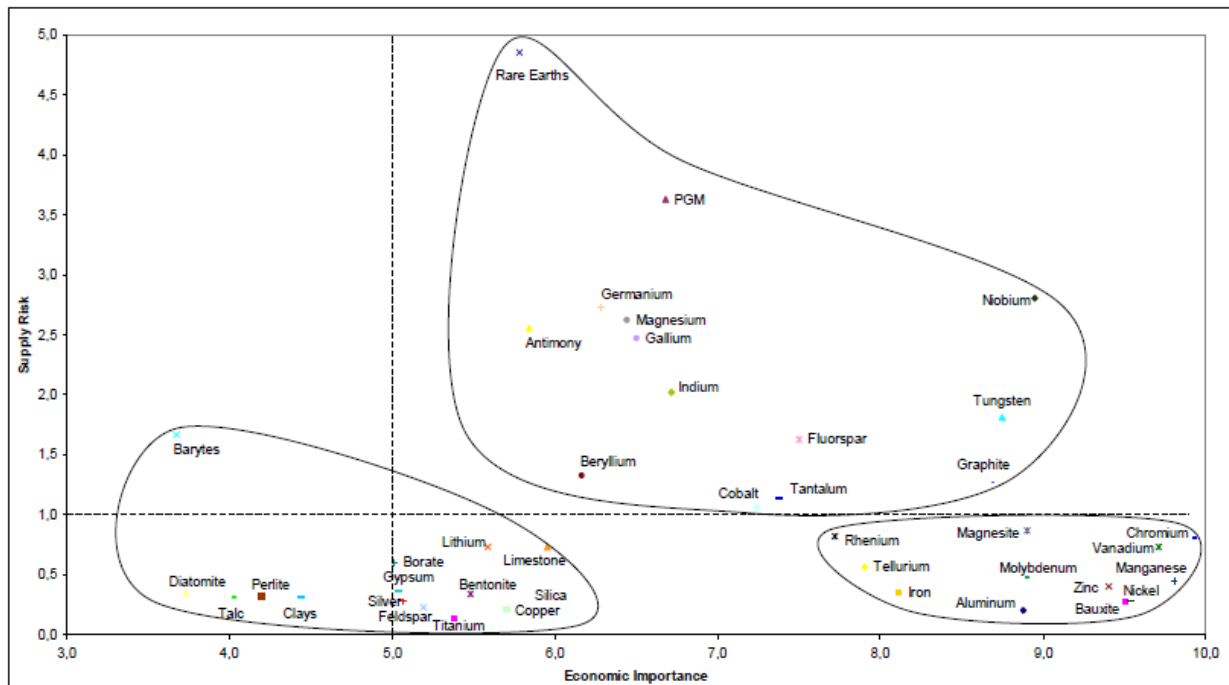


Figure 15: Economic Importance and supply risk of 41 materials with sub-clusters (European Commission 2010a 34).

The Y-axis reflects the positioning of the materials in relation to the supply risks and the Y-axis in relation to the supply risks that have been identified.

The results of this study to the criticality of materials are a good aspect for the development of an approach for improved recyclability of nanomaterials. For the evaluation of criticality of materials it is possible to take over the sub-cluster as a basis for decision making.

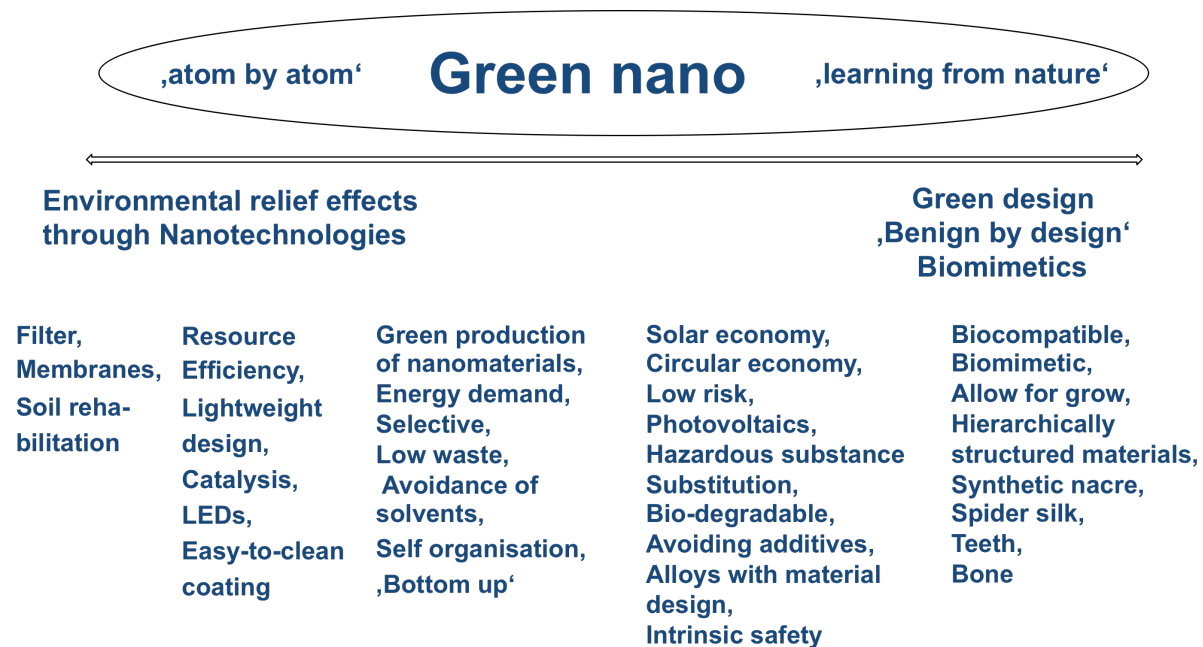
## 2.6 Sustainable nanotechnologies – 12 design principles for ‘Green nano’

In the context of the work of the German NanoKommission the Working Group on “Sustainable Nanotechnologies – Green nano” developed 12 design principles for ‘Green nano’, on the scientists of the Department ‘Technological Design and Development’ of the University of Bremen were instrumental.

The design of nano-based processes, products and nanomaterials on the basis of the shared paradigm of “Green nano” – as a responsible, voluntary approach to sustainable technology development (as opposed to a regulatory approach) – should gain more attention than in the past. They should be seen instead as one element in a broader effort to harness all available means to foster sustainable technology development and risk management based on the precautionary principle.

The design principles presented below relate to the goal of developing “sustainable nanotechnologies” or “green nano”, by which we mean explicitly taking into account environmental, health and safety considerations.

The paradigm of “sustainable nanotechnologies” encompasses a rather broad spectrum of options, ranging from emissions reduction and environmental remediation measures at one end of the scale to biomimetic sat the other. The goal is not only to minimize and prevent adverse effects (“design for safety”), but also to bring about positive benefits for human health and the environment (“benign by design”).



**Figure 16: Spectrum of options for ‘Green nano’.**

The developed design principles are broken down by four main fields (see Figure 17):

- I. Biomimetics
- II. Risk Poverty
- III. Resource Efficiency
- IV. Environmentally friendly use of nano in Energy and Environmental Technologies.

The level of innovation is expected to increase from bottom left to top right of the rule. The fourth main field ‘Environmentally friendly use of nano in Energy and Environmental Technologies’ describe the possibility of ecoefficiency in the conventional Energy and Environmental Technologies through nanotechnologies. The third main field ‘Resource Efficiency’ means the possible environmental benefits through new nanotechnological based process and product innovation. This environmental relief effects can quantified for this two fields with the method of life cycle assessment (see also the chapter 2.2-2.4). The second main field ‘Risk poverty’ has integrated the possible risk aspects of nanotechnologies (see also the other risk assessment tools in chapter 2.5.4-2.5.7). The first main field ‘Biomimetics’ has integrated extensive aspects of ‘learning from nature’. The Technology following nature’s example in cooperation with self-organization principles of nature.

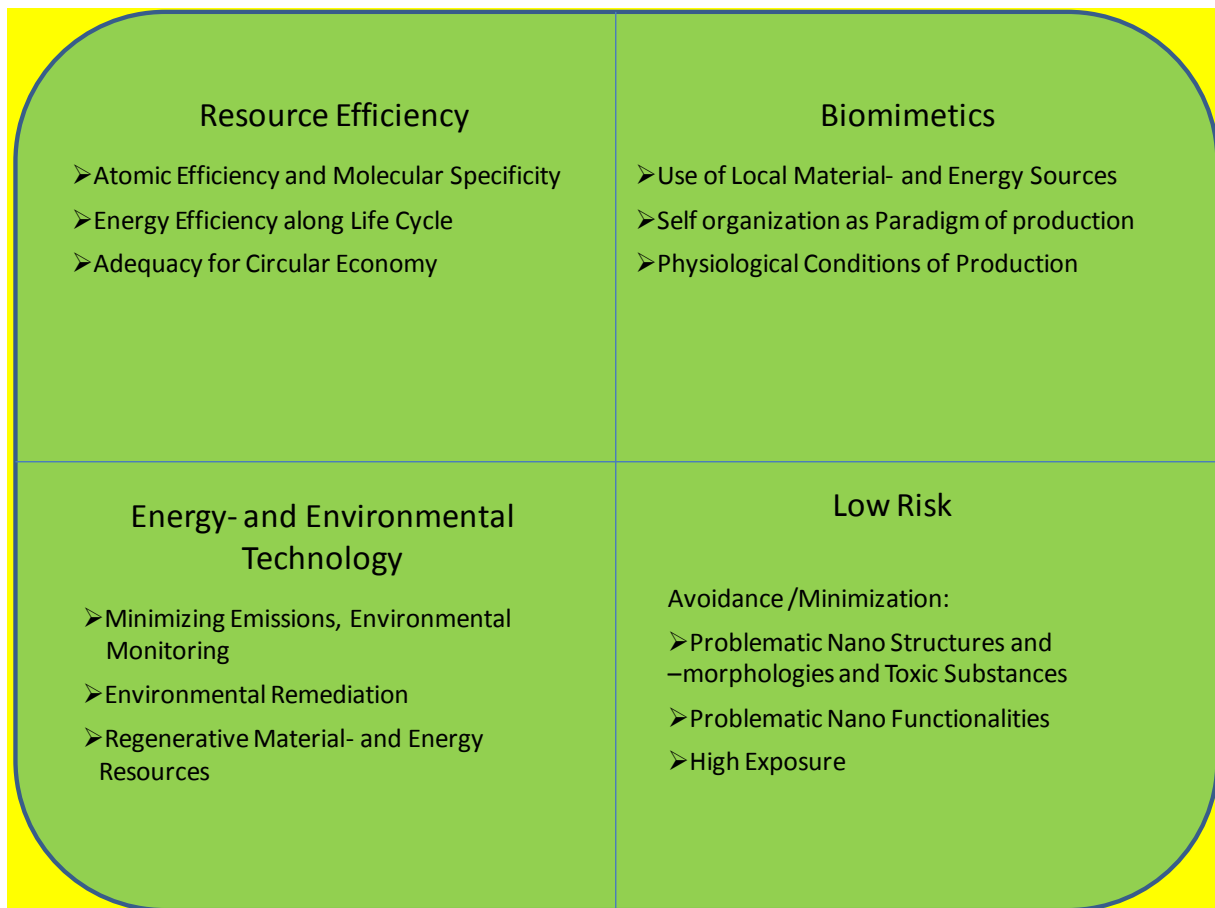


Figure 17: 12 design principles for 'Green nano' (NanoKommission 2010a 51).

## I. Biomimetics

### 1. Use of local materials and energy sources (energy and material opportunism)

**Prefer regenerative and obvious sources of energy and renewable raw materials and substances that circulate already in large quantities in bio-geo-chemical cycles anyway.**

Examples: solar power, waste heat, naturally occurring biogenic materials (e.g. cellulose, plant oils, etc.), limestone, etc

### 2. Self organization (bottom up) as a manufacturing paradigm

**Prefer the use of molecular self-organization and the context control in the production of complex structures and systems.**

Examples: Self assembly (e.g. self assembled monolayers, or SAMs), template controlled crystallization (biomineralization) for producing hierarchically structured, anisotropic, self-healing materials or complex molecular machines.

### 3. Physiological conditions of manufacturing

**Prefer physiological conditions of matter transformation.**

Physiological manufacturing conditions: "aqueous synthesis", pH 7, ambient pressure and temperature, avoiding aggressive and toxic chemicals.

## II. Risk poverty - Benign by design

### 4. Avoiding problematic nanostructures and nanomorphologies and toxic substances

**Prefer a low-risk design (benign by design, if necessary QSAR). Avoid problematic nanostructures nanomorphologies and hazardous materials.**

Examples of problematic morphologies and properties: similarity to asbestos. Examples of hazardous properties: ability to bioaccumulate, persistence, toxicity (to the environment), ability to cross cell membranes, cell reactivity, dust generating/explosive capacity. Possible basis for “benign design”: Quantitative Structure Activity Relations (QSAR).

#### 5. Responsible use of nano functionality

**Use the technically interesting nano functionality so that you have with them as low as possible problematic nano functionalities connected and / or so that existing technical or material risks avoided or be minimized (substitution of hazardous substances).**

Examples of problematic nano functionalities and surface properties of nanomaterials: ability to cross biological barriers, mobility in environmental media, reactivity. Ways of eliminating /minimizing/preventing problematic nano functionalities: selection of material and form, coating, surface functionalization using ligands, etc. Nanotechnologies offer interesting potential for substituting hazardous substances in e.g. solvents, flame retardants, metals, etc.

#### 6. Minimize exposure opportunities

**Make the nano-objects, systems, processes and products and their life cycle so that releases and exposure opportunities are minimized.**

Ways of minimizing/preventing exposure include ensuring that objects and materials are designed to minimize mobility and bioavailability, or are bound within a matrix. Exposure minimization/ prevention can also be incorporated into process and product design at a variety of levels – e.g. by means of containment, and not least by reducing the amount used in the manufacturing process or product to the lowest possible level. In addition to the other principles, further important considerations include preventing release of nanomaterials for which we have no biopersistence information, and preventing materials from being placed on the market unless methods are available for reliably identifying the substance in the body/in the environment and for determining on-site exposure.

### III. Resource efficiency

#### 7. Atomic efficiency and molecular specificity

**Customize the conversion processes and manufacturing processes and low-waste with low material intensity.**

Approaches to molecular specificity and atomic efficiency, in order to avoid / minimize side reactions, waste minimization, emissions have processes of molecular recognition, the (Auto) catalysis, enzymatic reactions and precision manufacturing and design.

Approaches to lower material intensity offer miniaturization / dematerialization, low requirements on purity, avoiding very rare materials, economizing on cleaning materials by using self cleaning surfaces, and preventing dissipative losses, e.g. by corrosion control.

#### 8. Energy efficiency

**Create processes and products with high degree of efficiency, high energy efficiency throughout the product lifecycle.**

Approaches to improving energy efficiency offer z. B. higher efficiencies (electricity, light, etc.), low process temperatures, minimizing entropy production (conversion into heat and heat loss), lightweight construction, etc.

#### 9. Cyclability

**Choose the materials and make the processes and products so that the materials can be carried out without great loss of quality in the technosphere in circles. Avoid / Minimize dissipative losses.**

Approaches to improving the recyclability offer: Low material variety, good separability/ modularity, minimization of additives and auxiliaries, avoiding dissipative use patterns, fugitive emissions and material impurities (contaminants).

A particularly interesting, 'Nano option' is e.g. in place to achieve by alloys and additives by selective influencing of crystallization (granulation) or polymerization different (anisotropic) material qualities.

#### IV. Energy and environmental technology

##### 10. Emission control and environmental monitoring

**Use the possibilities opened up by nanotechnologies to reduce emissions and environmental monitoring.**

Nanotechnological approaches to reduce emissions such offer as filters, membranes, precipitating agents and catalysts (off site, on site) as well as nanoelectronics for process monitoring and process control in the industrial sector.

Approaches to improving environmental monitoring offer e.g. nanosensors and assays.

##### 11. Environmental remediation

**Use situ in a responsible manner which opened up by nanotechnology opportunities for environmental remediation (soil, groundwater) ex and in situ.**

Approaches offer z. B. iron nanoparticles for the catalytic decomposition of petrochemical contamination or adsorption of arsenic.

##### 12. Switch to renewable materials and energy sources

**Use wherever possible renewable energy sources and renewable Roh substances.**

Opportunities nanotechnological approaches in photovoltaics in the solar thermal, the biomass conversion, etc.

#### Limits of sustainable design

At present, most innovations in the nanotechnology field remain technology-driven. Innovation processes are largely determined by new technological possibilities. Moreover, many innovation processes are still at a very early stage of development. This of course limits their scope just as much as the fact that very little is known at present about the potential benefits and risks of a given innovation.

Ultimately, however, it is not the technology alone that will determine the potential benefits and risks of nanotechnology-based innovations. The applications, operating conditions and contexts in which they are used are at least as important in this regard. The more the effects of materials, processes and products are determined by the purpose and context in which they are used, the greater the need to draw on additional design principles relating specifically to those purposes and contexts. The need for dialogue is thus likely to increase rather than decrease.

Finally, it must be emphasized that the orientation design principles possibly increase the likelihood of sustainable nanotechnology, but a corresponding success can't guarantee. The results of a sustainability-oriented design have been submitted to the usual technical and product policies.

#### Classification of the SUN case studies (see report D2.3) to the main fields of the design principles for 'Green nano'

The case study 5 'Nano-Titanium Dioxide (TiO<sub>2</sub>) air filter system' examines now a new developed nanoTiO<sub>2</sub> air filter system 'Phoebe' of the company COLORBBIA CONSULTING



S.r.l. to reduce NO<sub>x</sub> emission in gas.

Here is the focus clearly on the design principles of the field 'Energy and environmental technology' with the goal to reduce emissions.

The objective of the case study 1 'Nano-WC-Cobalt (Tungsten Carbide-cobalt) sintered ceramics' was to conduct a life cycle assessment for the nano-WC-Cobalt application in comparison to conventional coatings.

Here is the focus of the innovation clearly on the design principles of the field 'Resource efficiency'.

The application of the case study 3 is the integration of CNT in plastic with electrostatic properties for possible lightweight applications. Against this background the focus is also on the design principles of the field 'Resource efficiency'.

The other case studies

- Case study 2: Nanocopper wood preservatives
- Case study 4: Silicon Dioxide (SiO<sub>2</sub>) as food additive
- Case study 6: Organic pigment in plastics
- Case study 7: Nanosilver (Ag) in textiles

have examined nanotechnological based product innovations. In comparison to the conventional applications, no unique environmental or 'green' benefits are quantifiable. A classification is not possible.

### 3 Deviations from the Workplan

-

## 4 Performance of the Partners

All partners performed in satisfactory time and quality.

## 5 Conclusions

The main goal of the project is the development of the SUN Decision Support System (SUNDS) with the integration of nano-EHS data and methods for practical use by industries and regulators. For this tool information and data are needed from toxicological and risk analysis and LCA. This tool is an approach of the design and production phases of new nanotechnological based innovation (see Figure 18).

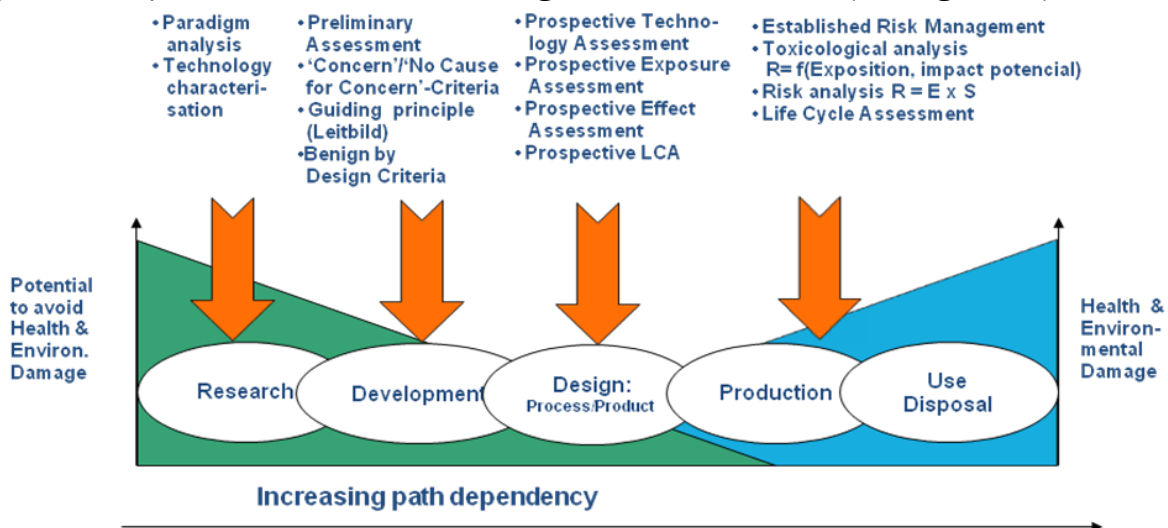


Figure 18: Approaches to technology assessment and engineering design according to the phases of innovation (in accordance with Steinfeldt et al. 2007)

On the other side the development of nanomaterials especially of the next generation of functionalized nanomaterials is still in an early phase of development. In view of the enormous knowledge problems of prospective technology assessments, the importance of concurrent approaches to specific developments of nanomaterials, -products and -processes must be emphasized. In early phases, the focus lays on what is already known, the technology, the materials and, if already in view, the products and processes that are based on them. In this situation, criteria and guiding principles for the shaping of green resp. sustainable nanomanufacturing processes and nanomaterials are needed. An analysis to environmental reliefs potentials of nanotechnology, an evaluation of specific manufactured nanoparticles, of nanomaterial based products and applications in LCA-studies, and a literature search and analysis to different 'green' and 'safer' approaches serves as a basis for the objective of the task 4.6, the development of criteria and guiding principles for green design of nanomanufacturing and nanomaterials.

As the result 12 design principles for 'Green nano' were developed.

The following design principles are broken down by four main fields (see also Figure 15):

I. Biomimetics

1. Use of local materials and energy sources (energy and material opportunism)
2. Self organization (bottom up) as a manufacturing paradigm
3. Physiological conditions of manufacturing

II. Risk Poverty

4. Avoiding problematic nanostructures and nanomorphologies and toxic substances
5. Responsible use of nano functionality
6. Minimize exposure opportunities

III. Resource Efficiency

7. Atomic efficiency and molecular specificity
8. Energy efficiency
9. Cyclability

IV. Environmentally friendly use of nano in Energy and Environmental Technologies.

10. Emission control and environmental monitoring
11. Environmental remediation
12. Switch to renewable materials and energy sources.

The fourth main field 'Environmentally friendly use of nano in Energy and Environmental Technologies' describe the possibility of ecoefficiency in the conventional Energy and Environmental Technologies through nanotechnologies. The third main field 'Resource Efficiency' means the possible environmental benefits through new nanotechnological based process and product innovation. This environmental relief effects can quantified for this two fields with the method of life cycle assessment (see also the chapter 2.2-2.4). The second main field 'Risk poverty' has integrated the possible risk aspects of nanotechnologies (see also the other risk assessment tools in chapter 2.5.4-2.5.7). The first main field 'Biomimetics' has integrated extensive aspects of 'learning from nature'. The Technology is following nature's example in cooperation with self-organization principles of nature.

It must be emphasized that the orientation design principles possibly increase the likelihood of sustainable nanotechnology, but a corresponding success can't guarantee. The results of a sustainability-oriented design have been submitted to the usual technical and product policies.

A classification of the SUN case studies (see report D2.3) to the main fields of the design principles for 'Green nano' is only partially possible.  
The product innovation of the case study 5 'Nano-Titanium Dioxide (TiO<sub>2</sub>) air filter system'

is clearly oriented on the design principles of the field 'Energy and environmental technology' with the goal to reduce emissions.

The product innovations of the case study 1 'Nano-WC-Cobalt (Tungsten Carbide-cobalt) sintered ceramics' and of the case study 3 'Carbon Nano Tube (CNT) in plastics' are clearly oriented on the design principles of the field 'Resource efficiency'.

The result of this task can be used as a part for the guidelines in workpackage 7.

## 6 List of Figures

Figure 1: Approaches to technology assessment and engineering design according to the phases of innovation (in accordance with Steinfeldt et al. 2007) .....	4
Figure 2: Nanotechnology-based products / applications on the market (Steinfeldt 2010) .....	5
Figure 3: Anticipated nanotechnology-based applications (Steinfeldt 2010) .....	6
Figure 4: Comparison of the cumulative energy requirements for various carbon nanoparticle manufacturing processes [MJ-Equivalent/kg material] .....	16
Figure 5: Comparison of the cumulative energy requirements for the production of various conventional and nanoscaled materials and components [MJ-Equivalent/kg product] (in parts own calculation) .....	17
Figure 6: Comparison of the global warming potential for the production of various conventional and nanoscaled materials [CO <sub>2</sub> -Equivalent/kg product] (in parts own calculation) .....	17
Figure 7: SWOT matrix summarising the results of the key indicators for the case example of “X-SEED” (material scenario) (Öko-Institut 2011). .....	21
Figure 8: The five principles of safer nanotechnology. ....	21
Figure 9: Nanotechnology risk mitigation matrix. ....	22
Figure 10: Model for the identification of of precautionary action by the state SRU (2011b, 12). ....	23
Figure 11: Decision tree for risk categorisation of nanoparticles and nanofibres SRU (2011b, 16). ....	23
Figure 12: Processing stages as part of the entire life cycle BAG/BAFU (2011b 10). ....	25
Figure 13: Parameters for estimating the precautionary need BAG/BAFU (2011b 15). ....	26
Figure 14: LICARA concept, and the interfaces between the guidelines and the tool (Som et al. 2014 4). ....	27
Figure 15: Economic importance and supply risk of 41 materials with sub-clusters (European Commission 2010a 34). ....	28
Figure 16: Spectrum of options for ‘Green nano’. ....	29
Figure 17: 12 design principles for ‘Green nano’ (NanoKommission 2010a 51). ....	30
Figure 18: Approaches to technology assessment and engineering design according to the phases of innovation (in accordance with Steinfeldt et al. 2007). ....	33

## 7 List of Tables

Table 1: Overview of studies about life cycle aspects of nanotechnology-based applications .....	6
Table 2: Overview of studies of published LCAs of the manufacture of nanoparticles and nanocomponents (based on Meyer et al (2009) and own data) .....	12
Table 3: Classification of the precautionary need BAG/BAFU (2011b 30). ....	26

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