Theme: Tailored Nanomaterials (NM)[i] and -structures[ii] in their Environment

0. General Introduction

"The advent of nanotechnology has been one of the most important transformations in recent material science. The National Science Foundation (NSF) projected that nanotechnology will become by 2015 "a trillion dollar industry" worldwide, the largest segment being nanomaterials, which will reach $ 340 billion annually.

The nanotechnology revolution essentially consists of the ability to control material features on the nanometer length scale. However, to see the economic impact of these new abilities we must continue to develop the basic science of nanotechnology, particularly in the area's that lead to practical production of useful products. One particular promising area in nanomaterials is the ability to **integrate** them into different hosts which offers a wide range of potential applications.

<u>In order to achieve this objective it is mandatory to join forces of the individual expert centers in Flanders (see annex 1) into a multi-disciplinary competence base to prepare, formulate (e.g. dispersions) and integrate nanomaterials into future commercially relevant systems</u>.

This objective is still valid in 2011.

However for most nanomaterials the desired organisation (nano-structural organization) and compatibility with the matrix often requires already preliminary engineering/design during their preparation or formulation.
Hence the result at system level (the micro/macro level) critically depends on the access to the required nano-sized building blocks (nano level) in combination with corresponding nanoformulations in sink with the final matrix (meso-mico level).

<u>On this level the critical gap for applying nanomaterial technology for SIM is situated</u>
Whereas the demands of the industrial SIM partners are situated at the macro side of the value chain, the universities and SOC's situate themselves at the supply side.

<u>The challenge for SIM is to forge this scattered expertise base into multi- disciplinary teams with a joint application oriented objective.</u>
This challenge is also still valid but there is some fundamental weakness detected if one wants to maximize synergy:

- The virtual organisation of SIM and the scatter of the teams over different organizations in the areas of synthesis and formulation of nanoparticles or structures and their integration slows down breakthroughs.
- Ideally, the nanosynthesis and nanoformulation with regard to a certain matrix /fluid carrier targets should be organized in one dedicated team with state of the art expertise and critical mass.

The required expertises to reach this goal are:

- to gain control over the synthesis and properties of nanomaterials, the corresponding formulations[iii] or ordered nano-structured (sub-) systems[iv].
- to understand and predict the processes and interactions of nanomaterials in their realistic environment (formulations and sub-systems) and to have the capability to draw structure activity relationships.
- to understand, predict and steer the integration of nanomaterials in the host or (sub-)system.

Cross-cutting support expertises required:

- to develop advanced characterization techniques for measuring structure and activity, advanced modelling, implementation of QSAR[v] techniques, experimental methodology[vi] and chemical additives[vii] to support the above targets.
- One major concern is the issues of health and environmental impact of nanoparticles. At present this is still poorly understood and represents a potential problem for development of products, due to either real or perceived risks. The objective within the nanomaterials theme is to support the ongoing work and keeping the team informed of the latest developments. Isolated research on the environmental and health impacts of nanomaterial will remain outside of SIM, since these are large issues that extend far from the SIM's materials focus.

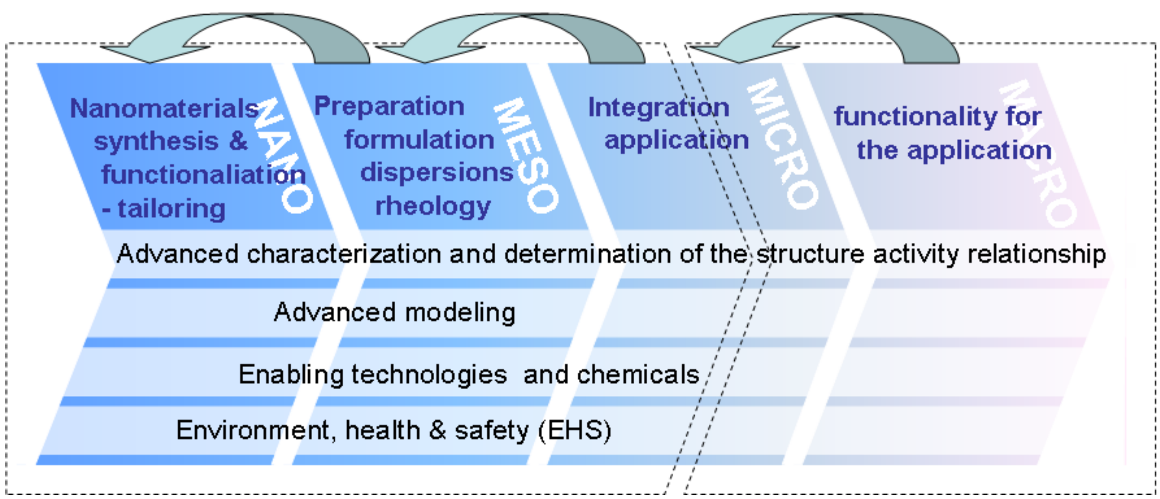


Figure 1: Value chain model used to describe the materials theme. The physical flow goes from left to right, while the demand driven information flow is driven from the application side (right to left: see top arrows). 4 cross-cutting themes are indicated (e.g. advanced characterization…).

The value chain for this nanomaterials theme is described in figure 1. In principle the process starts with the synthesis of the nanomaterial and ends with its integration in the dedicated system (PV[viii] cell, reinforced material...). However the nanomaterials can also be formed or functionalized in-situ during the formulation or the integration.

The nanomaterials workgroup welcomes multidisciplinary generic projects at all steps in the value chain preferentially for, but not limited to topics with the potential for valorization in the other SIM areas: Energy and Structural Materials. The nanomaterials theme does not focus on the developments in the MACRO part of Figure , but will make part of joined teams (e.g. from Energy or Structural Materials) working towards a final functionality or application (see vertical arrow in
Figure).

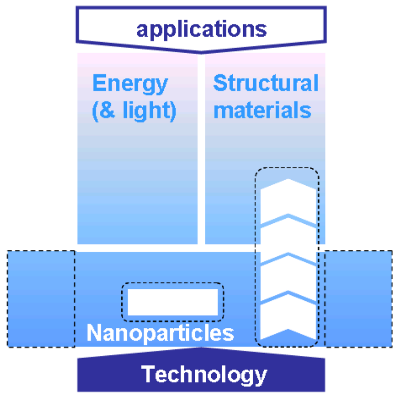


Figure 2: The nanomaterials theme is technology and science oriented but driven by the challenges from application oriented research activities such as Energy and Structural Materials. In some cases it may result in participation in these projects.

1. Nanomaterial synthesis and the nanomaterial/host interface

1.1 SHORT DESCRIPTION OF THE THEME, PROBLEM DESCRIPTION

This subtheme deals with nanomaterials (NMs) and the nanomaterial/host interface (NHI[ix]). Materials systems that show up through the SIM discussions are

- (Tailored) nanoparticle.
- 1D nanomaterials (nanofibres, CNT)
- Nanoporous materials.
- Nanoparticle assemblies.

An element that makes nanomaterials of interest is that their properties are determined by two elements:

1. the nanomaterial itself (core), and
2. the interface of the nanomaterial with the surroundings (NHI).

Taking the case of nanoparticles, physical properties like the interaction of the NP with light depend on the nature (metal, semiconductor) and the dimensions (size, shape) of the core. On the other hand, the nanomaterial/host interface is key to many chemical or physicochemical properties. Specific molecules (ligands) can bind to the NP surface and change its affinity for specific solvents, solid hosts or analytes.

The challenges faced by the field of nanomaterials synthesis and the NHI concern the development of synthesis routes for NMs,

- offering a perspective for upscaling,
- control over the nanomaterial dimensions – in the case of NPs: core size, shape and size dispersion – during synthesis,
- the analysis and understanding of the as-synthesized NHI and the manipulation of the NHI to get a specific functionality.

Meeting these challenges, should generate break-through knowledge, leading towards the realisation of innovative materials systems for applications in (preferentially but not exclusively) energy harvesting & storage and structural materials.

1.2 TIME-FRAME / ROADMAP

Development of nanomaterials synthesis schemes and control over the NHI are two elements that form the starting point of the *Nanomaterial Structure and Interactions* theme. Research in this context should start with the start of SIM. The aim is to build the synthesis-understanding-control chain for the nanomaterials requested, among others, by the energy and structural materials themes over a period of 5 years.

1.3 STATE-OF-THE-ART ANALYSIS

- Synthesis of nanomaterials
  - Wet chemical synthesis (hot injection, precipitation, hydrothermal synthesis, sol-gel) and deposition (spincoating, electrodeposition, dipcoating, printing…), preferably in non-hazardous solvents (e.g. water)
  - Vapor based synthesis methods and deposition (ALD, CVD…)
  - Precursor and reaction chemistry
  - Solid state synthesis
  - Electrochemical methods, anodization, electrospinning
  - (cold, atmospheric) plasma assisted synthesis and processing
  - Syntheses of nanostructures or by templates e.g. anodization, micelles, self assembly of polymers, zeolites, silica
  - MBE, (magnetron) sputtering, cluster deposition, ion implantation
- Surface functionalization of NMs
  - biofunctionalization
  - electro-optical properties at interfaces in photovoltaics
  - Chemical functionalization of colloidal nanoparticles
  - Electrochemical/plasma/organic functionalization of nanomaterials – tailored NPs for adsorptive separations.
- Identification and understanding of (bio)molecules at the nanomaterials surface.
  - ATR-FTIR, UV-Raman, ligand analysis based on NMR
- Directed or self-assembly based formation of nanomaterials superstructures.
  - formation and self organization of particles on surfaces/3D matrices.
  - chemical solution deposition and patterning of NP on surfaces
  - Formation and patterning of NP monolayers on surfaces.

1.4 S&T CHALLENGES

Specific industrial needs with regard to (1) nanomaterials synthesis and (2) the nanomaterial/host interface (NHI) have been identified, but are not limited to the potential applications listed below.

Topic	***application identified***
NM with improved, new, or a combination of functional properties	*Structural (*functional surfaces, multifunctional structural materials…*) photovoltaics, batteries, fuel cells…*
NM without toxic or strategic elements	*Photovoltaics* (TCO's without In, NP without Cd, Pb…)*, batteries, structural materials (*alternatives to Pb*)*
Controlled, reproducible and upscalable synthesis methods, large area deposition	*photovoltaics, batteries, fuel cells, structural materials*
Preparation of nanomaterials with control over nanostructure, morphology, crystal structure, addition of dopants and surface texture	*Photovoltaics, batteries, structural materials (*porous electrodes, more efficient and widened absorption, surfaces with superhydrophobic or other functionalities…*),*
Alternative hybrid material concepts	*Photovoltaics, structural materials* (multifunctional coatings, multilayers, NP

	reinforcement…*)*
Stability of NP dispersions (liquid)	*Photovoltaics* (nanoparticle inks)
Homogeneity of NP dispersions (solid)	*Energy storage* (cathode/anode materials for Li-ion systems) *Fuel cells* (homogeneous dispersion of catalyst particles) *Photovoltaics* (integration of NPs in solar cells) *Hybrid structural materials* (nano-reinforcement) *Functional materials*
Directing NP assembly	*Photovoltaics* (integration of NPs in solar cells)
Step-stone to hybrid organic/inorganic NMs	*Hybrid structural materials* (nanoparticle-nanofibre hybrids)
Provide functionality to NMs	*Energy storage* (thin film systems) *Fuel cells* (catalysts on nanoporous electrodes and membranes) *Sustainable processes* (recycling) *Functional materials* *Photovoltaics* (enhanced charge transfer)
Wet processing	*Energy storage* (thin film systems) *Photovoltaics* (printing of thin films)

1.5 OVERVIEW OF NEEDED COMPETENCES IN FLANDERS (TO BE REALIZED BY PROJECTS)

Most industrial needs deal with the formation of nanomaterials and the functionalization of the nanomaterial surface to obtain a functional nanostructure. We summarize this in a set of generic competences that follow a more or less logical order.

- Development of synthesis methods that enable rational synthesis of nanomaterials – examples are NP synthesis library with control over core shape, size, composition, surface characteristics, size dispersion; specific NPs like Cd- and Pb-free quantum dots or complex oxides; surface coatings of porous materials; the formation of 1D nanomaterials (wires, rods, fibers, tubes), in-situ synthesis.
- Understanding of synthesis mechanism. This is a key element of every synthesis effort within SIM.
- Synthesis approaches with a perspective for upscaling – this includes all aspects to achieve sustainable production processes (low toxicity precursors and end products, low energy consumption), low cost.
- Understanding the NHI – bonding of molecules to the NP/NM surface, organization of molecules at the NM surface. To what NHI do synthesis procedures lead?
- Methodology for in situ characterization of NHI. This is a key element to obtain a proper understanding of the NHI.
- Techniques for surface functionalization – How can we deliberately change the NHI to achieve specific functionality?

- Understanding the interaction between a NP/NM and its environment – What are the requirements for the NHI to achieve liquid dispersion stability, water solubility, solid dispersion homogeneity, to drive self-assembly? How stable are the NMs in their environment?
- Formation of nano/meso structures from nanomaterial building blocks.

Development of nanomaterial synthesis and processing schemes that enable the rational synthesis with control over size, shape and surface chemistry and that offer the perspective for upscaling. These materials should lead to innovative materials systems for applications in (preferentially) energy harvesting & storage and structural materials, but their application potential need not be limited to these elements.'

State of the art evolution 2011

Since 2008-2009, research has further extended the application domain of nanoparticles, especially for energy conversion and lighting. Examples include quantum dot based solar cells, which have reached efficiencies of 5%, the investigation at the industrial level and initial commercialization of quantum dots for white LEDs and the extending use of nanoparticles as precursor materials for wet-processed solar cells.

S&T critical challenges 2011

The growth of the application domain leads to:

1. An increasing demand for nanocrystals with well defined sizes at scales compatible with industrial R&D and applications
2. A need for acceleration at the level of synthesis understanding and development.
3. A post processing technology aimed at the incorporation of nanocrystals in solid matrices, thin films or colloidal dispersions.
4. Solving the 'ligands are good for synthesis and stabilization but bad for applications' paradox.
5. An enhanced need for alternative materials, *e.g.*, without Cd or Pb in the case of semiconductor nanocrystals.

Critical competences 2011 and following years

In line with the challenges, needed competences include:

1. Synthesis and formulation pilot upscaling – interaction between synthesis groups and chemical engineering groups.
2. An in depth understanding of actual synthesis recipes, *e.g.*, supported by kinetic and molecular reaction simulations and studies of reaction mechanisms.
3. Automated synthesis development enabling fine tuning of recipes and the development of novel synthetic routes.
4. (solution-based) methods for forming composite nanomaterials, e.g., incorporating nanocrystals in transparent oxide matrices.
5. Development of pre- or post deposition ligand exchange recipes, use of thermally decomposable ligands….
6. Adaptation of synthesis method to final application.
7. Development of improved synthesis routes for III-V or I-III-VI2 semiconductor nanocrystals.

1.6 OVERVIEW OF THE CROSS CUTTING THEMES NANO IN RUNNING SIM SIBO PROGRAMMES

1) NANOFORCE

CNT functionalization and formulation to polymer matrix
Nanoparticles loaded polymers (formulation?)

2) SHE

Selfhealing concepts bulk and coatings
Microcapsules
Formulation ?

3) SOPPOM

Nano CIS-CIGS precursors chemistries synthesis and formulation
Nano TCO precursors chemistries synthesis and formulation
OPV concepts on nanomaterials integration
iPV CIGS-CIS concept proof

2. Formulation of nanomaterials

2.1 SHORT DESCRIPTION OF THE THEME, PROBLEM DESCRIPTION

The fundamental question when dealing with dispersions of nanoparticles is: How can the individual nanoparticles be positioned in a controlled way, be it in the bulk (volume) of a material or at an interphase (surface). It is clear that in order to express the functionality associated with the nanoscale, the particles need to be brought into a well dispersed state by suitable processing operations and their surface chemical properties or formulation should be such that this dispersed state can be maintained.

2.2 TIME FRAME/ROADMAP

To achieve this, advances on different fronts are required. First, a methodology needs to be developed that allows a user to select a procedure to tackle the problem at hand, firmly based on methods that allow one to evaluate the (thermodynamic) efficiency of the dispersion process. Secondly, advances will need to be made in the technological methods to disperse aggregates and agglomerates of nanomaterials. Most likely this will require an intensification of existing methods, for example the use of combined 'fields', flow fields and ultrasound of electromagnetic fields. To this end, fundamental research will be required to understand agglomerate and aggregate break-up. The devices and new technologies will need to be scaled up and built into pilot plant scale devices. Finally, methods will need to be developed that enable one to quantitatively asses the dispersion quality e.g. in such combined fields.

2.3 STATE OF THE ART ANALYSIS

Currently, to disperse particles into a host matrix, different technological methods and procedures exist. However, most of these methods are batch processes (e.g. wet milling techniques), or involve a complex master-batch procedure. Although dispersing of particles is essential for each and every process involving particles in a host matrix, a rational basis for the design of technological methods is lacking and too often one resorts to energy intensive, ad-hoc solutions. For nanoparticles these methods often are insufficient or unreliable as, due to their small size, hydrodynamic forces are often insufficient to overcome the colloidal interactions. This results in loss of properties, even when the synthesis and functionalization of the nanoparticles have been properly designed and performed to give a thermodynamically stable dispersion. There is a clear need for an approach that enables robust, energy efficient and reliable dispersion processes.

2.4 S&T CHALLENGES

The **main issues raised** by the stakeholders of the SIM initiative were:

- How to efficiently disperse nanoparticles in highly viscous media (such as polymers and master-batches) or alternatively in low viscous materials.
- What are the best stabilizations strategies in aqueous media (e.g. coatings)
- How to stabilize inorganic materials in complex environments (high ionic strength, many chemical, polymer or metallic matrix…); developing a mechanistic understanding of the interactions of inorganic materials with surface active materials and their environment.
- How to formulate a nanocomposite system for a given application process and a final application
- How to strengthen en stabilize light-weight materials (such as foams and nanocomposites).
- Explore grafting via covalent bonding of inorganic nanoparticles on the organic part of an organic/anorganic multilayer.
- How to exploit self-assembly of nanoparticles in technological applications.
- Gain understanding of application processes of nanofilled materials (e. g. rheological behaviour at high shear rates, appropriate viscosities for printing applications…).

2.5 OVERVIEW OF NEEDED COMPETENCES IN FLANDERS (TO BE REALIZED BY PROJECTS)

Based on the technological opportunities summarized above, a non- exhaustive list of required competences is given below:

- Development and assessment of novel technological methods for the dispersion of nanoparticle agglomerates and aggregates by combination of external fields such as flow, magnetic, ultrasound and electromagnetic fields.
- Development of rational, science-based formulation strategies
- Quantification of the degree of dispersion of nanofillers in a complex host matrix e.g. determination of particle size distributions, development of rheological methods for in-situ characterization of dispersion quality (see also advanced characterization methods)
- Understanding the effects of dispersion quality of nanofillers on the properties of composites.
- Determination of adhesion and adsorption of dispersants on the surface of nanoparticles, e.g., by nano sensitive probe techniques such as AFM, SPM… (nano, meso, macro techniques)
- Formulation of stable dispersions with short chain ligands for photovoltaic applications and the homogeneous dispersion of nanoparticles in solid matrices.
- Design of additives and dispersants
- Exploitation of the formation and self-organisation of nanoparticles on surfaces e.g. for the stabilization of multiphase materials and foams.
- Understanding and modulating the thermodynamic forces that drive self-assembly, assisted by external fields such as flow, electric or magnetic fields.
- Understanding tailored nanoclusters and nanostructures in porous supports.
- …

2.6 OVERVIEW OF CROSS-CUTTING THEMES

Application areas include a wide range of materials such as: coatings, inks, adhesives, plastics, composites, foams…

The topics mentioned above are very generic and results will apply to a broad class of nano-particles related problems. Obviously there are links with the themes energy and structural materials. The main links are summarized below:

Links with energy:

- Photovoltaics (stable dispersions for wet processed adsorbed layers) and homogeneous embedding of nanoparticles in polymers.
- Energy storage: wet processing of thin films.
- Fuel cells: wet processing of nanostructured electrodes.
- Metal nanoparticles in solution for conductors and interconnects as well as plasmonic effects.
- Metaloxide nanoparticles in solution processable dispersions for interface layers.
- …

Links with sustainable materials:

- Embedding nanoparticles into the bulk or surface of a material can offer opportunities to change properties in the desired direction. This includes friction, bonding, environmental protection, self-healing and self-cleaning, but also bulk properties such as electrical, heat transfer….
- Embedded nanoparticles can be triggered to break down a material to recuperate for reuse.
- Mechanical properties of ultra-light structural materials such as foams can potentially be drastically improved by the incorporation of nanoparticles.
- There is great potential for multiscale structural hybrid materials such as nanoparticles in short fiber reinforced thermoplastics or carbon nanotubes in long fiber reinforced thermosets.
- Sustainable manufacturing-wet processed thin films versus vacuum techniques.
- …

S&T challenges anno 2011

- Linking the synthesis of nanoparticles and –structures to formulation, both on a scientific level as well as on a multidisciplinary team level. Different teams need to work really closer together to obtain high-quality results within a reasonable timeframe
- Although dispersing of particles is essential for each and every process involving particles in a host matrix, a rational basis for the design of technological methods is still lacking and too often one resorts to ad-hoc solutions.
- It is essential that advances be made in the technological methods to disperse aggregates and agglomerates of nanomaterials. Most likely this will require an intensification of existing methods, for example the use of combined 'fields', flow fields and ultrasound.
- Scaling-up of the devices and dispersion technologies into pilot plant scale devices needs to be performed.

Overview of needed competences in Flanders anno 2011

Based on the technological opportunities summarized above, required competences are:

- Development and assessment of novel technological methods for the dispersion of nanoparticle agglomerates and aggregates with scaling potential
- Development of rational, science-based formulation strategies
- Design of nanoformulation additives and dispersants
- Fundamental knowledge on agglomerate break-up
- Engineering knowledge on scaling-up of (new) dispersion technologies.

We see a clear lack/gap of knowledge/competence centers in Flanders concerning all these challenges. Although some of these issues are (remotely) touched in other (SIM) projects/programs for various applications*, there is almost no fundamental knowledge in Flanders on how to improve, generalise, and scale-up the dispersion process of nanoparticles.

* For example VITO has developed two dedicated prototype systems for atmospheric pressure plasma functionalization and coating of micron- and nano-sized particles.

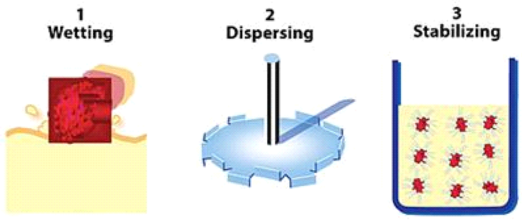
Apart from these challenges, it has been observed that dispersions of nanoparticles are becoming available on the market, offered by various (small) companies. E.g.:

- Mknano
- Nyacol
- Nanophase
- Nanoamor
- Byk

Major S&T challenges 2011

- Recently: commercial availability of e.g.:
  - High concentrated dispersions prepared by smart dispersion processes

Michael Berkei van BYK Chemie (D) stelt een betere manier voor om koolstofnanobuizen te dispergeren door gebruik te maken van additieven die de schade aan de nanobuizen kunnen beperken. Eerst en vooral is een goed bevochtigingproduct nodig dat in de agglomeraten kan binnendringen. In een tweede stap is het belangrijk een beperkte, optimale hoeveelheid energie te gebruiken om de buisjes te ontwarren. Ten slotte is het van zeer groot belang de buisjes te stabiliseren tegen herflocculatie. BYK heeft efficiënte bevochtings- en dispergerende additieven ontwikkeld die hen in staat stellen hooggeconcentreerde (tot 10 procent) dispersies van meerwandige koolstof nanobuizen te ontwikkelen in water en organische solventen. Wanneer deze dispersies toegevoegd worden aan coatings, kunnen antistatische, transparante lagen gemaakt worden bij slechts 0,5 procent koolstofnanobuizen (oppervlakteresistiviteit: 10^6 Ohm). Door hogere concentraties (1,5 procent) toe te voegen, worden elektrisch geleidende lagen bekomen (oppervlakteresistiviteit: 10^4 Ohm).



De verschillende stappen in het dispersieproces van koolstofnanobuizen (Bron: BYK Chemie)

Bron: Techniline 29/04/11: De nieuwste ontwikkelingen in functionele deklagen: slimme, functionele en nanogebaseerde coatings. European Coating Congress 2011.

Mostly these dispersions relate to widely available nanoparticles like silica, titania, etc. but they don't offer a general dispersion strategy.

Moreover, the question can be raised to what extent these dispersions lead to the desired end properties in the application: often the dispersion medium or functionalisation agents need to be adjusted to the specific application because they are incompatible with it.

3. Integration of nanomaterials in the host or sub-system

3.1 SHORT DESCRIPTION OF THE THEME, PROBLEM DESCRIPTION

Structuring nanomaterials within materials to provide the desired functionality is a major challenge due to inherent properties associated with the small size scale. This may involve:

- self-assembly,
- thermodynamically driven structuring,
- the application of external forces such as flow stresses, electric fields, or magnetic fields during coating, printing or mixing,
- coatings (e.g. nanoparticles in polymer or other host matrix),
- …

However, for most nanomaterials the desired organisation (nano-structural organization) and compatibility with the matrix often requires already preliminary engineering/design during their preparation or formulation.

Hence the result at system level (the micro/macro level) critically depends on the access to the required nano-sized building blocks (nano level) and corresponding formulations (meso level).

<u>On this level the critical gap for applying nanomaterial technology for SIM is situated</u>

Advances are needed in the fundamental understanding, characterization and modelling capabilities in order to optimize the integration of nanomaterials in the host without compromising the unique properties that the nanomaterials impart.
Methods of in-situ preparation of nanomaterials within organic matrices are promising but currently limited to only certain combinations of nanomaterials and matrix chemistries.

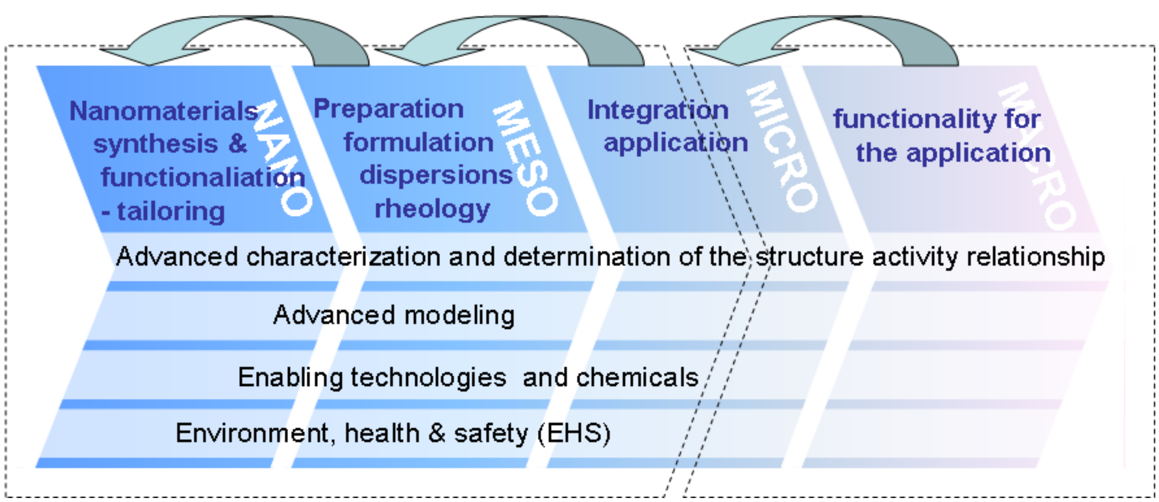


Figure 3 Value chain model used to describe the nanomaterials theme. The arrows accentuate the necessary feedback loops in the model.

3.2 TIME-FRAME / ROADMAP

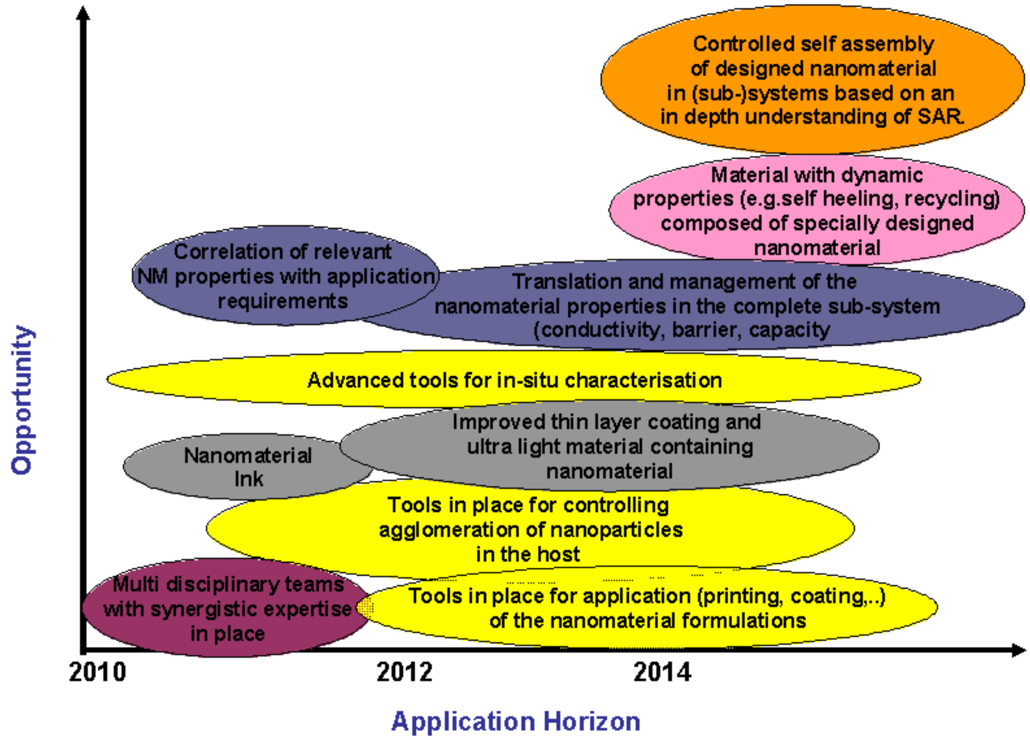


Figure 4 The theme will first focus on developing tools, multi-disciplinary teams, building blocks to evolve ultimately in the controlled (self-) assembly of hybrid nanomaterials based systems with dynamic properties.

3.3 STATE-OF-THE-ART ANALYSIS

Report A amply demonstrates that the Flemish knowledge base in materials science is very strong both in the industry and the universities and SOC's[x] (see Annex 1).

But although there are several collaborations they are usually bilateral and restricted to very specific projects. In general the potential for collaboration and synergy is not exploited. Already one of the major benefits of the SIM feasibility study is the growing mutual awareness of competences and needs.

Whereas the demands of the industrial SIM partners are situated at the macro side of the value chain, the universities and SOC's situate themselves at the supply side both at the nano and the meso level. The challenge for SIM is to forge this scattered expertise base into multi- disciplinary teams with a joint application oriented objective.

This challenge is still valid but there there is some fundamental weakness detected if one wants to maximize synergy:

- The virtual organisation of SIM and the scatter of the teams over different organizations in the areas of synthesis and formulation of nanoparticles or structures, and their integration slows down breakthroughs.

- The project leader capacity on the side of the universities is limited
- Ideally the nanosynthesis and nanoformulation with regard to a certain matrix /fluid carrier targets should be organized in one dedicated team with state of the art expertise and critical mass.

3.4 S&T CHALLENGES

- Understanding how the interaction of the nanomaterial with the matrix will influence the optical, electronic, mechanical, chemical, biological and degradation properties of the (sub-)system including the behaviour at the interfaces (e.g. for coatings)
- Understanding how the behaviour of nanomaterials can be triggered during application (coating, printing, injecting, mixing...) by temperature, magnetic or electric fields, moisture…
- Efficient, cost effective characterization of the behaviour and structure of nanomaterial in the host
- Prediction in order to define the application-driven information flow:
  - the required structure of the nanomaterials. This includes definition of required surfaces (e.g., 100 vs. 111), alternative morphologies (e.g., cubes, octahedral, or even ribbons and tubes), composition (e.g., alloys, core-shell structures, addition of dopant, partially or entirely ordered phases), and overall distribution of all of these within a large sample.
  - the required surface functionality or chemistry of nanomaterial in order to obtain a better control over the interaction with the environment (e.g., to adhere more strongly to a surface they must protect).
  - the required properties of formulations in order to improve the application in the system (e.g. rheological properties of nanoparticle inks).
  - the required properties of the functionalized nanomaterials to conform with the host
- Controlling of nanoparticle behaviour (e.g. agglomeration, adhesion, cross-linking, self-assembly...) in the host.
- Developing techniques (printing, coating, injecting…) for (un)patterned deposition of the nanomaterial or its formulation in the host.

3.5 OVERVIEW OF NEEDED COMPETENCES IN FLANDERS (TO BE REALIZED BY PROJECTS)

- In situ analysis capability on nano-ordered/structured morphologies in the host. Develop and tune complementary characterization techniques (microscopy, electro-optical, NMR, X-ray techniques, rheological) and combine them in an overall analytic strategy to get a full picture of the system and the integration of the nanomaterials in it (see also generic characterization and modelling chapter for in depth elaboration).
- Modelling toward required structural features of the nanomaterial and their formulations in order to meet the design requests of materials and systems (as input for the synthetic and formulation subtopics).
- Develop and understand the role of chemical additives (dispersing agents, synergists, reagents...) for controlling the incorporation (agglomeration, low temperature annealing, bonding, self-assembly...) of the nanomaterials into the host without degrading the required property (conductivity, absorption, charge separation…)
- Understand and develop techniques for the mastering the properties of nanomaterial containing layers in complex systems (adhesion, defects, flexibility…).
- Develop strategies and techniques for the patterned application of the nanomaterial formulations (printing, lithography, “functionality on demand” ...).

- Develop strategies and techniques for steering the (self-)assembly of the nanomaterial in a nano-structured sub-system.
- Develop strategies for triggering the behaviour of nanomaterials (conductivity, barrier properties, self-heeling, recycling...) in the host through heat, addition of chemicals, electromagnetic radiation, corrosion, etc…

3.6 OVERVIEW OF CROSS-CUTTING THEMES

Energy & Light:

- Defining the structure / performance relationship of nanomaterial based hybrid inorganic/organic barrier layers for (organic) solar cells
- Nanoparticles/porous electrode synthesis for hybrid solar cells.
- Large area / hi throughput printing of inks of inorganic nanoparticles for inorganic solar cells (CIGS or CdTe based)
- (Self) organisation of inorganic nanoparticles (CIGS) in the active layer of the inorganic solar cell.
- Application of dielectric/metal layers with nanoparticles for thin film silicon PV-cells.
- Development of nano-structured, conductive coatings for advanced cathode materials in batteries.
- Nano-structuring of particles of active materials with proper composition and selection of inert stabilizing components (metallic, ceramic, polymer, glasses …) for anode materials in batteries

Structural Materials:

- Development of nanomaterials with a triggering function, that allows improved recycling of starting materials from hybrid systems.
- Developing nanomaterial based composites with increased durability (anti-corrosion, self-cleaning, low friction, resistant to high and low temperatures) and sustainability (ultralight structural materials).
- Developing high performing (ultra-)thin coatings based on nanomaterials.
- Identifying and adjusting the reactivity of the nanomaterial towards the chemistry of the host matrix to allow for a strong interface bonding thus creating improved compression strength and shear stability of the resulting hybrid (e.g. in foams).

In annex 1 an overview of the nanomaterials research at IMEC is presented.
Compared to the SIM program on nanomaterials the IMEC program is focused on:

- Semiconductor, sensor and biomedical applications
- The use of Vaccum deposition and growth techniques for integration
- Biofunctionalisation of nanoparticles

4. Generic characterization and modelling methodologies for tailored nanomaterials in their real environments for realizing new SAR knowledge platforms for SIM

4.1 SHORT DESCRIPTION OF THE THEME, PROBLEM DESCRIPTION

The SIM-program on Energy & Light and on Structural Materials will use tailored organic, inorganic and hybrid nanomaterials with nano/micro/meso structuring as basic concepts to realize their targets. The final functionality and the durability of the device (for instance a fuel cell, rechargeable battery or photovoltaic cell) or the structural material (for instance, microstructured polymer foam loaded with functional nanoparticles) will be largely dependent on how the nanomaterial (in the broad SIM definition) behaves in its real operational environment. For instance, the functionality of the electrocatalyst in a fuel cell will depend on how the nanoparticle behaves in the electrolyte as part of a polymeric membrane or on the surface of a microstructured carbon paste. The same can be said for nanoparticles in microstructured polymer foam, where the local adhesion between the nanoparticle and the foam will be decisive for its long lasting durability. Electric charge transport in rechargeable batteries can be drastically improved by interaction between the nanoparticles and conducting media making even poorly conducting substances to become perspective materials. So knowing and to be able to characterize and model the nature and behaviour of the nanomaterial *in its real environment* is of the utmost importance when it comes to understanding its functionality, and ultimately the device and/or material performance over time.

Hence, the ultimate goal is to gain multiscale understanding of the performance of a nano-structured device or material on system/subsystem/nanolevel, linked to the knowledge of the local atomic/nano/meso structure. We aim to achieve this goal by building *generic characterization and modelling methodologies* for tailored nanomaterials in their *real environments*, by combining and developing ex-situ and in-situ analysis and modelling approaches.

With the '**real environment'** we mean the functionalised state of the nanomaterial in the application conditions, or conditions as close as possible to the real application environment. *For example*, for nanoparticles used in a certain device or structural material, the following real environments (not exhaustive) -on the various system levels- should be considered:

- Nano-level: the nanoparticle in a liquid dispersed state, and in its functionalised formulation before structuring or coating;
- Meso-level (subsystem): the nanoparticle in its host matrix (for example, in an (in)organic coating or in a (in)organic nanostructered (porous) foam);
- Micro level (system): the subsystem in the device or the structural material;
- Macro level (operation): the subsystem in the device or the structural material under operation.

With '**generic methodologies'** we mean the development of methodologies which can be used for many different nanomaterials in many different applications. Characterization and modelling will be performed to determine the morphology and the composition of the nanomaterial, as well as its functionality, on the various system levels. The in-situ approach in the real environments of the nanomaterials is seen as the main and most challenging innovation.

4.2 TIME-FRAME / ROADMAP

The vision is to develop in a timeframe of 5 to 10 years -in parallel with other SIM projects- a technology platform for submicron in-situ molecular and functionality characterization and modelling. This will be a joint effort of the existing characterization and modelling platform in Flanders, already quite advanced in ex-situ approaches.

A roadmap -indicated by the arrow in the table below - is proposed, crossing the various characterisation and modelling aspects for the various system levels with increasing complexity and more demanding competences (from left to right).

	Ex-situ*	In-situ	Interface between nanomaterial/ surrounding medium	Functionality SAR	Dynamic processes
Nanolevel	X	X	X	X	X
Subsystem level	X	X	X	X	X
System level		X	X	X	X

*Especially still challenging for soft matter analysis

Time frame and roadmap are still valid and up to date in 2011.

4.3 STATE-OF-THE-ART ANALYSIS

Multiple techniques are available to get insight in the nature and functional properties of the nanosystems in both ex-situ and in-situ conditions. However, many of the techniques (SEM, TEM, XPS, SIMS, STM, AES…) providing unique information on the atomic structure, morphology, composition and interfaces between the nanoparticles and their hosts are realized mostly in ex-situ conditions (require high vacuum and customized specimen preparation) and have limited applicability for investigation of nanomaterials in their real environment. By applying this ex-situ approach, the important details on the real extreme surface surrounding nature and interaction between nanoparticles and their surrounding can be missed or artefacts can be produced due to intervention of the specimen preparation techniques and influence of the specimen environment during measurements. Another drawback of this approach is that the nanosystems can be drastically affected by high energy radiation used for the measurements that limits the variety of potential objects for investigation, concentrating mostly on more robust inorganic substances.

In Flanders, state-of-the-art analysis equipment for such ex-situ characterization is available in the different knowledge centres (see report C of the Initial SIM proposal).

In-situ characterization of nanomaterials involves three aspects: characterization of (i) the nanomaterial (structure, morphology, composition, and functionality), (ii) the matrix (surrounding medium of the nanomaterial) and the nanomaterial/matrix interface (compatibility, bonding…), and (iii) the comportment of the nanomaterial subsystem in the device.

In-situ molecular material characterization is emerging in Flanders, as well as worldwide, and uses different approaches than the ex-situ approach, such as advanced NMR methodologies, local electrochemistry, in-situ TEM, AFM in liquids, SERS Raman, FT-Raman, advanced ESR-EPR methodologies under excitation, FTIR, UV-VIS. For example, for the chemical characterization of *interphases* formed between and at nanomaterials, synchrotron based techniques are being evaluated. Merging the ex-situ and in-situ approaches by combining their strengths in one expertise center is a feasible concept.

Additionally, some of the SIM material concepts will also be oriented to soft matter (organic polymer based), where still ex-situ characterization challenges remain, that can be addressed within SIM using the state-of-the-art ex-situ techniques (TEM, XPS…) in Flanders. Advances in 3D imaging and chemical analysis at nanoscale are emerging, and even imaging at atomic scale is considered feasible providing further developments in analysis techniques can be realized. 3D studies at the atomic scale will be of

great importance in future nanotechnology as they can provide more realistic structural input for theoretical modelling of nanoscale structures and interfaces, leading to a better insight in the relationship between the structure and properties of nanoscale materials.
A complete and effective utilization of information obtained from various ex-situ and in-situ characterization techniques requires a multiscale modelling approach, where this information will serve as input for better understanding the properties and behaviour of the nanosystems. Internationally more attention is going to the role of modelling on different spatial scales in the development and the understanding of nanomaterials with functional properties. Again joining together the advanced characterization techniques and modelling approaches in one expertise center will lead to pronounced synergetic effect. The existing modelling competence in Flanders embraces first principle calculations of electronic and optical properties of various nanomaterials (including carbon-based nanostructures), modelling of growth processes and deposition of coatings, multiscal modelling, efficient modelling and simulation of production/fabrication processes, deterioration mechanisms and/or damage mechanics, risk analysis and life cycle analysis etc.

4.4 S&T CHALLENGES

The major challenges of this proposed subtheme can be expressed as questions on the various system levels. Some are more oriented to the individual nanomaterials (particles, tubes, fibers…); others also apply to the nanoporous materials and assembled nanomaterials.

Nano-level: the nanomaterial in the dispersion (fluids) and in its formulation (formulation ready for deposition or for structuring, nano-ink formulation, nano-pastes …)

What does the surface of the nanomaterial in the dispersed state and in its formulation look like in-situ, and what does this mean for the structure-activity-relation? Some examples of questions demanding specific competencies:

- What is the structure of the nanoparticle at an atomic scale? Is it possible to get a 3D image of the nanoparticle at an atomic scale as input for theoretical modelling approaches?
- Which functional groups are present at the surface of a functionalised nanoparticle?
- What is the local molecular structure of the dispersant on the nanoparticle surface? Is it possible to model the dispersant's molecular structure on the surface, or to model the optimal dispersant architecture for a certain matrix?
- Is there a dynamic exchange between the nanomaterial and surrounding liquid/formulation?
- Are there re-organisation issues or instabilities on the molecular level as a function of time that can be appropriately detected and understood by monitoring in real time during formulation and structuring?
- Can the functional property of the nanoparticle be modelled on the nanolevel taking into account the real environment?
- How to adapt existing or develop new simulation and modelling approaches for this study?

It is vital to implement the right sample preparation methods to avoid modification of the nanomaterial's surface in order to mimic as close as possible the real environment.

Subsystem level: the nanomaterial in its surrounding matrix after deposition (nanoparticles in polymer coatings, inorganic foams, coated nanoparticles), with special attention for the nano-structured polymer *subsystems (soft matter OPV problem), interfaces between the nanoparticles and substrates and interaction between the nanoparticles and their functionalizing coating layers.*

- How to prepare the subsystem for characterization without changing its structure during sampling?
- What is the interface, compatibility, bonding… between the nanomaterial and its surrounding medium? What is a reliable methodology which gives us structural and chemical information on the submicron level in the subsystem?
- "Soft-hard matter" nanostructured composites: how to characterize their structure on the molecular/atomic scale? What is the limit of high resolution techniques in such cases?
- Can the functional property of the nanoparticle be modelled on the subsystem level taking into account host/matrix interactions?
- How can the activity of the nanoparticle best be measured (for example, leaching effects from a polymer matrix)? Can this behaviour be adequately predicted based on theoretical models? How to adapt existing or develop new simulation and modelling approaches for this study?

System (and operation) level: the nanomaterial as part of a subsystem in a device or structural material

Is it possible to set-up methodologies which are able to prepare the device in such a way than we can use or extrapolate the methods developed for the characterization of the nanomaterial at the subsystem level also on the system level?

4.5 OVERVIEW OF NEEDED COMPETENCES IN FLANDERS (TO BE REALISED BY PROJECTS)

Some examples of desired competences (list is not exhaustive):

- Characterization of structural and chemical properties of soft matter and soft-hard matter composites in 2D and 3D by ex-situ high resolution techniques;
- Soft matter modelling (for example, the nanoparticle and its ligand-polymer surrounding, starting from the dispersant problem), by expanding multiscale modelling to the meso-scale;
- Molecular modelling as a virtual characterization tool (structural as well as functional);
- Preparation techniques for nanomaterials on the various system levels to be able to characterize them in or close to their real environment;
- Advanced NMR, EPR, AFM, synchrotron (dynamic, under controlled flow conditions…) and spectroscopy methodologies for monitoring the nanomaterial properties in its fluid or formulation;
- A methodology which gives molecular information on the submicron level in a subsystem or a system/device;
- Functionality characterization of nanomaterial on nanolevel and subsystem level. (See the following section on cross-cutting themes for some examples)

4.6 OVERVIEW OF CROSS-CUTTING THEMES

Some examples (list is not exhaustive):

For structural materials:

- Self-cleaning, optical (appearance, colour), anti-bacterial, barrier, self-healing properties (+ corrosion inhibitor release properties) of a coating containing nanoparticles
- Behaviour of nanomaterials under (environmental) stress

- Fracture phenomena in nanomaterials (filled with micro/macro fillers versus unfilled)

For energy & light applications:
- Thermal resistance of nanomaterials
- Electric transport, magnetic and thermoelectric properties of nanoparticles
- Electric conductivity and diffusion in the nanosystems
- Catalytic properties of nanoparticles and nanostructured materials
- Optical absorption properties, appearance of a coating containing nanoparticles

For bio-medical applications:
- Bio-compatibility of nanomaterials
- Anti-bacterial coatings containing nanoparticles

5. Create awareness & strategies among project teams to deal with environment, health & safety aspects

5.1 DESCRIPTION OF THE GUIDELINE

The unique chemical and physical properties of nanomaterials and –structures lead to concerns about potential health risks and adverse interactions with ecosystems. Risks for human health or the environment should not go unnoticed. At the same time it should be avoided that these concerns might turn into a rejection of nanotechnologies and a negative image, or might lead to unnecessary and costly prevention and remediation actions. Therefore it is advisable to integrate a strategy to deal with environment, health & safety aspects, i.e. risk assessment and management, already in the initial stages of development of new materials and technologies. This will assure that the choices made in these initial stages, will not be jeopardized by EHS issues in a later stage of development.

But the traditional risk assessment methodology has not yet been applied to nanoparticles. At the moment, there are no official guidelines on what is an appropriate testing procedure. The commercial manufacture and use of nanoparticles is relatively new and there is very little data available on dose-response relationships and exposure measurements.

Available data are subject to methodological uncertainty, because actual standard methodologies to assess exposure, fate and toxicity of chemicals are not a priori suitable for nanomaterials. Initiatives are running both at international level (e.g. EU, OECD, CEFIC …) and at national level (e.g. national action programs in Germany, UK, and Netherlands…) to fill in this knowledge gaps and come up with standardized methods step by step. Important running FP7 NMP Nanosafety projects are for example Q-Nano, MARINA, NanoValid and NanoDevice.

These 4 projects are considered as a main driving force in Europe to boost future innovations in the field of nanosafety in the following main areas:

- fabrication of reproducible ENMs and standardization of reference materials;
- development and validation of accurate measurement and testing methods for ENMs;
- development and validation of new approaches for hazard and exposure assessment;
- design of new strategies for risk and life cycle assessment applicable to ENMs;

• build-up of a European knowledge hub and scientific database;
• development of new alternative non-animal in vitro and in silico testing methods.

Systematic application of:

The Defense in Depth Principles;
The ALARA principle;
The Precaution Principle;
The Control Banding method;

5.2 ROADMAP

Until now, only limited tools are available to perform a quantitative risk assessment yet. In case of the absence of firm toxicological and exposure data, control banding (CB) strategies offer simplified qualitative solutions for controlling worker exposures. CB is a generic technique to prioritize occupational situations based on exposure bands (likelihood of exposure) and hazards bands (potential hazard, such as skin/eye irritant, very toxic, carcinogenic, etc) combining them into risk bands (next figure) Based on the overall results, a risk reduction scenario or control scenario can be designed reducing the risks.

Hazard band / Exposure band	A	B	C	D	E
1	3	3	3	2	1
2	3	3	2	2	1
3	3	2	2	1	1
4	2	1	1	1	1

Figure 5: Priority bands - Hazard: A = lowest hazard, E = highest hazard /Exposure: 1 = lowest exposure, 4 = highest exposure / Overall result: 1 = highest priority, 3 =lowest priority.

Because most CB-models will only focus on worker inhalation exposure also a precautionary matrix can be drawn up. The precautionary matrix enables to estimate the nano specific “precautionary need” of ENMs and their applications for employees, consumers and the environment based on selected parameters. The matrix facilitates a structured approach and allows the major potential sources of risk to be identified. Thus it also provides the basis for early decision making on how to proceed with new products and processes.

5.3 INDUSTRIAL NEEDS AND TECHNOLOGICAL CHALLENGES

Experience exists on the systematic application of safety methodologies: (1) The Defense in Depth Principles; (2) The ALARA principle; (3) The Precaution Principle; (4) The Control Banding method.

Research teams within SIM should be encouraged to take notice of the above safety methodologies, or even consider applying them. For example apply a control banding model (worker) and/or draw up a precautionary matrix (worker, consumer, and environment) for the development, production, use and disposal of synthetic nanomaterials. Because of the large variability in types of nanoparticles, production processes and end-products and the complexity of the control banding model and the precautionary matrix, this should be done in a pragmatic way, on a case-by-case basis, making maximum use of available data and knowledge, and results of current research activities.

It is advisable, that members of SIM projects will be assisted in:

1. Translation from basic research findings to applications in safety evaluation or methodologies
2. Benchmarking the current work procedures to identify and review potential EHS related aspects in the different stages of the development or application of the ENM;
3. To enhance capabilities for adequate exposure control strategies to effectively and efficiently ensure minimal risk for the worker, the consumer and the environment;
4. Building up a network related to EHS, especially on the EU level, in order to:
    a. collect and assess available data and knowledge;
    b. get access to current research activities and information sources at national and international level (e.g. EU, OECD, CEFIC…);
5. Establish an interdisciplinary framework for excellence centers outside SIM (e.g. experts on exposure measurements, (eco)toxicologists, risk assessment, life cycle analysis…) for specific EHS research;
6. Outline a plan on how to initiate societal and scientific debate between R&D professionals, environment and health scientists, legislators, relevant stakeholders…

---

[i] Nanomaterials (NM) are here defined as an object, which is in one of its dimensions nanosized such as nanoparticles (NP), nanofibres (NF), etc. For a full description of definition see also Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate (ISO/TS27687)

[ii] Nanostructure (NS) is an ordered system of NM whether or not embedded in a matrix.

[iii] Such as dispersions, aerosols or pastes.

[iv] The host or sub-system is to be considered as the (structured) assembly of NM's - with or without a matrix (e.g. polymer, metal) - in a coating, surface layer or as a bulk material.

[v] QSAR: Quantitative Structure Activity Relationships

[vi] This includes fast screening techniques as well as new or improved analytic equipment.

[vii] Potential enabling chemicals are dispersants, binders and synergists for modifying the crystal surface.

[viii] Photovoltaic cell.

[ix] NHI : Nanomaterial/Host Interface

[x] SOC : Strategisch OnderzoeksCentrum (VITO, IMEC, VIB)