NanoRoadMap is a project co-funded by the 6th Framework Programme of the EC

Draft Roadmap Report on Nanoporous materials

This version is circulated within the Delphi Panel to clarify open issues
Please read carefully and provide feedback wherever you see fit

Statements are preliminary – pending Expert panel approval
Responses are not linked to individuals participating in the Delphi panel

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18th of July 2005

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1 Introduction

1.1 Background

The NanoRoadMap (NRM) project, co-funded by the European Commission (EC), is aimed at roadmapping nanotechnology related applications in three different areas:

- Materials
- Health & Medical Systems
- Energy

Within the project, an international consortium consisting of eight partners covering seven European countries and Israel, has joined forces to cover the time-frame for technological development in this field up to 2015. The results of the NRM project are to be used by any European entity interested in planning an R&D strategy taking into account nanotechnology. An important potential user is of course the EC itself in the preparation of the 7th Framework Programme (FP7) for research and technology development.

For additional information on the NRM project, please refer to www.nanoroadmap.it

1.2 Goals

The primary objective of NRM is to provide coherent scenarios and technology roadmaps that could help the European players to optimise the positive impact of nanotechnology on society, giving the necessary knowledge on its future development and when technologies and applications will come into full fruition.

The key users of the reports are mainly European SMEs, research organisations, public bodies in general and the EC in particular. Even though a special focus is put on SMEs, these roadmaps are also meant to be useful for larger corporations.

This report is one of the three final deliverables of the NRM project (together with the reports on the field of Health & Medical Systems and Energy) and it is aimed at providing a thorough overview of specific topics selected for roadmapping within the field.

1.3 Methodology

1.3.1 Collection and synthesis of relevant existing information

A report was published in October 2004, as the most important deliverable of the first stage of the project. It was based on the collection and synthesis of existing public sources in 31 countries and was published as key input for the celebration of the First NRM International Conference held in Rome the 4th – 5th of November 2004. The full report can be downloaded for free on the project web site.

The report focused on reviewing the different types of nanomaterials, describing the topic, its most remarkable properties, current and future markets & applications, and leading countries & highlighted R&D activities in the field. A general review of non technological aspects (social, legal, ethical and health and safety aspects, but also economical aspects and infrastructures requirements) was also performed.

The 12 topics identified, even not being completely homogenous in terms of scope or materials classification, were intended to adequately cover the field of nanomaterials. The following list was agreed upon the different partners of the NRM project (similar classifications can be found in the existing bibliography):

- Nanostructured materials
- Nanoparticles / nanocomposites
- Nanocapsules
- Nanoporous materials
- Nanofibres
- Fullerenes
- Nanowires
- Single-Walled & Multi-Walled (Carbon) Nanotubes
- Dendrimers
- Molecular Electronics
- Quantum Dots
- Thin Films

1.3.2 Selection of topics

Another major goal of that report was to set the basis for discussion and selection for roadmapping of 4 out of the 12 topics identified above. A preliminary selection of topics was presented during the First International Conference in November, 2004.

After a thorough discussion, which involved international experts in the field of nanotechnology, four topics were selected (and validated in dialogue with the European Commission). The topics chosen are:

- Nanoporous materials
- Nanoparticles / nanocomposites
- Dendrimers
- Thin Films & coatings

1.3.3 Roadmaps elaboration

One draft roadmap has been prepared for each of the four aforementioned topics. The present report gathers all the work executed during this phase, and can be considered as the deliverable for this activity till now. The results of these roadmaps will be presented in 8 National Conferences and one International Conference to be held in September – November, 2005.

A Delphi-like approach (referred to as Delphi panel in the future) has been used for the preparation and execution of the roadmaps. The methodology followed consisted of 2 cycles, and it was the same for the four topics. The Delphi exercise consisted in:

1. Selecting top-international experts on the field
2. Preparing a dedicated on-line questionnaire for each topic to be roadmapped
3. Circulating the questionnaire and gathering experts' responses (1st cycle)
4. Preparing a first draft roadmap document based on the input gathered from the experts and personal interviews with some experts
5. Circulating the draft roadmap document, asking for feedback (2nd cycle)
6. Elaborating the final version of the roadmap

2 ‘Nanoporous materials’ Roadmap

2.1 Definition of nanoporous materials

Nanoporous materials can be distinguished between bulk nanoporous materials and membranes. As a general characteristic, they are materials with holes less than 100 nm in diameter. Within this report, following the IUPAC classification, mesopores are those with 2 to 50 nm in diameter and macropores are pores with 50 to 100 nm.

PICTURE

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Nanoporous materials could have open (interconnected) pores or closed pores and could have amorphous, semi-crystalline or crystalline (e.g. lamellar, cubic, hexagonal) frameworks. These two characteristics very much influence the applications a specific nanoporous material is suitable for.

Nanoporous materials could be natural or synthetic, organic or inorganic and hybrid materials. Examples of materials considered for bulk materials and membranes are, amongst others, carbon, silicon, silicates, polymers, metal oxides, organic/metals, organic/Silicon, etc. Materials specifically considered for membranes include materials such as the widely used Zeolites (modified zeolites called electrides for catalytic applications but also with interesting electric, magnetic and optical properties) or the so-called schwartzites (carbon rings with higher porous size than activated carbon).

Figure 2.1.1 shows the materials background of the experts that participated in this roadmapping exercise.

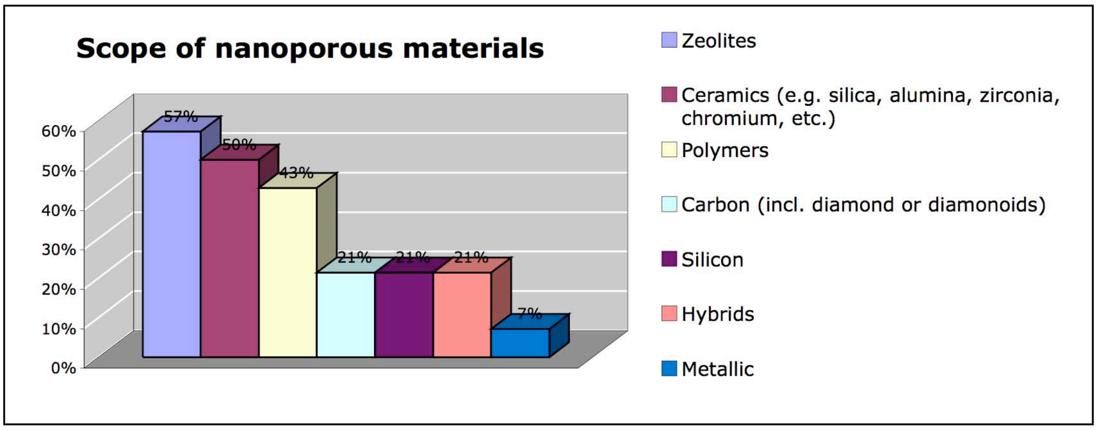


Figure 2.1.1 Scope of nanoporous materials

Not surprisingly, most experts work on the field of zeolites (a research field for over 70 years without being named “nano”), ceramics (good properties but some others limited by bad mechanical behaviour) and polymers (low temperature processes and with large chemical and oil companies heavily investing in this area).

Noticeable, development of hybrid organic-inorganic nanoporous materials is attracting more and more attention. Typical advantages of organic polymers are flexibility, low density, toughness, and formability whereas inorganic ceramics have excellent mechanical and optical properties such as surface hardness, strength, transparency, and high refractive index. The major driving force behind the intense activities in this area are the new and/or enhanced properties that the traditional macroscale composites do not have: for example, nano-composites are often still optically transparent materials.

2.2 Most remarkable properties

Nanoporous materials combine the advantages of porous materials with the physic-chemical-biological functionality of the material itself. Materials' properties are enhanced or inhibited by the nanometer-sized porous structure but still depend on the material chemical composition.

Above all the others, most remarkable properties are: high specific surface area, control over pores' size, morphology and distribution and broad possibilities for surface chemistry (directly relating to adsorbent properties). These properties are relevant both for bulk materials as well as for membranes.

Figure 2.2.1 summarizes those properties considered more relevant by the experts for membrane-related applications.

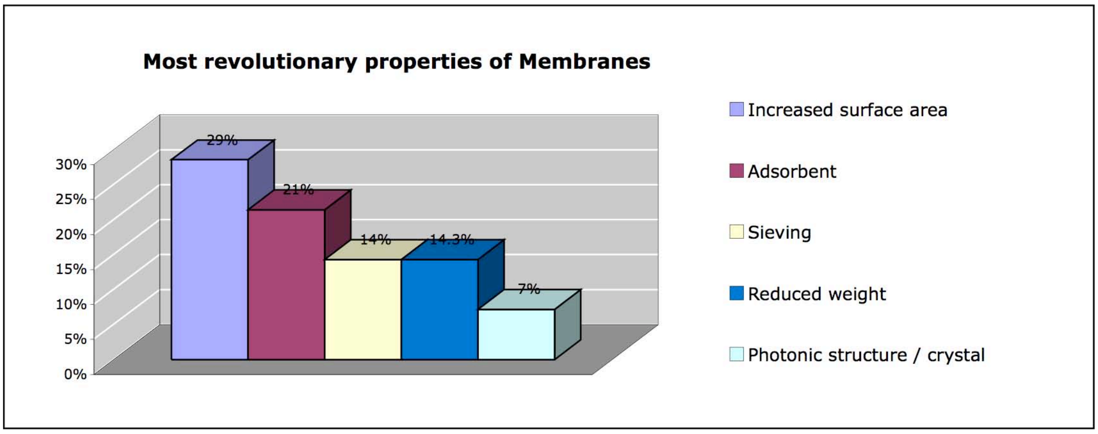


Figure 2.2.1. Most revolutionary properties of nanoporous membranes

Figure 2.2.2 summarizes those properties considered more relevant by the experts for applications of bulk nanoporous materials.

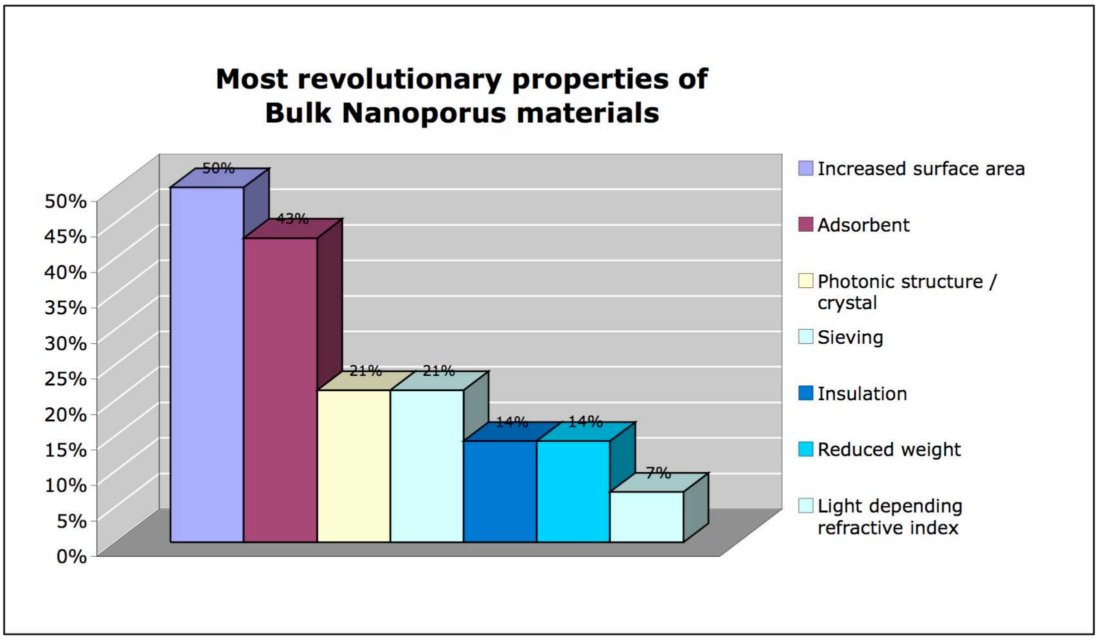


Figure 2.2.2. Most revolutionary properties of nanoporous bulk material

Below, the properties ranked as being important are briefly explained.

Increased surface area

Probably the most relevant property of nanoporous materials is the increased surface area per unit volume. Overall, this leads to increased pores' surface able to interact either with adsorbents (e.g. CeO_2 for catalytic applications), with particles embedded into the pores (e.g. Li+ electrolytes into metal oxide matrixes) or the flow passing through the material (e.g. polluted water). Nanotechnology is already enabling improved control on pores' morphology and size as well as on pores' size distribution (e.g. combining nanoporous and mesoporous structures) that combined with increased surface areas enables enhanced absorption and adsorption properties and ultimately leads to substantial improvements on applications such as catalysis, membranes or electrodes.

Adsorption

Adsorption of a substance is its concentration on a particular surface. The result is the formation of a liquid or gas film on the surface of a solid body. In the bulk material, all the bonds (ionic, covalent or metallic) of the constituent atoms of the material are filled. However, the surface represents a disruption of these bonds and is energetically favourable for these bonds to react with surrounding liquids or gases.

In catalysis, the adsorption of reactant/s to the catalyst surface creates a chemical bond, altering the electron density around the reactant molecule and allowing it to undergo reactions that would not normally be available to it.

Other fields where the adsorption property is of high interest are the storage of large amounts of gases (e.g. methane or hydrogen used as fuels), CO_2 separation from fuel gases or environmental remediation (e.g. CO_2 caption).

Nanotechnology provides the tools for a better fundamental understanding of the surface interaction phenomena and thus sets the ground for a precise control of the active sites morphology and size distribution whilst enhancing the control over surfaces energy (surface chemistry). This would help overcoming the needs to reach a better customisation of adsorbents to complex molecules as well as shed light to the development of predictive methods.

Sieving

Sometimes known as molecular sieving, it makes use of the absorption and adsorption properties of nanoporous materials by enabling liquid or gases to pass through the nanoporous structure while retaining specific particles or molecules. Customised porous structures have the ability to discriminate between and organise molecules. Zeolites are probably the best-known molecular sieves. Nanotechnology provides greater control over the pore morphology and enables the creation of complex morphologies that could be used for increasing its selectivity (prime objective of fine chemical industry). The development of mesoporous structures enables the separation of larger and complex molecules. Applications include water/solvent separation, hydrogen production/separation, fine chemicals production or pollutants caption. Sieving (together with the increased surface) is probably the most relevant property of nanoporous material and probably the most commercial significant area.

Reduced weight

Nanoporous materials contain more voids within their structure whilst keeping most of the properties of the solid material (e.g. mechanical). Applications benefiting from it include windows or furnaces (achieving better insulation with less weight) as well as metal foams being developed/used for automotive semi-structural applications. The combination of the reduced weight and the insulating properties, plus the radically improved strength of some nanoporous materials is potentially very valuable in aerospace applications (where cost is a less limiting factor).

Photonic (Band Gap)

Nanoporous materials could be designed to exhibit photonic crystal’s properties: certain frequency or energy cannot propagate through the material. However, this property is also achievable in non-porous materials that have a periodic (lattice) structure with different refractive indices.

For controlling the light, materials have to be opaque and do not absorb the light. Although this material may not exist in nature, it could be artificially created by creating photonic gaps in materials with enough variable refractive index and with the appropriate geometries. Nanotechnology enables the creation of nanostructured materials at sizes below the light/optical wavelength and therefore enables the creation of opaque materials. Once the light is trapped inside the material, nanotechnology techniques can introduce defects (changing materials’ refractive index) on the structure along which the light will move (waveguides) or to control light emission or light caption. Possible applications are a.o. high-speed optical switches, low-power lasers, light-emitting diodes, optical transistors, optical mirrors, wave guides and many other components used in the optical communication and computing industries.

Thermal insulation

Prevents or inhibits heat transfer across the material. Heat transfer through porous materials occurs via the sum of three different mechanisms; 1) solid phase conduction, 2) gas phase conduction, and 3) radiation.

In nanoporous materials, thermal conduction through the solid portion has weak temperature dependence and is hindered by the small size of the connections between the particles making up the conduction path (complicated three-dimensional networks). Thermal conduction by liquids or gases inside the solid is possible, although conduction paths are only the size of the mean-free path for molecular collisions. When the size is smaller than the wavelength of visible light, molecules collide as much with other liquid/gas molecules as with solid molecules, virtually eliminating thermal conduction. The third component, radiation, can be highly temperature dependent depending upon whether the insulation is sufficiently opacified with infrared absorbing and/or scattering materials. Further exploitation of the kundsen effect could enable the creation of very low-density materials (below 200 g/l) with extremely low thermal conductivity.

Among others, thermal insulation applications include industrial heating applications (e.g. furnaces) as well as windows. Materials considered are nanoporous ceramics based on alumina, mullite, zirconia, chromia and silica. High temperature infrared opacification is achieved by adding other materials' fibres and powders.

Stability in time

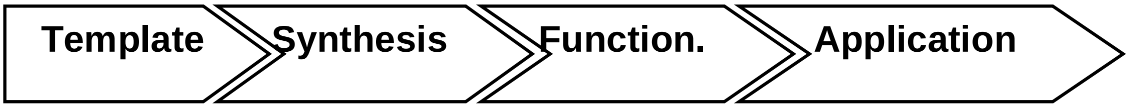
Physical and/or chemical stability is required to ensure a uniform performance over time (e.g. catalysis, separation) or to enable the nanoporous material to be used as a template (e.g. for other nanostructures production). Durability and reliability are crucial performance indicators in, a.o. fine-chemical industries.

Nanotechnology could provide a better control over the pore physical, chemical and hydrothermal stability, minimising pore’s shrinkage and degradation and hence maintaining the material performance over time.

Regarding bulk nanoporous materials, instability (e.g. leading to materials degradation) is very much appreciated in applications such as bio-implants for structural or drug delivery purposes where materials might have to be destroyed or removed after fulfilling their function.

2.3 The nanoporous materials pipeline

This section reviews the different steps in the nanoporous materials' pipeline: template preparations, synthesis and functionalisation. The later step is intended to provide the nanoporous material with the properties required for the final application.



However, it should be underlined that nanoporous material production does not always follow this linear approach with subsequent independent steps. In fact, in many occasions steps are integrated, combined or skipped. In many cases, each and every different application uses one or few specific templating, synthesis and functionalisation processes that lead to the desired properties whilst fulfilling other industry specific requirements (e.g. cost, throughput, flexibility).

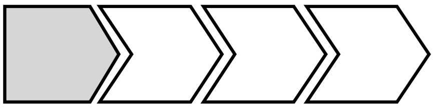
Within this roadmap exercise, most of the attention has been paid to the initial steps of the value chain where the material is designed and produced and functionalised. However, an overview of different end-users application is given in section 2.3.4. this section also includes information on the benefit for each application to move into nanotechnology as well as the most suitable type of nanoporous material.

Table 2.3.1 summarises the production techniques considered within this chapter. For each of them a brief description is given and main bottlenecks outlined.

Template preparation	Material synthesis	Functionalisation
• Mesoporous structures • Colloidal suspensions • Block Copolymers	• Solution precipitation • Self-assembling • Liquid Crystal routes • Swelling • Supercritical fluids • Lithography	• Solvents for templates' removal • Etching • Post-modification/grafting

Table 2.3.1. Overview of processes considered

2.3.1 Template preparation



The production of nanoporous structures with controlled pores' size, morphology and size distribution or crystalline framework usually involves the use of tailored templates.

The use of templates is to provide the conditions for raw materials’ self-assembling in the desired way and is absolutely required for long-range arrangement of the nanoporous materials (especially for the mesostructure). When these templates are removed the porous material is obtained.

Templates' preparation methods can be grouped in 2 main groups: substrates which pattern and/or structure is reproduced in the nanoporous material (e.g. mesoporous structures for carbon nanoporous material) and particles' suspensions (containing surfactants or not) that act as precursors of the pores and around which the nanoporous material is formed.

This chapter briefly describes the fundamentals of the 3 main processes used for preparing templates, main bottlenecks identified and possible research paths. However, due to the variety of nanoporous materials applications and required properties, many different template processes are being researched or customised to specific applications.

Figure 2.3.1.1 shows the processes that experts are more familiar with:

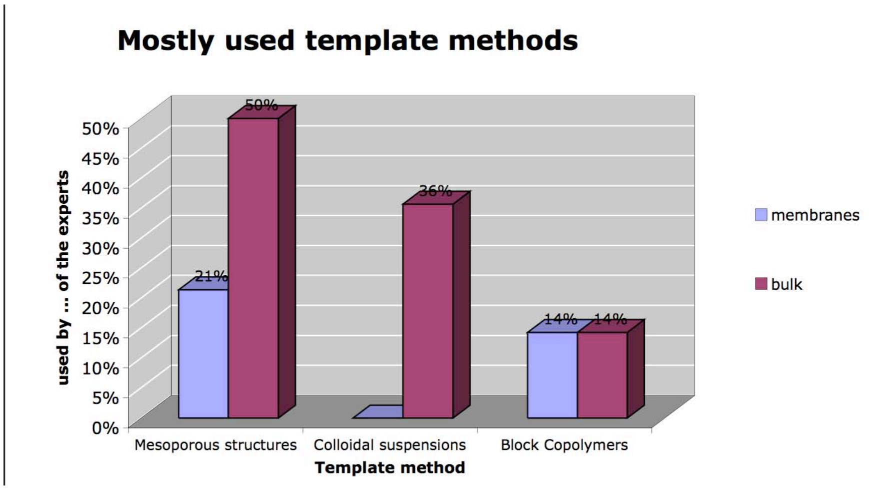


Figure 2.3.1.1. Mostly used template methods

2.3.1.1 Mesoporous structures

This method consists on using nanoporous structures as templates for creating new nanoporous materials. For instance, mesoporous silica with 3-D connected pores' network is used to produce non-siliceous mesoporous materials such as carbon. The initial pores are used as reactors inside which the carbon is deposited. After that, the Silica framework is burned off and the carbon mesoporous material remains.

Another application of using mesostructures as a template is to build up bi-modal structures. This is combining mesoporous (e.g. created by means of BCP templates) with a macroporous structure (e.g. produced via emulsion process).

Main barriers to success and research paths

Most of the experts highlighted that the main barrier for this process development is price (especially for bulk materials). However, the lack of suitable block co-polymer templates has also been highlighted.

The use of block co-polymers that provides silica material with microporous structure seems not that suitable for non-siliceous materials because they’re normally not robust enough to maintain the mesostructure upon the formation of the oxide. However, the use of inorganic salts (instead of alkoxides or organic metal complexes) has led to impurities' free structures which are thermally stable thank to the thicker inorganic walls.

Many non-siliceous materials have been synthesized; however, these materials have a significantly lower surface area and pore volumes than siliceous materials, probably due to disordered domains or appearance of blocks within the pores’ networks. One research path could be the use of post-treatment methods (e.g. re-crystallisation). Another crucial problem is that most of the metal oxides being researched are not thermally stable.

Also for non-siliceous materials it is much more difficult to obtain crystalline frameworks. It’s well known that a crystalline structure is essential in many applications such as photocatalyst or photonic crystals. Possible research path include considering different inorganic precursors or applying different thermal processes.

2.3.1.2 Colloidal suspensions

This template method is mostly used for the production of bulk material. Most widely used colloids are Silica and polystyrene latex (both commercially available). Advantage of Si colloids is that it can be dispersed in water or ethanol and can be etched by acid solutions. Advantage of polymer latex colloids is that they could be removed by heat or solvent treatment. Over last years, polymer colloids are also being functionalised leading to core-shell PS spheres with Silica onto their surface that offers the possibility to make 3D photonic crystals with tunable optical properties.

Main applications for colloidal suspensions are their use for photonic crystal and advanced catalyst production. For the production of photonic crystals is part of a 5 step process: (1) colloids production; (2) fabrication of artificial opal; (3) Annealing of artificial opal; (4) infiltration; (5) template removal.

Main barriers to success and research paths

According to the experts, main bottlenecks refer to price and availability of suitable monodisperse inorganic/organic colloidal suspensions. Monodispersion of the colloids ensures a highly ordered defect-free opal structures required for photonic crystals, one of the biggest challenges on photonic crystal production.

2.3.1.3 Block Copolymers

Block copolymers (BCP) are macromolecules made up of two or more distinct blocks covalently bonded together. This template process is based on the so-called cooperative assembly, where the surfactant (BCP) interactions with the inorganic material drive the creation of the nano/mesoporous structure.

BCP have the ability to self-assemble into predictable highly ordered structures by means of altering process temperature, chemical composition, and molecular architecture. Moreover, BCP have rich structural properties and phase behaviour.

Surfactants aggregate to micelles in a solution above their critical micelle concentration and a network enclosing the hydrophobic part of the micelle is formed. After removal of the template, pores are established with shapes according to the aggregate’s morphology. The resulting nanoporous materials have many potential applications including catalytic conversion, separation media, inner-layer dielectrics, and templates for the synthesis of other materials (see section 2.3.1.2).

Recently, research has mostly focused on non-ionic block co-polymers instead of ionic or neutral amine surfactants because they are non-toxic, biodegradable and can be produced at relatively low-cost. However, BCP do require non-aqueous media to avoid hydrolization of metal alka-oxides.

According to the experts, the main bottleneck for nanoporous materials’ development is the lack of suitable BCP templates. Presently available templates lack the robustness required for maintaining the mesoporous structure created around them and the lack of knowledge on the phase diagrams for complex (e.g. tri-block) BCP. Knowledge on phase diagrams is crucial to be able to design nanoporous materials with predicted properties. Even for, in theory, well-known BCP, there are very few recipes leading to well-defined porosity.

The need to develop templates with high hydrophilic-hydrophobic contrast withstanding the sol-gel process temperature was also pointed out. The self-assembly of the surfactants may suffer damage due to the harsh conditions present in some processes (e.g. sol-gel). Therefore, more stable aggregates (e.g. unimolecular amphiphilic structures) are also being used as templates.

Besides that, there’s the need to improve the crystallinity of the mesoporous structures. One possible research path could be the use of ionic block co-polymers functionalised with amine groups. These amine groups could play an important role in the formation of crystalline frameworks.

None of the experts pointed to cost factors hindering BCP templates exploitation, although one expert highlighted that synthesis of block copolymer templates has not yet reached industrial production.

2.3.2 Nanoporous material synthesis

A broad range of methods could be used for synthesising nanoporous materials; however, few of them get most of the attention (see figure 2.3.2.1).

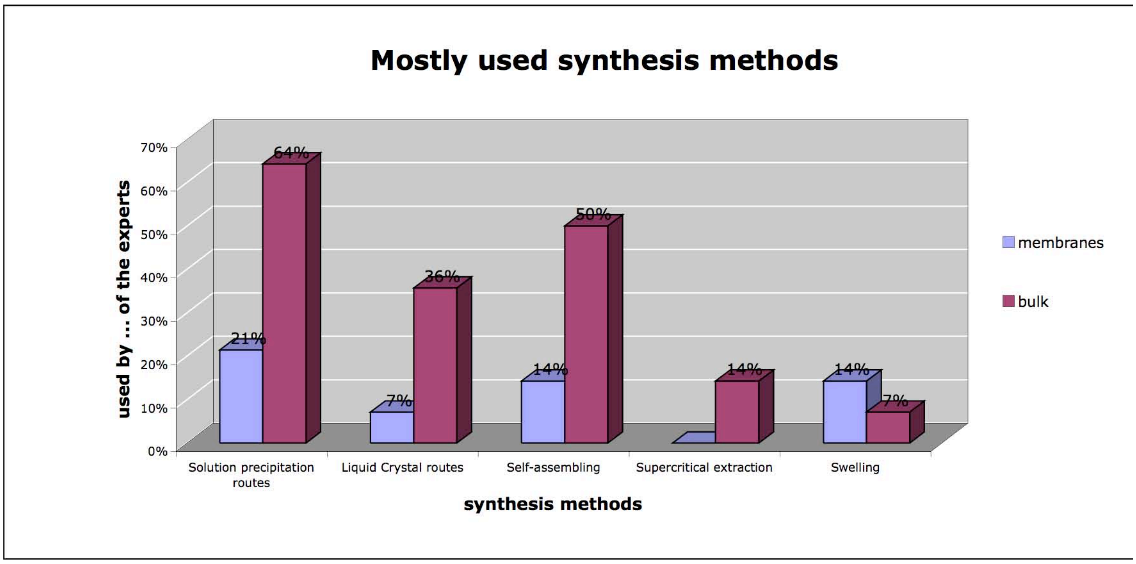


Figure 2.3.2.1. Mostly used synthesis methods

2.3.2.1 Sol-gel method / Solution precipitation routes

In solution precipitation routes, the precursor of the nanoporous material is dissolved in the solution and precipitates due to chemical reactions (normally accelerated by means of catalysts).

In the Sol-gel method, the precursor is in the form of micro-sized particles (usually inorganic metal salts or metal organic compounds such as metal alkoxides) mixed with a solvent (e.g. water or alcohol). When mixed, a suspension is formed.

The sol-gel process works at room temperature and consists of 4 main steps: hydrolysis, condensation and polymerisation of particles, growth of particles and agglomeration and formation of networks. The outcome of the process depends on several factors that influence the hydrolysis and condensation rates. Among them, there are few that are considered to have a greater impact: ph, nature and concentration of catalysts, H_20/precursor molar ratio and temperature.

The sol-gel process could be used to produce a wide range of materials structures such as nanoporous membranes and aerogels. Besides that, the sol-gel process could be used to produce nanostructures such as thin film coatings, ceramic fibres, powders, etc. The fact that the process works at room temperature (and close to neutral pH) enables its use in bio encapsulation-related applications.

The production of hybrid materials via the sol-gel process is receiving substantial attention. The inorganic material provides the framework of the nanoporous material (incl. chemical and thermal stability) whereas the organic material is used to functionalise the pores surface giving the required functionality/ies. The functionalisation could be done either by direct synthesis (incorporating the functional groups to the reactants) or by post-processing methods.

Main barriers to success and research paths

Although for some experts this is a well-established process, several technical barriers have been identified:

- Reproducibility of the process
- Purity of the nanoporous structure
- Difficulties for adapting the material characteristics to specific applications

The price factor has also been indicated as a bottleneck for the sol-gel process.

Regarding membranes, hydrothermal stability is required for gas separation or membranes reactors. In these applications gas streams may contain water vapour that reacts with the hydrophilic sites in the membranes. This causes both chemical and structural instability that drastically reduces the membrane performance and durability (absolutely required in the chemical industry). Therefore, improving the hydrophobicity (whilst maintaining their selectivity and permeability as well as thermal stability) of nanoporous membranes should be the main focus of research initiatives.

Suggested research areas of interest are: (1) the acquisition of experimental data for membranes performance as nano-reactors that could be used to validate computer simulations and (2) studies of water vapour permeation and adsorption as well as (3) studies of membranes' resistance to water vapour at high temperatures.

2.3.2.2 Self-assembling

Self-assembling processes is a bottom-up approach that basically consists on designing atoms and molecules that undergo a physical, chemical or biological process that ends up with the atoms and molecules being at the right place forming the right structure. It lies on the principle that energy forces drive atoms and/or molecules: they will naturally go to a place where they can minimize their energy.

Main advantages of self-assembly processes are that they don't require scaling down the manufacturing tools presently required (and used in all top-down production approaches) and, because they are a bottom-up approach, in principle they require less raw material and produce less waste.

Main barriers to success and research paths

One of the main challenges is to design molecules so they assembled in the desired way and to scale up these processes. IBM already demonstrated (Nov 2003) a flash-memory chip created via self-assembly using special polymer molecules. The development of templates or structure directing agents for directing the self-assembly process is pointed out as one of the main bottlenecks to be addressed.

The other main challenge is to make complex systems by hierarchical self-assembly where self-assembled building block can undergo further self-assembling processes. Main barrier to overcome is the design (probably through several production cycles) of these complex systems.

As a long-term research field, the price factor is also highlighted by most of the experts. Although self-assembly is a long-term ambition, many research projects do have a self-assembly component. Also large companies like Merck, Pfizer, 3M, IBM or Hewlett Packard are heavily investing in self-assembly.

2.3.2.3 Liquid Crystal routes

Liquid crystal phases, at high enough concentrations, can replicate their liquid crystalline structures, thus repeating distance and mesophase of the liquid crystal phase. This could lead to large continuous domains (in the range of mm) of mesoporous structures. That's advantageous as compared to template methods based on the cooperative assembly principle.

Main barriers to success and research paths

According to the experts there are price and technical barriers both for membranes and bulk materials. The need for new templates also involves costly synthetic procedures.

2.3.2.4 Swelling (e.g. for polymers)

Swelling is the increase of volume of material, usually due to absorption of a solvent. The swelling behaviour of polymer cross-linked matrices (e.g. derived from block co-polymers) depends on the degree of cross-linking of the blocks. For instance, the presence of double bonds in the nanoporous polymer facilitates a controlled introduction of functional groups onto the pore walls, which leads to the opportunity of controlling the internal surface characteristics of the nanoporous cavities. Several morphologies (templated from the self-assembled diblock copolymer structures) are conserved in the resulting cross-linked matrix.

Main barriers to success and research paths

According to the experts there's one main technical bottleneck to be address: pore collapse upon solvent removal.

2.3.2.5 Supercritical fluids

The unique physical characteristics of supercritical fluids (e.g. CO_2) are used to produce well-defined nanostructures for potential applications in a.o. inorganic catalyst supports. Main benefits of supercritical fluids are that they minimize the surface tension and capillary forces (between the solvent and precursors) that have shown to be highly destructive at the nanoscale. Processes based on supercritical fluids offer a very good control over solvent variables such as density, dielectric constant and polarisability. Changing pressure conditions instead of temperature performs control of processes' variables. This is highly advantageous as pressure propagates much faster than temperature. However, according to the experts there are still price and technical barriers to be overcome.

The possibility to avoid the use of organic solvents may make this method attractive for producing biocomposite materials.

This process could also be used for functionalising the pores. The highest viscosity of supercritical fluids allows and easier penetration into the porous structure providing a complete and more homogeneous functionalisation

2.3.2.6 Lithographic approaches

Main lithographic approach consists on bombarding a material with light (through a mask) to physically change its surface (or the part of the material attacked). The wavelength of the light being used limits the minimum achievable feature size, which is around 30 nm.

Traditional light-based lithographic processes have been widely used in the semiconductors' and MEMS/NEMS industries but are getting close to their limits.

Approaches using electrons, ions or atoms for bombarding the material are also being developed and some of them already applied in pilot plants. These approaches do not require masks and are able to directly modify the surface. These approaches could lead to close to nm precision; however, they are serial approaches (cannot create structures simultaneously) and very expensive. Therefore, they’re presently used for creating masters for soft nanolithography or for preparing templates used in self-assembling production methods.

Regarding nanoporous materials, lithographic approaches are considered for the production of photonic crystals. Materials known as 3-D photonic crystals or band-gap do not absorb light and do have a periodic spatial structure on an optical scale length. These photonic crystals inhibit light emission (using band gaps) and manipulate the flow of electromagnetic waves in three dimensions.

Main barriers to success and research paths

These materials could be produced using lithographic techniques but these are too time-consuming, expensive and facing difficulties when creating thick 3-D structures. The bottom up approach consisting of self-assembled colloidal micro-spheres spheres into ordered artificial opals (opals are non-crystalline varieties of silica that can be almost any colour and contain varying amounts of water) that are used as templates where the photonic crystal is grown (inverse opal).

2.3.3 Post-treatment and functionalisation

Most applications of nanoporous materials do require special characteristics (specially on the pores' surface) that could not be achieved by means of standard processes.

There are 2 main approaches for providing the required functionality: post modification (so-called grafting method) or direct synthesis (co-condensation of the functional groups). The co-condensation method is mostly applied to the sol-gel process and basically consists on adding the functional groups to the sol so they undergo the normal production process. This process allows a high load of functional groups but has a negative impact on the long-range order of the mesoporous structure. In addition, only limited functional groups could be applied with this method and there's also the risk of losing part of the achieved functionality during template and solvent removal.

Besides these processes, this section addresses the post-processes required for completing the production of nanoporous materials (incl. solvent and precursors removal)

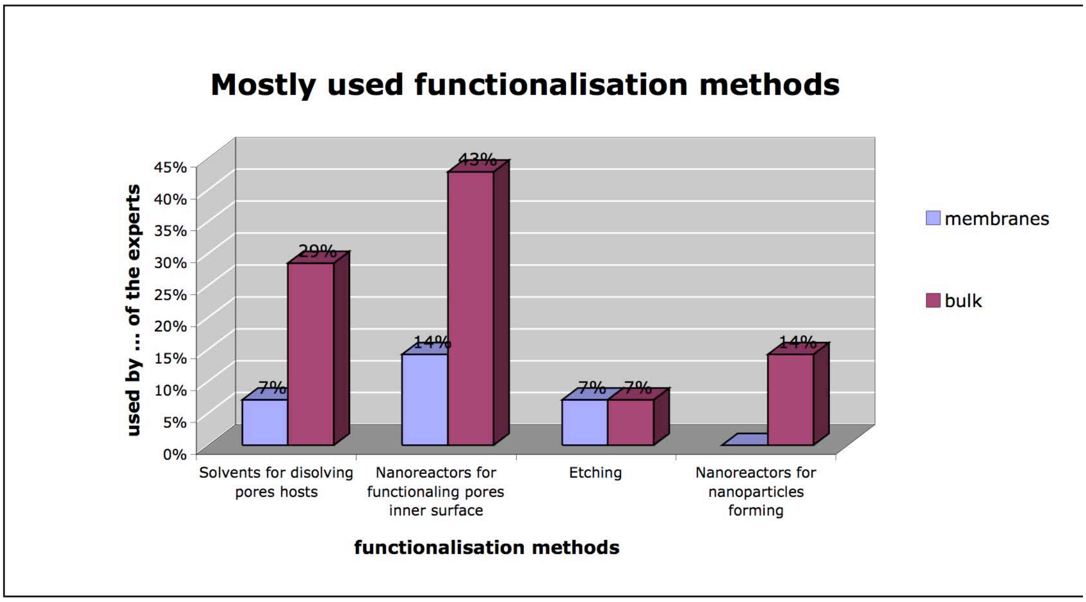


Figure 2.3.3.1. Mostly used functionalisation methods

2.3.3.1 Solvents for dissolving pores' hosts/precursors

Many nanoporous production methods make use of templates or structure directing agents (Structure Directing Agents) to achieve the required nanoporous material. Once the material has grown, the pores' precursors remain inside and need to be removed for achieving the final porous structure.

The use of solvents for dissolving pores' precursors is widely used but has an important drawback: in many cases the SDA are destroyed during the process. These SDA are tailored to the specific shapes and morphology and therefore are normally very expensive. Also the process undergone to eliminate the pores' precursors (e.g. high temperature processes) may endanger the resulting nanoporous structure. According to the experts, this process has also a negative environmental impact.

Main barriers to success and research paths

Finding the right type of solvent (especially for semiconductors' applications) normally implies very long-term research activities. Some experts from industrial organisation have also highlighted price as a showstopper.

The challenge is to achieve a low temperature process that enables the recovery of the pores' precursors.

2.3.3.2 Etching

The nanoporous material is obtained by passing an electric current through the semiconductor or metal material that is in contact with a strong acid solution. The acid reacts with the material leaving behind a sponge-like structure that is full of linked pores. The current used controls the fraction of the material that dissolves where the front of acid has reached; therefore, it's possible to vary the porosity form place to place by changing the current as the etching progresses. Thus is easy to produce multi-layered structures (e.g. with different pores size and refractive index).

According to the experts, micro/nanoporous structures in A3B5 semiconductors as thick as 50 mkm in self-organized mode are prepared by anodic etching. Main barrier to be overcome is the need of experimental equipment for programmed etching.

2.3.3.3 Post-modification / grafting

The so-called grafting method allows the functionalisation of pores' surface with various chemical functionalities, both organic and inorganic whilst maintaining the mesostructure after the functionalisation has been made; however, the density of functional groups to be added is limited and not uniform due to the constraints for acceding the pores. Moreover, this type of functionalisation reduces the surface area and the pores' volume.

In open nanoporous materials, pores are part of an interconnected network in which connections are normally smaller in diameter than the pores they connect.
Because most of the times the functionalising substances are molecules, their size is too big to let them pass through the nanoporous interconnections. Therefore, the only way to get them in is to separately feed the different components of the functionalising molecule and make them react inside the pore (which is acting as a chemical reactor of nanometre size).

As previously highlighted, stability is one of the main requirements for nanoporous materials and therefore is one of the requirements to be fulfilled after the functionalisation has been completed. In the case of surface alumination, for instance, different pathways are available (supercritical, dry and wet grafting) each of them providing different surface areas and pores' volumes (being supercritical grafting the one providing higher values).

Main barriers to success and research paths

According to the experts new organic synthesis strategies have to be found for linking organic moieties to highly condensed metal oxide pore surfaces. Also research is needed to avoid side reactions outside the mesopores (i.e. on particle surfaces). Finally, price is also considered an important bottleneck by half of the experts.

2.3.4 Applications

2.3.4.1 Introduction to main applications and identified bottlenecks

The two main basic application areas for nanoporous materials are as membranes and as bulk materials. Membranes based on nanoporous materials could be used for gas separation, chemicals synthesis, water remediation or fuel cells membranes. Applications of bulk materials include insulating windows, photonic crystals or bio-implants.

Whereas for membrane-related applications the pore is the crucial part of the nanoporous material, for bulk applications, the material structure (e.g. amorphous or crystalline) also plays an important role in the material's performance.

Before entering into the details of specific applications, experts have been asked to identify crucial bottlenecks for membranes and bulk material applications. Experts' opinion about membrane-related bottlenecks is summarized in Figure 2.3.4.1.1

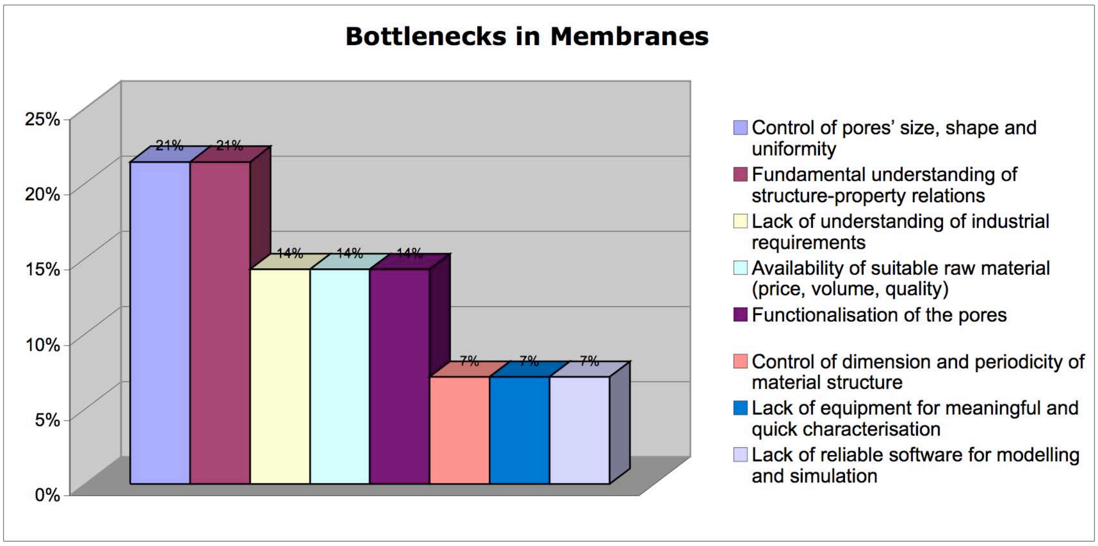


Figure 2.3.4.1.1. Main bottlenecks in nanoporous membranes

Bottlenecks for bulk materials' applications are summarized in Figure 2.3.4.1.2.

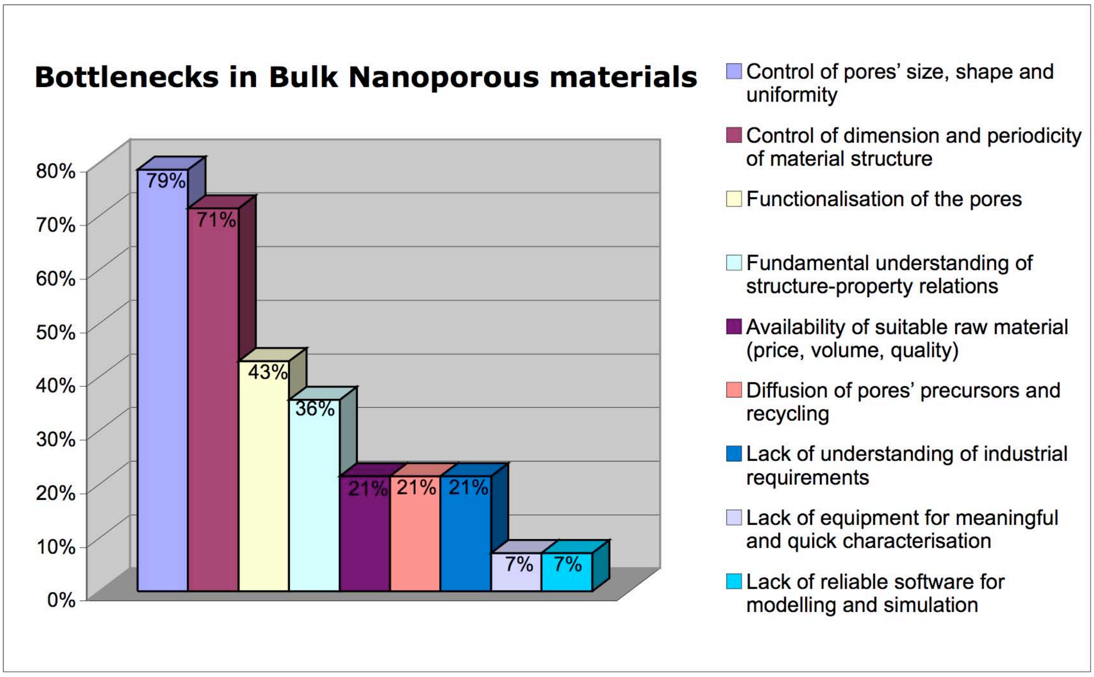


Figure 2.3.4.1.2. Main bottlenecks in bulk nanoporous materials

According to the experts there are 4 main bottlenecks, some of which could be addressed by means of nanotechnology:

- Fundamental understanding of structure-property relations: new instrumentation being developed could shed more light into this relationship; however, it's also highlighted that such instrumentation is not yet able to provide meaningful and quick characterisation.
- Control of pores' size, shape and uniformity
- The availability of suitable raw material seems to refer to the availability of suitable templates. This has already highlighted in section 2.3.1.
- The lack of understanding of industrial requirements is worrying and cannot be addressed only by means of nanotechnology.

Other bottlenecks highlighted by the experts are:

- Functionalisation of the pores (see section 2.3.3)
- Lack of suitable software for modelling and simulation: it's linked to the lack of understanding of the structure-properties relationships.

Other concerns raised by the experts include the reproducibility of the formulas for porous materials with well-defined porosity and the availability of suitable templates for mesoporous (2 to 50 nm) material production. In general, uniformity, quality and throughput are essential for reaching large volume production at decreasing costs. Fabrication of crystalline metal oxides without pore collapse has been specifically pointed out as a bottleneck for bulk nanoporous materials.

2.3.4.2 Overview of applications considered

The following is a list of most relevant applications of nanoporous materials.

- Membranes
- Catalysis
- Gas storage
- Thermal insulation
- Photonic crystals
- Electrodes
- DNA sequencing / Single-molecule analysis
- Tissue engineering / bio-implants
- Drug delivery / bio-encapsulation
- Sensors

2.3.4.3 Timeline for applications development

The following paragraphs give an integrated overview of the different stage of development of the applications listed above. The following three paragraphs each cover one "snapshot" of the overall nanoporous materials' roadmap. One for the current state of the art, one for the state of the art as predicted in five years from now (2010) and one in ten years from now (2015). The following distinctions have been made in the following figures:

- *Basic Research & Development Phase (Basic R&D)*

Applications in this phase have received the interest of at least one, or more researchers in the world. Some applications might still be in early development, while others are tough to develop and need a lot of basic research to be fully understood. The object of basic R&D is to validate the original hypothesis. Most of nanoporous materials' applications are currently in this phase as researchers are still struggling to understand basic interrelations between properties and structure and to have a greater control over pores' characteristics.

- *Applied Research & Development Phase (Applied R&D)*

After the hypothesis is validated, research typically (but not necessarily) moves from pure research labs to more commercial labs and companies. Applied R&D will eventually result in a proof of concept, a successful demonstration model. While the production issues might not have been solved yet, a successful prototype / model has been validated.

- *Production Research & Development Phase (First applications)*

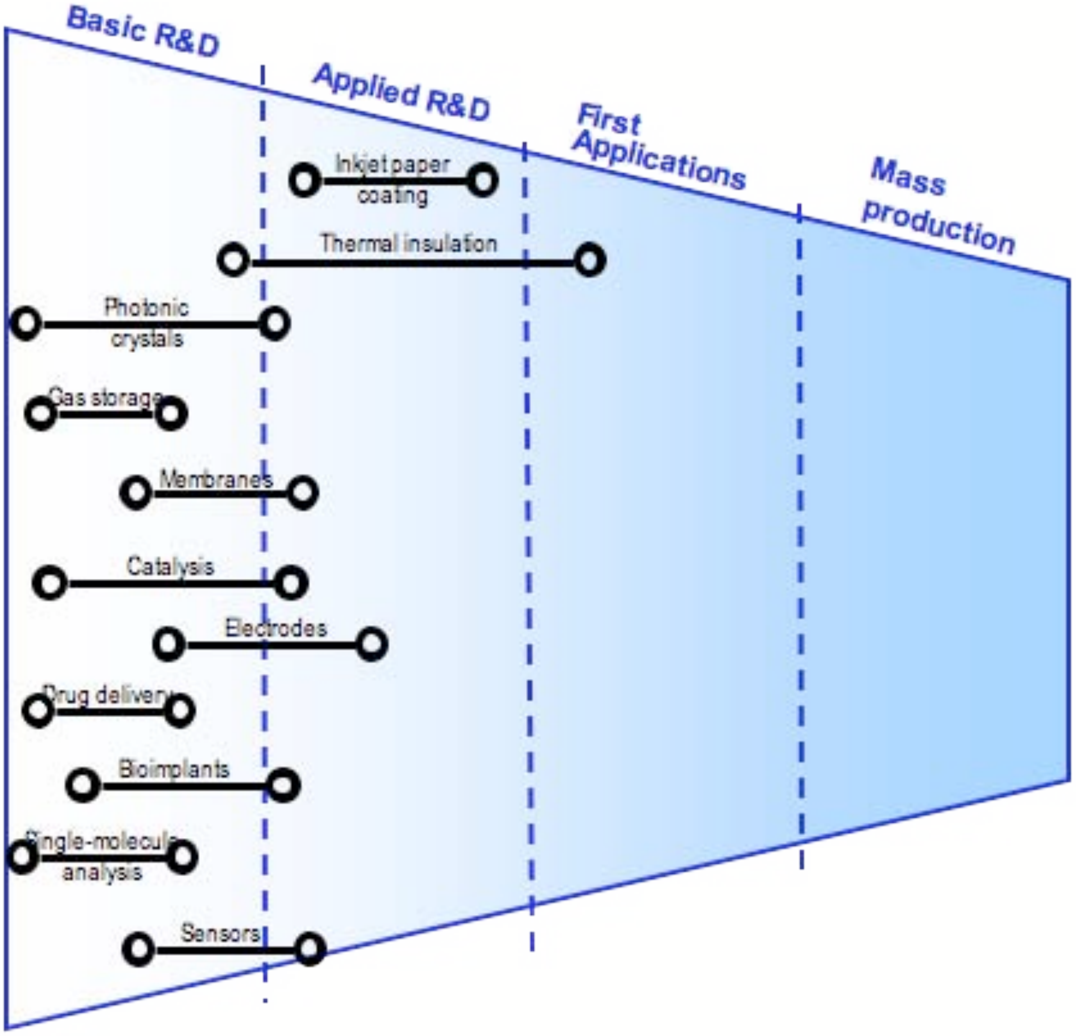
After first demonstrator models and prototypes, initial, usually prohibitively expensive, small amounts of products may be produced. At the same time, if these prove successful, companies will seek to upscale production processes. Generally at some point, demand increasing sufficiently to offset the investment needed to start bulk production. This phase ends at that point when is clear and possible to start this bulk production.

- *Mass production and incremental research (Mass production)*

The final development phase, in this phase production has reached bulk amounts and research focuses on incrementally improving the products. After this phase even more phases can be discerned (market maturity, end of life cycle, etc.) but these have not been taken into account when creating the following figures.

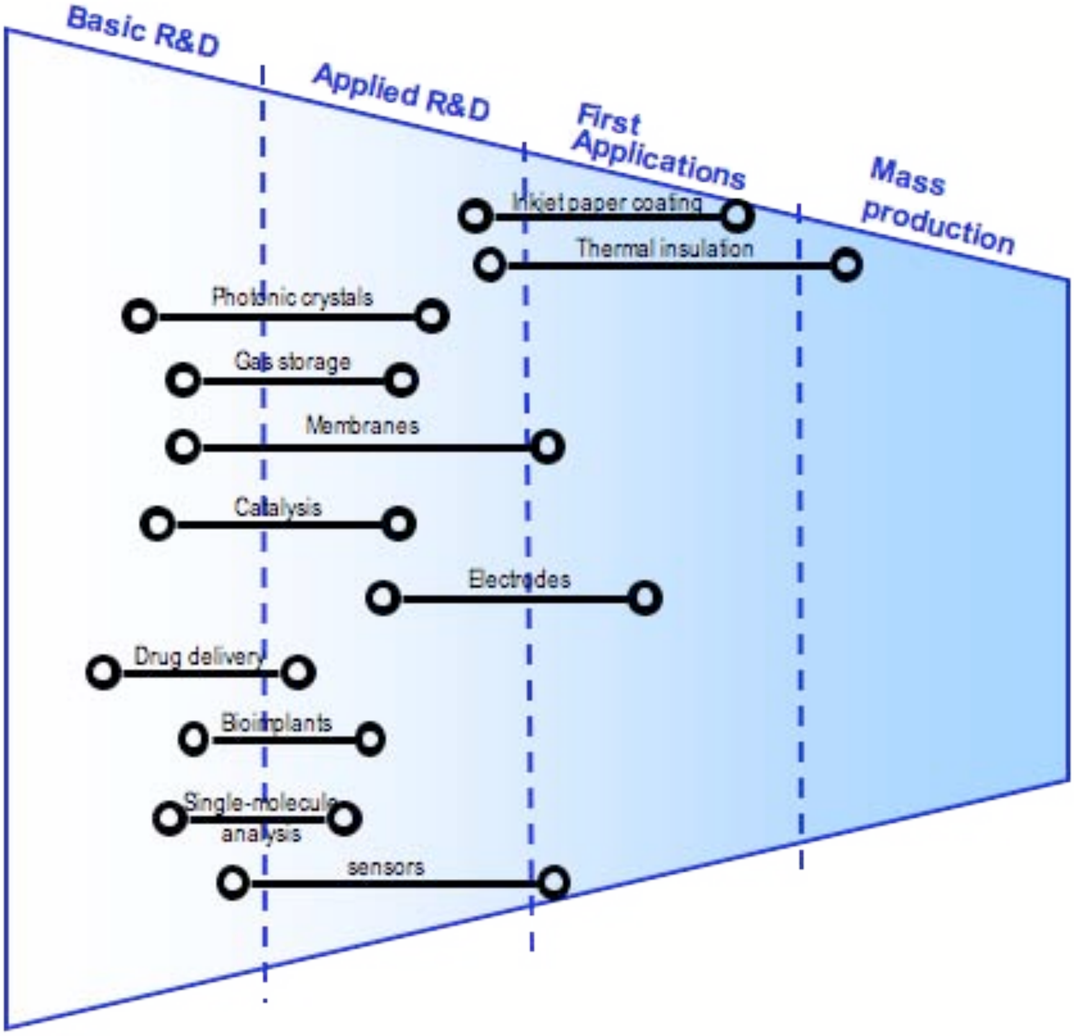
Overview of current applications (2005)

The following figure is an overview of the current state of development of different applications of nanoporous materials.



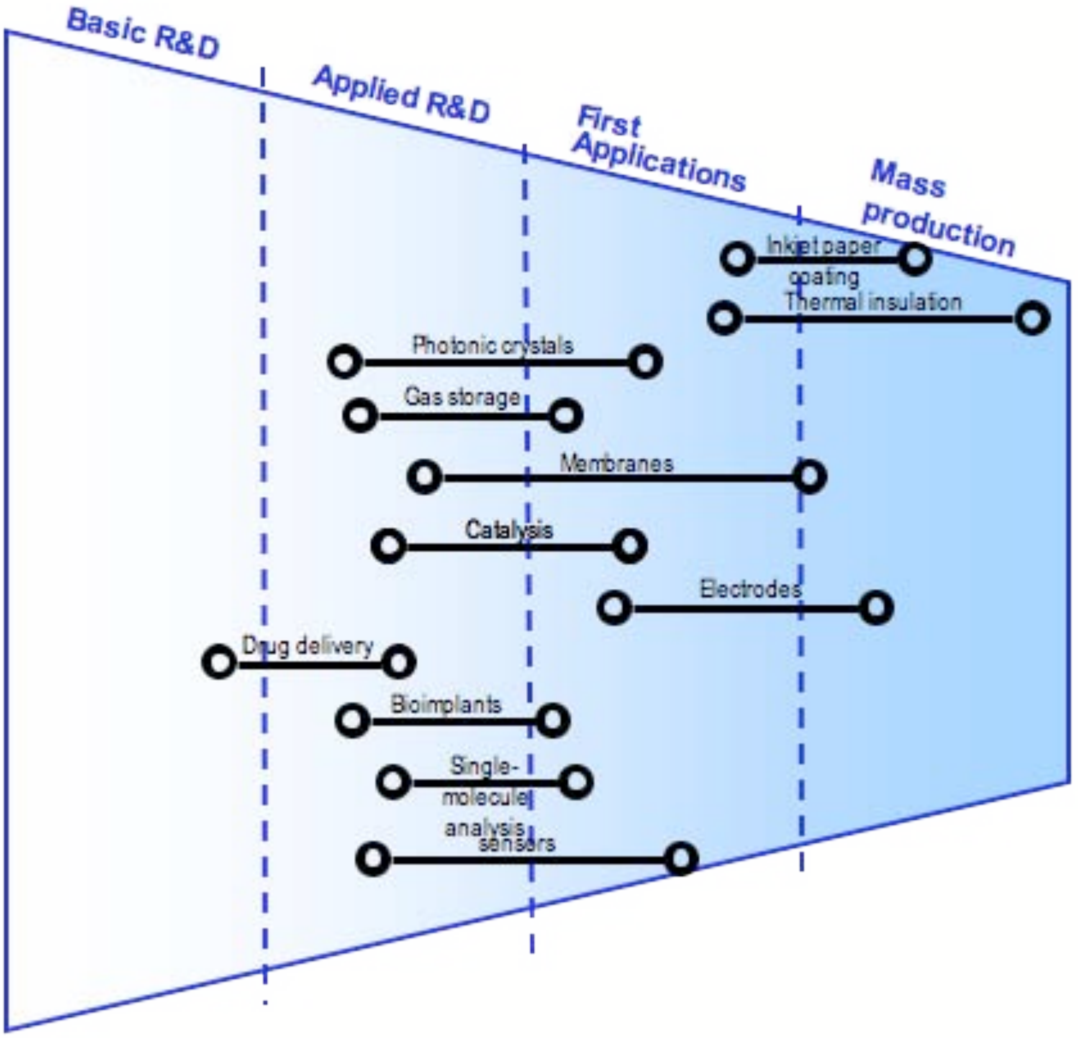
Overview of applications in 2010

The following figure is an overview of the expected state of development of different applications of nanoporous materials in year 2010. After five years many more applications will have come into fruition.



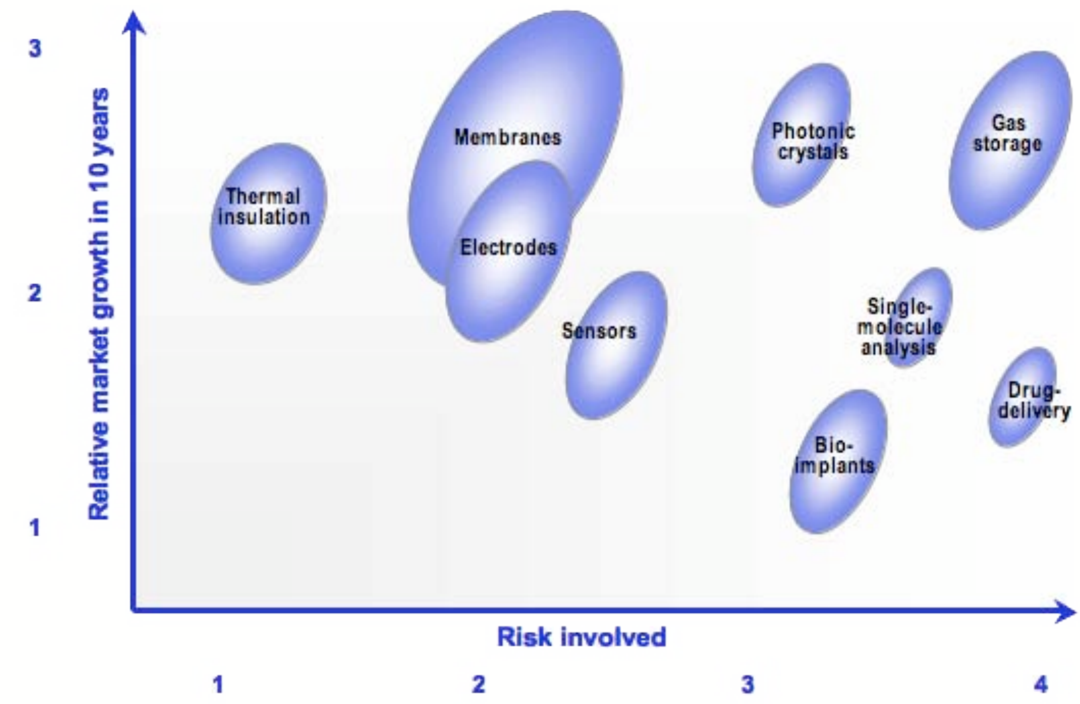
Overview of applications in 2015

The following figure is an overview of the expected state of development of different applications of nanoporous materials in year 2015.



2.3.4.4 Risk involved vs. market growth in 10 years

The next picture shows an estimation of (technological plus market) risk associated to each of the above-mentioned applications vs. the estimated market growth in the following ten years.



2.3.4.5 Description of main applications

Membranes

Membranes based on nanoporous materials could be used for gas separation, chemicals synthesis and water remediation or fuel cells membranes. Specific requirements for these applications are:

- Membranes for gas separation (e.g. CO2) do require materials that combine high selectivity and permeability as well as good mechanical stability at high pressures and temperatures (specially against vapours).
- Proton Exchange Membranes or Phosphoric Acid Fuel Cells benefit form an increased surface to volume ratio and would benefit from the possibility to work at higher temperatures (aprox. 120 ºC instead of 80) to reduce the adverse effect of CO over the catalyst and increase reaction kinetics. This requires the materials to be thermally stable (minimising their degradation) assuring a high proton conductivity.
- In the fine-chemical industry are essential high throughput, low capital investment and operating costs, long-term durability and reliability.
- In addition to the above-mentioned requirements, membranes' application for environmental remediation does require high adsorption/absorption properties and robustness in dirty environments.

The added value of moving into nanotechnology is the increased surface to volume ratio, the improved control over pores' morphologies (required for molecular sieving), size and distribution and having the ability to modify chemical and physical characteristics of materials (thus having a direct impact on its adsorption properties.

Table in section 2.2.4.1 summarizes the main general bottlenecks for the development of nanoporous materials' membranes. Other concerns raised by the experts in the field of membranes include the reproducibility of the formula for porous materials with well-defined porosity and the availability of suitable templates for mesoporous (2 to 50 nm) material production. Also the lack of robust enough block copolymer templates able to maintain the mesostructure upon the formation of the oxide is considered an important barrier.

Catalysis

Most of the catalysts used are highly porous materials with a large surface area and consist of an active phase and a passive phase ('heterogeneous catalysts"), the latter being made of a chemically and thermally stable material (e.g. alumina). Main benefits for moving to nanotechnology are an increased surface to volume ratio and better control over active sites (pores' morphology, size, distribution).

One of the main barriers for catalysis development is the lack of understanding of the surface morphology and how do they interact at the atomic level. Recently developed techniques such as Scanning Tunnelling Microscope and others should contribute to unveiling this. Models being developed so far mostly focus on the interrelation between the structure and its reactivity.

Although Silica nanoporous materials could be used as catalysts' support, a better chemical and thermal stability has to be reached in order to compete with complex oxides (HfO_2, ZrO_2, CeO_2) that are chemically much more stable and more suitable for catalysis than silica. Also parameters like throughput, catalyst selectivity and active sites needs to be improved. Nanoporous materials with customised pores' catalytic functionalities might be able to compete with catalytic nanoparticles because they do not require catalyst separation after the process and avoid the agglomeration of catalytic nanoparticles. Accordingly, main research lines focus on achieving stable structures as well as materials with identical structure and composition in active sites.

Gas storage

Nanoporous materials could be used for storing different liquids or gases in a safe efficient way. There is the need of new materials able to store large amounts of gases, such as methane or hydrogen, used as fuels in replacement of liquid fuels.

H_2 storage seems to be main application for gas storage as it is likely to be the fuel of the future and H_2 storage has not yet been solved; however, there are several possibly competing routes.

In general, gas storage is a “high risk – high reward area”. Market potential is huge but also the risk of not reaching requirements.

Thermal insulation

Thermal insulation applications include industrial heating applications (e.g. furnaces) as well as windows and more sophisticated applications such as in aerospace (where the combination with improved mechanical properties is required; e.g. lightweight insulation for cryogenic propellant tanks).

Thermal insulation can be achieved by filling in pores with air or other gases therefore avoiding heat convection process. Thermal insulation materials have low conductivity (or low dielectric constant), low solid density, high porosity and high surface area.

One of the main barriers is that porous insulating materials have partial near infrared transparency. This causes them to exhibit radiant heat transfer and thus reduces their insulation capacity. Research paths for improved insulation involve both the use of opacifiers as well as attempts to further reduce materials' density.

By means of nanotechnology, nanoporous materials could be designed to drastically reduce heat transfer (conduction, convection and radiation) by designing the pores, the material framework and adding the required functionality for infrared absorbing. In principle this could be combined with a high transparency and very low material density that would enable applications in windows.

Another barrier is the high cost associated to the use of alkoxides as precursors but alternative preparations using commodity feed-stocks are being researched and promise raw material cost reduction.

Availability of software for modelling and simulations seems not to be a key barrier for thermal insulation developments. For customising materials' properties to specific insulation applications there are analysis programs that enable the simulation of various insulation and refractory configurations.

Materials considered are nanoporous ceramics based on alumina, mullite, zirconia, chromia and silica. High temperature infrared opacification is achieved by adding other materials' fibers and powders. Most promising material (low cost compared to others) seems to be Al_20_3/Cr_20_3.

Photonic crystals

One of the most promising added-value of nanotechnology is to move from electronics (electron-based) to photonics (photon based). This seems to be within reach by means of the development of photonic crystals with tunable bandgaps. Photonic crystals inhibit light emission (using band gaps) and manipulate the flow of electromagnetic waves in three dimensions. Thus, it would be possible to create channels which are less than 5% of optical fiber width and which have radius thousands of times smaller than presently used optical fibers.

Foreseen applications include high-speed optical switches, low-power lasers, light-emitting diodes, optical transistors, optical mirrors, waveguides and many other components used in the optical communication and computing industries. Also application in solar cells is possible.

Nanotechnology enables the creation of nanostructured materials at sizes below the light/optical wavelength and therefore enables the creation of opaque materials. Once the light is trapped inside the material nanotechnology techniques can introduce defects (materials with high refractive index) on the structure the light will move along (waveguides) or to control light emission or light caption.

According to the experts, from the production point of view, photonic structures are important for the planar integration of the opto-electronic elements like negative refractive index materials, superlenses, etc. Moreover, Epitaxial Lateral Overgrowth (ELO) over porous silica substrate is able to extend critical layer thickness and prepare highly mismatched hetero-structures. ELO over micropores could improve defect structure of the deposit.

Electrodes

Electrodes could be used, a.o. in fuel cells, batteries, super-capacitators or solar cells. The electrode supports the catalyst that allows for efficient ionization and increased electrical conductivity. In order to raise catalyst efficiency, a porous carbon material with a large surface area is needed

DNA sequencing / Single-molecule analysis

Pores within a nanoporous membrane could be used for single molecule analysis either by means of voltage change detection. The approach consists on pulling DNA or RNA strands through the pore and applying a voltage across the pore. Then the current intensity could be measured by measuring changes in the ion flow or changes in tunnelling currents across the pore so each letter (4 letters in total) of the genetic alphabet could correspond to a given current and therefore the human genome could be sequenced (long term expected throughput: hours per human-genome). The application for protein analysis could also be feasible

Tissue engineering / bio-implants

As matrix to either induce surrounding tissue or cells in-growth or to serve as temporary scaffold for transplanted cells to attach, grow and maintain differentiated functions. Nanoporous structures' design is considered the most suitable for cell growth and proliferation. Up to now only applied in dermis and cartilage (because they do not need intrinsic blood vessels)

The matrix material has to be biocompatible, non-toxic, non-brittle and surgically easy to handle and therefore biodegradable polymers play an important role in most applications of tissue engineering and regenerative medicine. Also hybrid materials (silica with polymers for improved toughness) are suitable for this type of application.

Drug delivery / bio-encapsulation

The principle of using nanopores to let some molecules pass but not others holds potential for drug delivering both via pills or implants. The concept may offer the possibility of shielding drugs from digestive enzymes (e.g. could not enter the nanoporous structure).

Hosting of drugs or bio-encapsulation is possible thank to production process working at room temperature and near neutral pH. The availability of non-surfactant templating routes offers almost endless possibilities for election (e.g. glucose, fructose, etc.) in a direct synthesis processes for bio-encapsulation of bio-active substances such as enzymes, proteins, nucleic acid or cells. For releasing the encapsulated compounds, nanoporous materials could be designed to open or close their pores under external stimuli (e.g. light, pH, temperature, ions, molecules, enzymes or viruses)

Barriers being addressed are the need to have membranes with well-defined pores' channels and to be able to produce well defined monolith structures. Besides that, the use of non-surfactant techniques enables the possibility to avoid the use of toxic (and expensive) surfactants and avoid harsh process conditions that hinder the encapsulation of bioactive substances: high pressures and temperatures or strong acidic or alkaline media for template removal.

Most suitable types of nanoporous material are hybrid materials (based on silica) or metal-oxides.

Sensors

The high surface area and high sensitivity to changes in their environment that could be achieved by nanoporous materials opens up their application as sensors and actuators. Most important sensors' application includes gas sensors (detection of change in electric resistivity) and biological sensors (e.g. immobilizing molecules onto the surface so they can be used for biological detection).

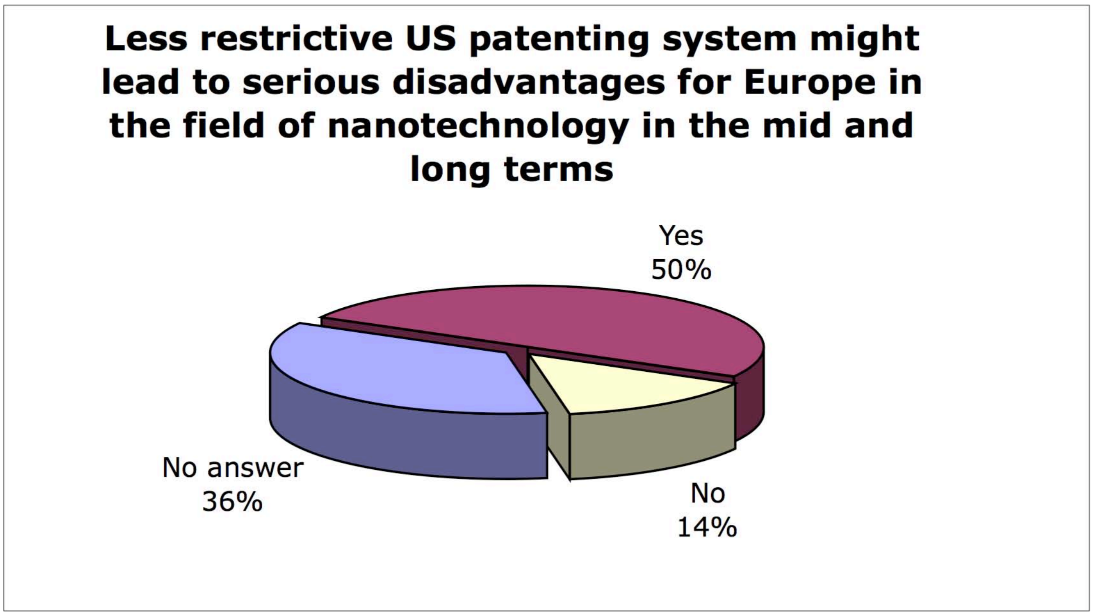
The main benefit for moving to the nano-level is that of increased surface area and precise design of porous sensitivity via surface functionalisation.

The most suitable types for sensors include SnO_2, TiO_2 or ZrO_2

2.4 Non technological aspects

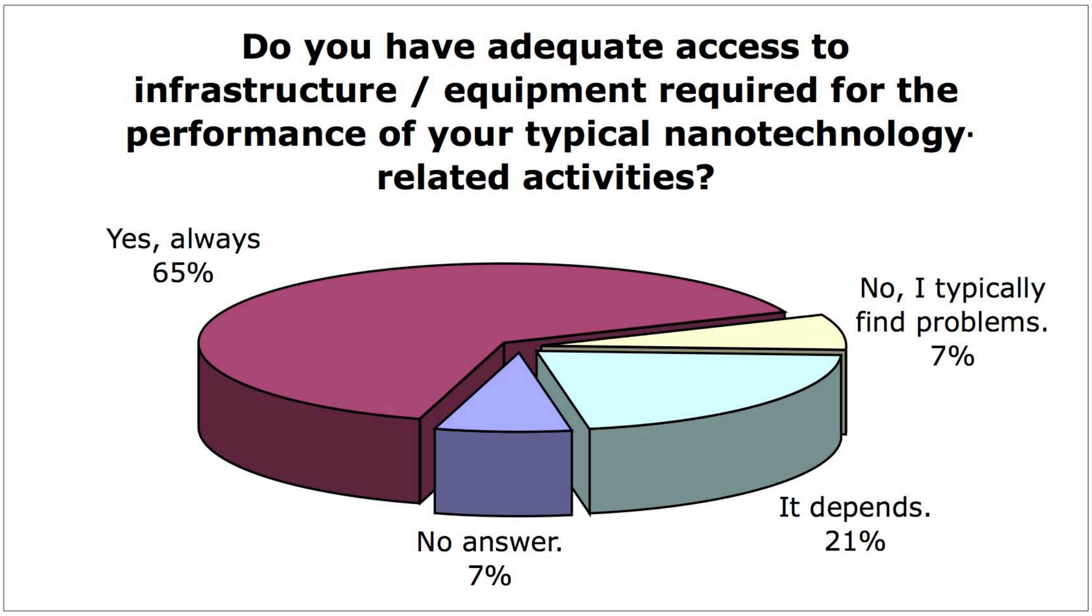
2.4.1 Legal aspects (incl. patenting systems)

One of the key aspects for nanotechnologies development is the protection of the intellectual property. 55% of the experts in the Delphi panel (including all experts from industries) think that differences between EU and US patenting systems (with the latter being less restrictive in terms of patent granting) will lead to disadvantages for Europe in the mid/long terms in the field of nanotechnology. Only 18% of the experts having answered the question do not think this would lead to disadvantages.

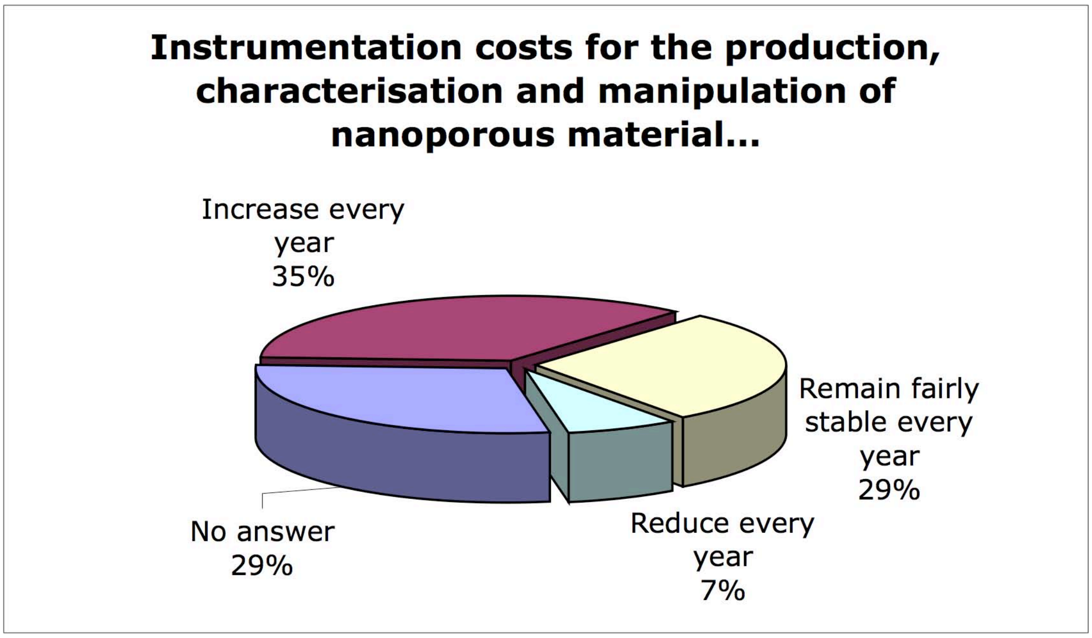


2.4.2 Infrastructure requirements and instrumentation cost

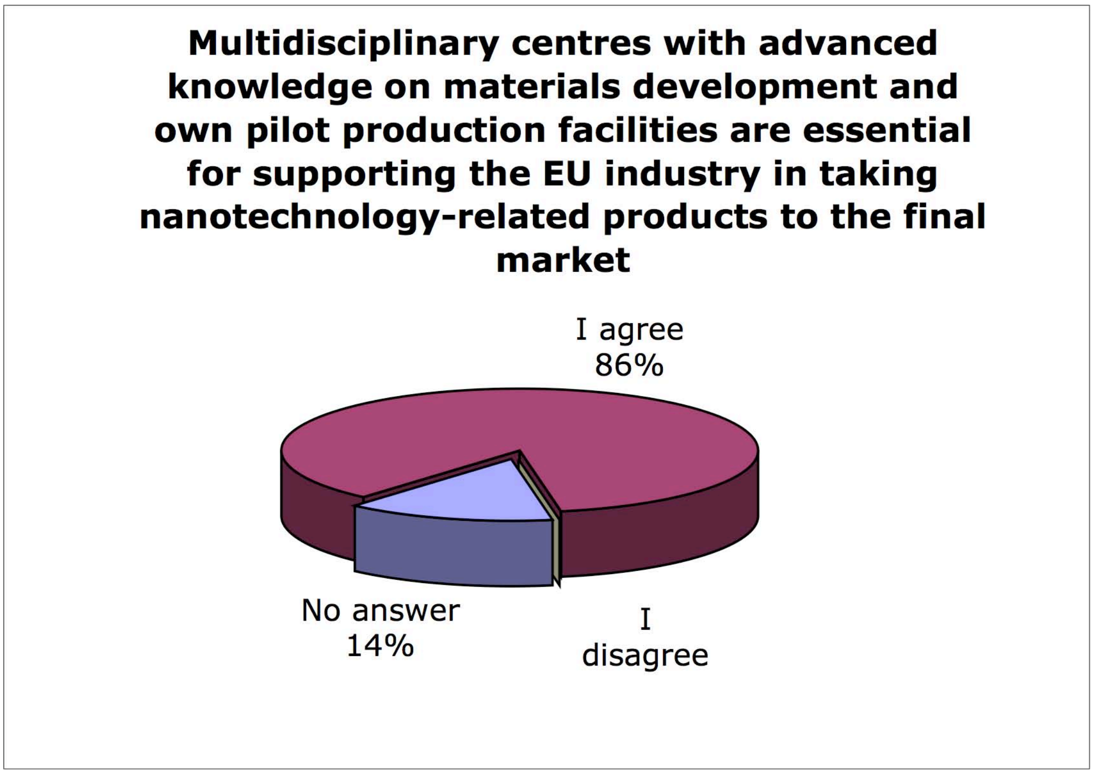
When asked about infrastructure needs required to perform the nanotechnology day-to-day work, most participants (64%) in the Delphi panel agree that they have adequate access to facilities (either internal or through existing collaborations). Less than 20% finds problems on specific situation but normally get access to the required infrastructure by partnering or collaborating with others. Experts from Eastern European countries find more problems in their day-to-day work.



Linked to the accessibility to infrastructure / equipments, experts were asked about the price evolution of the instrumentation required for the production, characterisation and functionalisation of nanoporous materials. As the figure shows, only one expert indicates that instrumentation cost is decreasing every year. All experts from industries consider that costs are steadily increasing.



Finally, experts were enquired about the suitability of having production pilot plants besides the research labs. This approach is already implemented in some advanced research centres and is proving successful. Not surprisingly, all experts agree that this type of set-up would facilitate nanotechnology up-take by European industries.



2.4.3 Health, safety and environmental aspects

In principle there are no health or safety issues deserving special attention (as is the case for nanoparticles). However, according to the experts, the recovery /recycling of either the solvents or structure directing agents needs to be considered.

Surprisingly, experts have not pointed out the need to consider the waste generated or the comparably high-energy consumption of some of the processes being considered.

2.5 Conclusions

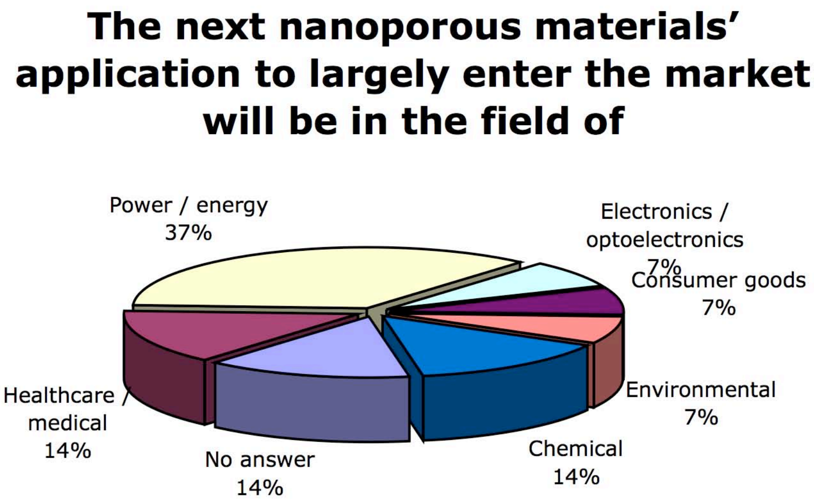
2.5.1 Most relevant applications

The fact that crucial bottlenecks identified by the experts are fundamental (e.g. understanding of structure-properties' relationships, control of pores' size, etc.) is an indication that the development of market applications of nanoporous material is not as advanced as for other nanomaterials.

In general, many of the applications could be applied in many different markets with very different requirements. For instance, nanoporous membranes could be applied in fuel cells for portable equipment but also in the chemical/petroleum industry industry. Therefore, the timing for the realization of these applications (if ever occurs) could very much vary. Also the market volume and risks associated to each of these developments might be substantially different,

Amongst the most developed applications, thermal insulation windows are already in the market, although applications combining thermal insulation properties with mechanical properties (e.g. for space applications) are still in their infancy.

According to 37% of experts, it's considered that applications related to power and energy (namely membranes and electrodes) would be the next to largely enter the market followed by health/medical and chemicals-related applications. There are no clear indications on what would come next as there are still basic research bottlenecks to be overcome.

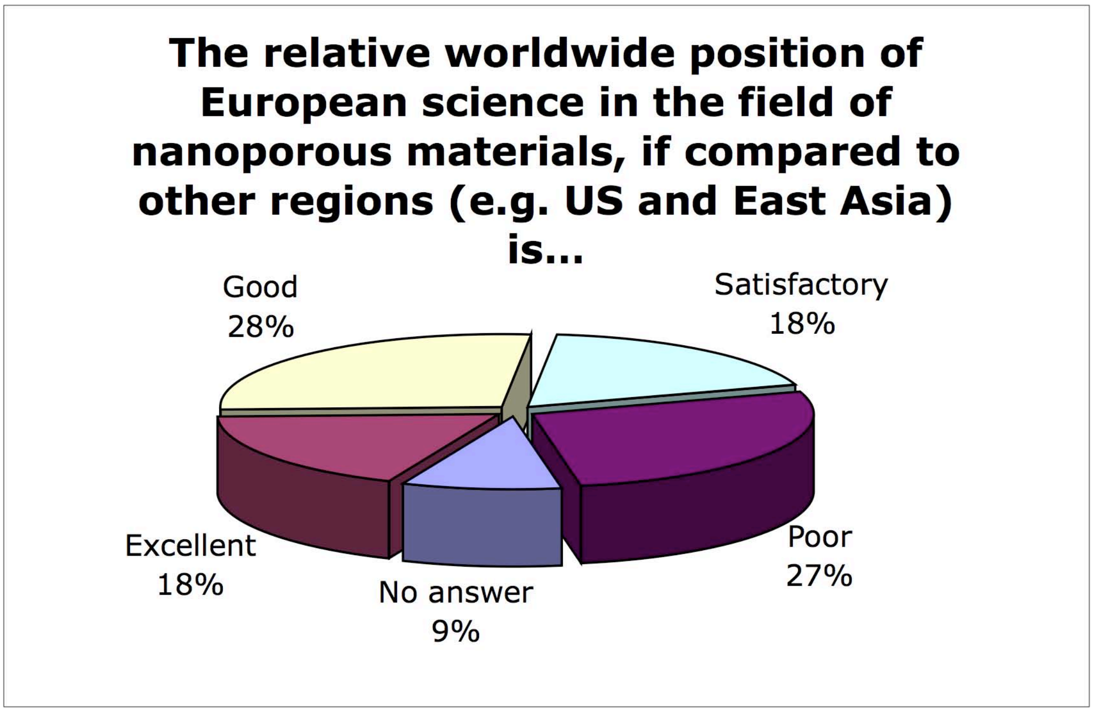


One factor that is perhaps underestimated is that most of nanoporous material applications refer to large industries (electronics, chemical, pharmaceutical). Most of these industries mostly produce commodities for which the production facilities require very high investments and long pay-off returns. Therefore, even if nanoporous materials replace existing ones (e.g. membranes), the implementation path would take several years.

Another important issue is safety and reliability. Applications such as new drug delivery systems would need to go through formal approval process by Public Authorities even if they are technologically feasible. This means passing through all clinical trials as other drug compounds do.

The case of gas storage (and especially Hydrogen storage) has got a lot of attention over last years. The fact that the hydrogen-based energy sources may at some time replace energy sources based on fossil fuels has risen the need for proper hydrogen storage. However, besides nanoporous materials, other competing solutions are being research and this substantially increases the risk of not reaching the market. Finally, the development path and market entrance (if any) would strongly depend political decisions: how heavily would governments support research on Hydrogen storage? How much environmental regulations would push industries to use cleaner power sources?

2.5.2 EU positioning in the field



According to the experts, many of the companies to be considered key players in the nanoporous material industry are large global corporations. Most cited names are DuPont, BASF, DOW and General Electric.

Among the companies cited by the experts, it’s important to notice that industries producing final products are also playing a key role in nanoporous material development. Examples include companies like Unilever, Procter & Gamble, 3M, Canon or Toshiba.

2.5.3 Final conclusions and recommendations

Main barriers

Nanoporous materials have been investigated and applied for many years prior to the word “nano” developing its present impact. Zeolites are perhaps the most well known example. Therefore, researchers focus on what nanotechnology is now able to bring them: better understanding of how materials work on a molecular/atomic scale, improving their ability to tailor pores’ characteristics (size, shapes, etc.), etc. Nanotechnology, instead of new materials, has delivered a set of tools for understanding the phenomena that occur in materials.

At this present stage, researchers are still struggling for getting the right raw materials (e.g. precursors, templates, etc.) and process set up for getting the desired properties. The lack of equipment for meaningful and quick characterisation (and not the access to equipment) is slowing down nanoporous development.

For membranes related applications, main barriers to overcome are control over pores’ characteristics and pores’ functionalisation. For applications as bulk materials, main bottlenecks are related to the pores’ framework (especially crystallinity).

In many cases pores’ collapse after templates removal is an issue of crucial importance. The availability of suitable raw materials (namely templates) both in quality and price and the reproducibility are key showstoppers to be addressed.

According to the experts, there’s a lack of understanding of industrial requirements. The fact that substantial research is devoted to get a better understanding of structure-properties' relations and not on processes development poses the risk of the production processes not being aligned to industrial requirements.

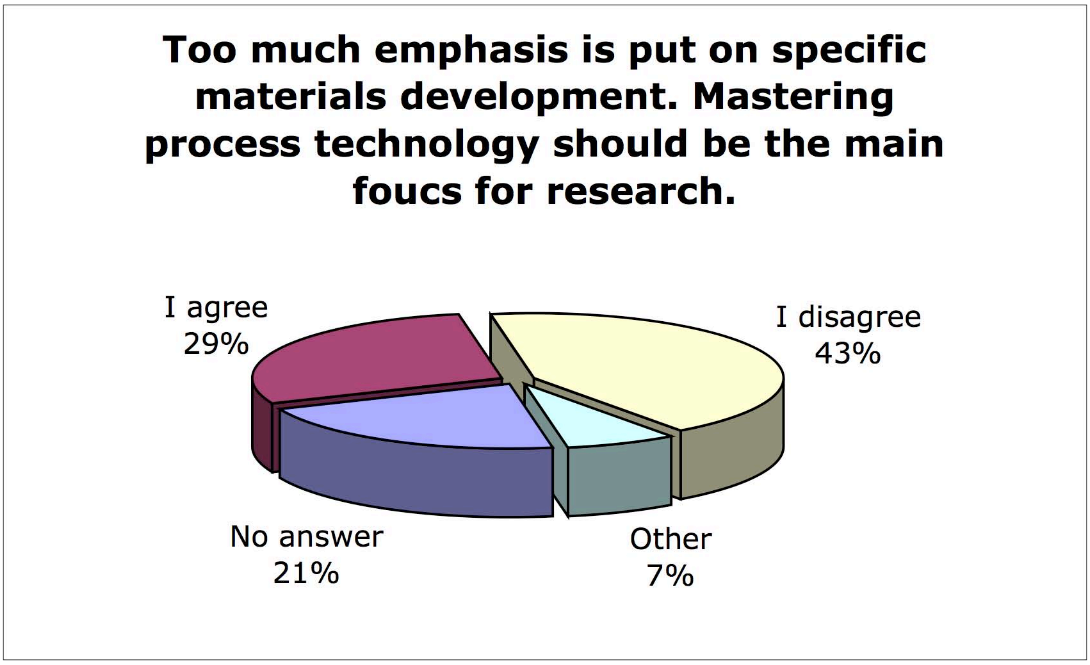
The other way around, it might be difficult for industrial organisations to understand the possibilities offered by the broad range of technologies and materials being researched. The agreement on a common terminology for production processes and even for the classification of nanomaterials would probably shed more light into the subject.

Scenarios for further development of nanoporous materials

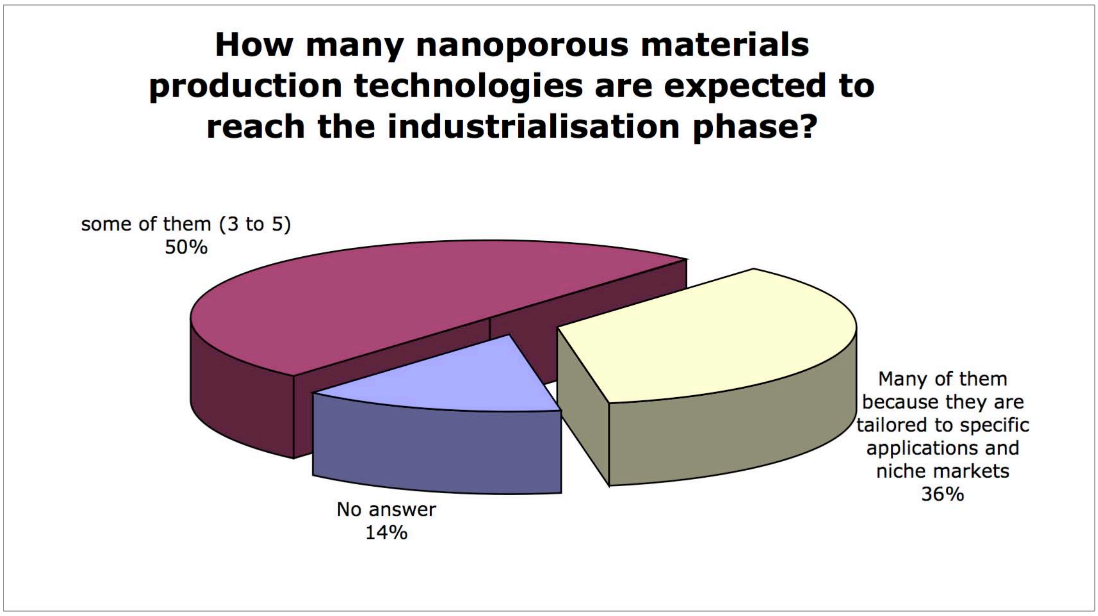
Nanoporous materials research and technology development is not as advanced as in other areas of nano-materials: only a limited number of applications would reach the first application or mass production development stage.

Besides that, there’s little interest in scaling up process technology, there are no clear “winners” identified and there’s also little awareness of environmental impact issues related to mass production.

When asked about the need to shift some efforts from materials’ research to processes’ development, most of the experts consider that efforts should still be maintained on materials’ research. This might be also an indication that there are still several bottlenecks to be addressed prior to focusing on process development. Actually, in all processes there’s at least one expert pointing out a technical bottleneck.



As pointed out in several application-oriented roadmaps (e.g. for nanoelectronics), it’s likely that many of the presently researched production techniques will never get out of the lab. However, according to the experts, there would be at least 3 production technologies reaching the industrialisation phase. None of the experts believes that 1 or 2 technologies would become technology platforms around which nanoporous materials would be developed and many still believe that many technologies will be applied by industries.



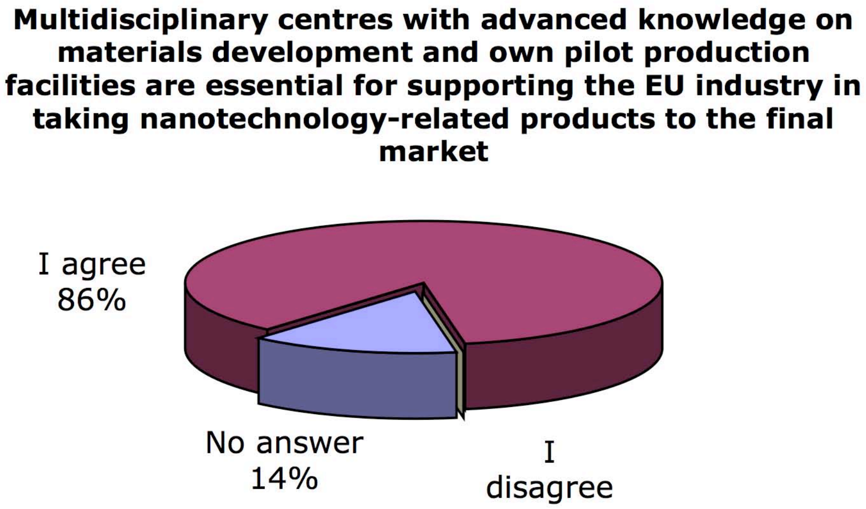
In W&W opinion, although several production technologies have the potential to provide the required material properties, industrial production requirements will very much limit the number of technologies finally adopted by industries.

Preliminary / Final recommendations

Materials & processes development will at some point in time come together and then decisions on further development would be driven by multi-criteria choices: material properties and processes/market requirements. Therefore, the sooner these multi-criteria are considered the better.

- The involvement of industry in basic research networks needs to be strengthened. Some industries are already part of networks' steering committees but that's still not a common practice. Even if they do not have voting rights when defining networks' priorities, industries could have an influence at a very low cost.
- Basic R&D projects should contain a feasibility analysis component. Dedicating a small amount of resources in this area could have a significant impact. This is especially important in public funded projects, where funding limitations normally lead to this type of work being downsized or even eliminated to have enough resources to perform the research. The fact that feasibility analyses are normally not 100% funded may also explain the lack of interest of researchers on this issue.

Anticipating that some of the materials and technologies fulfil the expectations and there's the need to scale up production technologies, W&W suggests favouring the creation of pilot production plants in (or nearby) research centres. All experts that gave their opinion on this recommendation agree that this is essential to support EU industries in taking nanotechnology related products to the final markets.



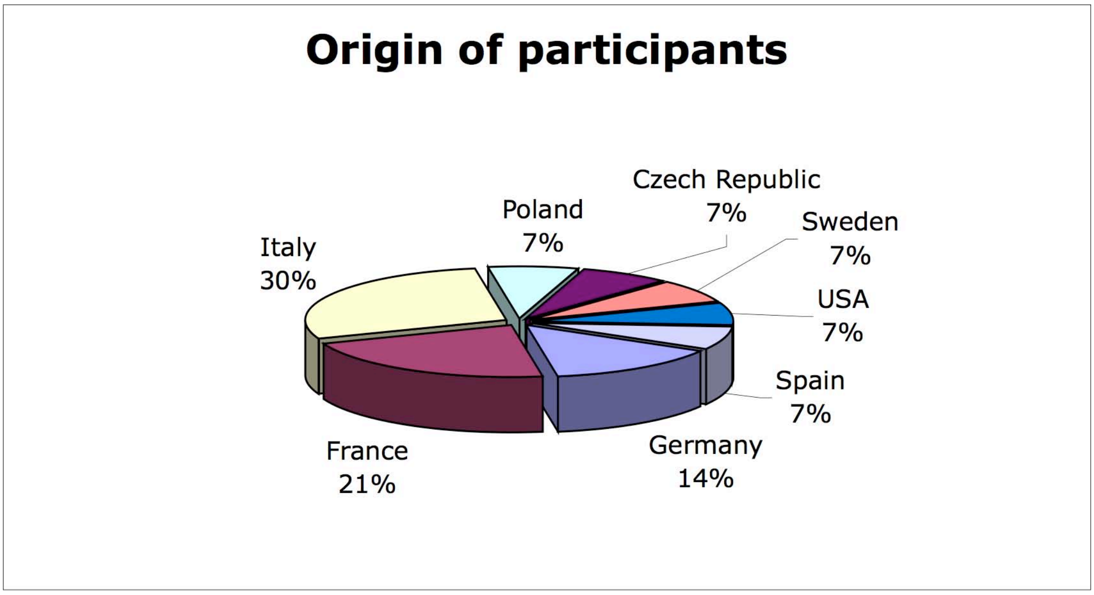
In many application areas it seems too early for SMEs to be involved. The time-to-market for many applications is too long to fit within SMEs' usual financial conditions. W&W recommend to mostly focusing SMEs' involvement in very specific/high-tech fields such as instrumentation and equipment. In this area there's a critical bottleneck to be addressed and time-to-market is much shorter. Accordingly, modelling and software tools are already needed and may become even more crucial for widespread application of nanotechnologies once other bottlenecks have been addressed.

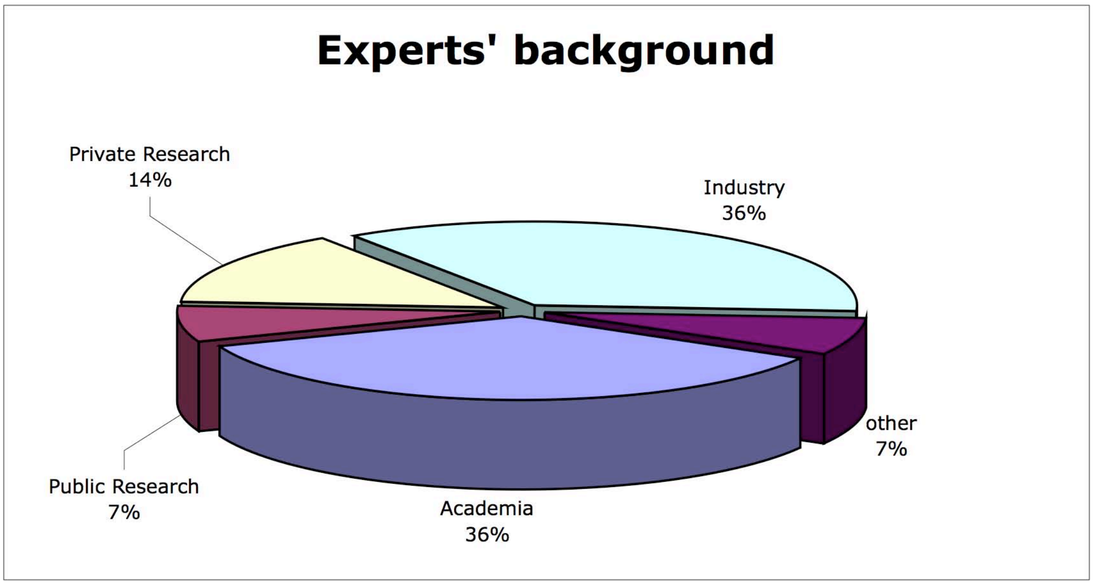
Once some of the basic bottlenecks are addressed, W&W recommends increasing the risk capital to support the scaling up of production technologies. In case those production pilot plants are built up around universities/ centres this venture capital would complement the seed capital (usually public funds) normally available for universities spin-outs.

For increasing the involvement of traditional SMEs (or even large industries), W&W recommends that sectoral organisations are actively involved in identifying and communicating business and technology opportunities derived from nanotechnology. It’s presently almost impossible for someone without a scientific background to get some clarity on what’s going on: there are many materials and many processes to get them. Above all, there is neither an even a common classification of materials nor of the processes. From a traditional company everything is too fuzzy to be able to make decisions on where to focus on.

We strongly recommend to perform a thorough analysis of all nanomaterial fields to enable a sound comparison that provides the basis for decision-making at all levels.

Annex I. Participants' background





NanoRoadMap is a project co-funded by the 6th Framework Programme of the EC

Roadmap Report on Nanoparticles

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The present document is a roadmap report prepared by Willems & van den Wildenberg (W&W) in the framework of the NanoRoadMap (NRM) project, co-funded by the 6th Framework Programme (FP6) of the European Commission.

This roadmap report is mainly based on the input received by experts participating in the Delphi-like panel. It is one of the key deliverables of the NRM project and is issued for discussion and information purposes. The views expressed do not necessarily reflect those of the European Commission.

Table of contents

1 Introduction

1.1 Background

The NanoRoadMap (NRM) project, co-funded by the European Commission (EC), is aimed at roadmapping nanotechnology related applications in three different areas:

- Materials
- Health & Medical Systems
- Energy

Within the project, an international consortium consisting of eight partners covering seven European countries and Israel, has joined forces to cover the time frame for technological development in this field up to 2015. The results of the NRM project are to be used by any European entity interested in planning an R&D strategy taking into account nanotechnology. An important potential user is of course the EC itself in the preparation of the 7th Framework Programme (FP7) for research and technology development.

For additional information on the NRM project, please refer to www.nanoroadmap.it

1.2 Goals

The primary objective of NRM is to provide coherent scenarios and technology roadmaps that could help the European players to optimise the positive impact of nanotechnology on society, giving the necessary knowledge on its future development and when technologies and applications will come into full fruition.

The key users of the reports are mainly European SMEs, research organisations, public bodies in general and the EC in particular. Even though a special focus is put on SMEs, these roadmaps are also meant to be useful for larger corporations.

This report is one of the three final deliverables of the NRM project (together with the reports on the field of Health & Medical Systems and Energy) and it is aimed at providing a thorough overview of specific topics selected for roadmapping within the field.

1.3 Methodology

1.3.1 Collection and synthesis of relevant existing information

A report was published in October 2004, as the most important deliverable of the first stage of the project. It was based on the collection and synthesis of existing public sources in 31 countries and was published as key input for the celebration of the First NRM International Conference held in Rome the 4th – 5th of November 2004. The full report can be downloaded for free on the project web site.

The report focused on reviewing the different types of nanomaterials, describing the topic, its most remarkable properties, current and future markets & applications, and leading countries & highlighted R&D activities in the field. A general review of non-technological aspects (social, legal, ethical and health and safety aspects, but also economical aspects and infrastructures requirements) was also performed.

The 12 topics identified, even not being completely homogenous in terms of scope or materials classification, were intended to adequately cover the field of nanomaterials. The following list was agreed upon the different partners of the NRM project (similar classifications can be found in the existing bibliography):

- Nanostructured materials
- Nanoparticles / nanocomposites
- Nanocapsules
- Nanoporous materials
- Nanofibres
- Fullerenes
- Nanowires
- Single-Walled & Multi-Walled (Carbon) Nanotubes
- Dendrimers
- Molecular Electronics
- Quantum Dots
- Thin Films

1.3.2 Selection of topics

Another major goal of that report was to set the basis for discussion and selection for roadmapping of 4 out of the 12 topics identified above. A preliminary selection of topics was presented during the First International Conference in November 2004.

After a thorough discussion, which involved international experts in the field of nanotechnology, four topics were selected (and validated in dialogue with the European Commission). The topics chosen are:

- Nanoporous materials
- Nanoparticles / nanocomposites
- Dendrimers
- Thin Films & coatings

1.3.3 Roadmaps elaboration

One roadmap has been prepared for each of the four aforementioned topics. The present report gathers all the work executed during this phase, and can be considered as the key deliverable for this activity. The results of these roadmaps will be presented in 8 National Conferences and one International Conference to be held in October – November 2005.

A Delphi-like approach (referred to as Delphi panel in the future) has been used for the preparation and execution of the roadmaps. The methodology followed consisted of 2 cycles, and it was the same for the four topics. The Delphi exercise consisted in:

1. Selecting top-international experts in the field (see Annex I for more information)
2. Preparing a dedicated on-line questionnaire for each topic to be roadmapped
3. Circulating the questionnaire and gathering experts' responses (1st cycle)
4. Preparing a first draft roadmap document based on the input gathered from the experts and personal interviews with some experts
5. Circulating the draft roadmap document, asking for feedback (2nd cycle)
6. Elaborating the final version of the roadmap

2 ‘Nanoparticles / nanocomposites’ Roadmap

2.1 Definition of nanoparticles

Water-repellent effect nanoparticle coating

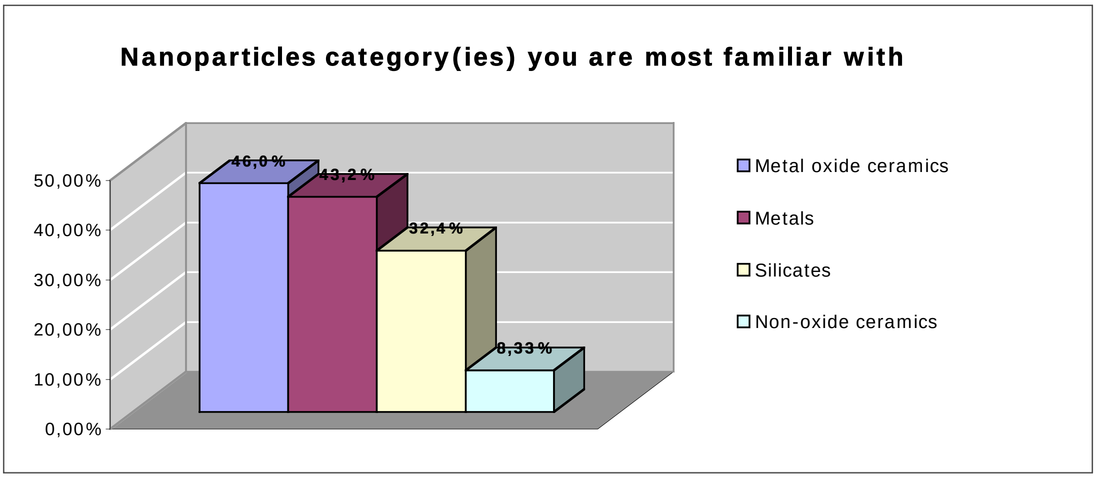
Courtesy of BASF

Despite the fact that a unique definition does not exist for nanoparticles, they are usually referred to as particles with a size up to 100 nm[1]. It can be argued that below that size, the physical properties of the material don't just scale down or up, but change. Nanoparticles exhibit completely new or improved properties based on specific characteristics (size, distribution, morphology, phase, etc.), if compared with larger particles of the bulk material they are made of.

Nanoparticles can be made of a wide range of materials, the most common being metal oxide ceramics, metals, silicates and non-oxide ceramics. Even though nanoparticles of other materials exist, e.g. those based on polymer materials or compound semiconductors, the former categories count for the most part of current applications.

Nanoparticles present several different morphologies (flakes, spheres, dendritic shapes, etc.). While metal and metal oxide nanoparticles in use are typically spherical, silicate nanoparticles have flaky shapes with two of their dimensions in the range of 100-1000 nm. They are generally designed and manufactured with physical properties tailored to meet the needs of the specific application they are going to be used for.

According to the participants in the Delphi panel, these are the categories of nanoparticles they are most familiar with:



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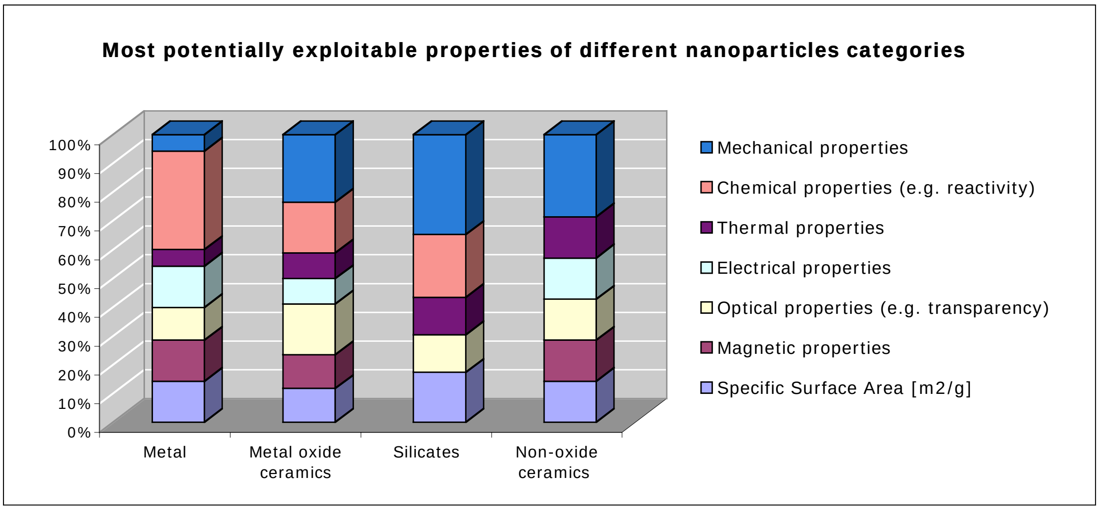
[1] It should be noted here that there are two signficant areas of application where the critical dimension is substantially above the 100 nm range: biological and light-related applications. Substantial work using nanoparticles for drug delivery uses particles up to 400 nm or more, which is still small enough to be biologically significant. For light-based applications, it is worth remembering that light wavelengths (UV and visible) are measured in hundreds of nm.

Some other nanomaterial categories could fall within the category of nanoparticles (e.g. spherical fullerenes, dendrimers or quantum dots). However, for concreteness purposes, these have not been included in this roadmap.

2.2 Most remarkable properties of nanoparticles

Nanoparticles exhibit completely new or improved properties based on specific characteristics (size, distribution, morphology, phase, etc.), if compared with larger particles of the bulk material they are made of.

According to the experts that have participated in the Delphi panel, the most potentially exploitable properties of nanoparticles are:



Specific Surface Area [m2/g]

Nanoparticles present a higher surface to volume ratio with decreasing size of nanoparticles. Specific surface area is relevant for catalytic reactivity and other related properties (e.g. sensors), although stabilization of the surface area, nanoparticles topology (roughness) and interface with support-material are also relevant aspects.

Good examples of this are *noble-metal* based catalysts where very high surface areas and high support porosity lead to superior catalytic activity compared to state-of-the-art catalysts. This property is also exploited in *metal oxide* catalysts (e.g. cerium oxide for automotive catalysts).

As specific surface area of *metal particles* is increased, their biological effectiveness in certain applications can increase as well due to the increase in surface energy. Silver nanoparticles, for example, are used in antimicrobial applications. In addition, an increase in specific surface area decreases sintering temperature of metal nanoparticles.

For use as polymer filler, high surface area gives strong polymer/filler interaction, resulting in more efficient reinforcement at lower loadings. This results in improved material performances and can result in cost reductions through use of less material, though increased cost of nanoparticles can offset this.

The sheet like structure and the ability to get a very high specific area for a relatively low addition of *silicates* to a polymer material can create a physical structure that serves as a barrier to gases (low gas permeability) or low Mw substances by vastly increasing the average path the molecule needs to permeate the material. This can be used in automotive fuel systems and films for a variety of applications including food and chemical packaging. It is also relevant for flame retardancy applications. Nanoparticles show considerably higher flame retardant capabilities for relatively small surface area, converting them into a suitable replacement for halogen-based flame retardants.

Magnetic properties

The decrease of the particle size to the nano-range results often in improved magnetic behaviour (as compared to their bulk counterparts). For example, there are excellent soft magnetic materials (applicability in transformers, various sensors, etc.) and also hard magnetic materials (so called exchange spring magnets), which are composed of nano-sized building blocks.

Two major applications benefiting from the above are high density media storage and medical applications. Nanoparticles can be used as data storage materials, if uniformly dispersed in a matrix or substrate. *Metal* nanoparticles have use as marker materials (ferrofluidics) for biofluids. Individual metallic magnetic nanoparticles (often with core / shell structure) can exhibit super-paramagnetic behaviour and they could be used in various medical applications such as drug delivery (e.g. Ni and Fe), hyperthermia and MRI contrast agents. Polymer composites with nanoparticles such as ZnO, TiO, CdS, CdSe, ZnSe and PbSe can be also used in medical imaging and genetic materials manipulation.

Optical properties (e.g. transparency)

The absorption or emission wavelength can be controlled by size selection, interaction with ligands and external perturbations. For example, transparency can be achieved if the nanoparticle size is below the critical wavelength of light.

This makes nanoparticles (e.g. metals, silicates or metal oxide ceramics) very suitable for barrier films and coating applications, combining transparency with other properties (UV, IR-absorption, conductivity, mechanical strength, etc.). In addition, interesting optical (light absorbing/filtering) properties can be used for cosmetic applications.

Optical properties are also especially relevant for *surface plasmon resonance*. *Metal* nanoparticles have been used for high-sensitivity sensors and for enhanced imaging in microscopy of biological samples.

Metal oxide ceramic nanoparticles are high band gap materials that can be doped with suitable emitters. Rare earth oxide matrices doped with an emitter are being researched in order to decouple the optical properties of the matrix from those of the dopant. In this perspective, having large gap matrices is an advantage that covalent semiconductors materials cannot provide. Other examples of optical applications of oxides include zirconia (ZrO_2) nanoparticles, which are being used as *index matching* and improved scratch resistance or ceria (CeO_2) nanoparticles, used as a transparent abrasion/UV resistant coating.

Electrical properties

Transport can be controlled via the individual properties of the nanoparticles. For example, the chemical nature and the size control the *ionic potential* (IP) or the *electron affinity* (EA). When self-assembled, a further control is possible via the magnitude of the inter particle coupling through the ligand nature and length or by applying mechanical pressure, which is relevant for electronic and logic applications.

Metal nanoparticles, as opposed to non-metal ones, typically have more point-to-point contacts available, allowing for a thinner layer and a more reliable electrical path. This is applied in conductive silver ink and other electronic and opto-electronic applications.

Metal oxide ceramic nanoparticles can be used to obtain special devices with special response to electromagnetic waves. Very high surface areas of this type of particles together with surface treatment might dramatically improve performance in insulation systems such as field grading properties and break down strength. These nanoparticles have potential uses in novel electronic packaging materials.

Thermal properties

If homogeneously disseminated, metal nanoparticles can achieve significant improvement in thermal properties for polymer systems, leading to faster processing time. Sintering and melting temperature decrease with decreasing size of nanoparticles. For example, the sintering temperature of silver nanoparticles below 100 nm can be as low as 150 ºC.

High thermal conductivity is required for some applications. Small particles may be incorporated better in base matrix (e.g. without reducing strength) and provide better thermal conduction.

It is widely known that layered *silicates* generally improve the heat deformation temperature of a thermoplastic compound, i.e. the temperature where an object of certain dimensions begins to deform under a specified load. This can widen the use of low cost thermoplastics to environments where only far higher-cost polymers have been used. For example, cheap polypropylene compounds could replace more expensive polyamides in applications under the bonnet in a car. Whether the thermal stability (oxidative stability) can be improved is under dispute since it is clear that highly accelerated tests benefit from the barrier effect that the silicates provide to the degradation products formed within the matrix and hence shifting the equilibrium away from degradation. In real life however, silicates actually seem to promote degradation in most cases.

Silicates can influence[2] the flammability of polymers, increasing the *Glass transition Temperature* (Tg) and the *Heat Deflection Temperature* (HDT). Such properties can be useful for the building and the mining industries.

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[2] Silicates can sometimes act synergistically with traditional flame retardants. This synergism can be exploited so that more economical formulations can be made (by using less amounts of expensive flame retardants). Also more environmentally friendly formulations can be made if the synergism makes it possible to use less amounts of an environmentally hazardous component. In addition, the mechanical performance is often improved when adding silicates, because traditional flame retardants typically reduce the mechanical performance of the composite.

Chemical properties (e.g. reactivity)

Reactivity can be considered the most relevant aspect for catalysis and related applications (sensors, etc.). Combining reactivity and catalytic activity hits some important application fields, such as fuels (and fuel additives), fuel cells and explosives. Catalysis is enhanced by high surface area / volume ratio and potential homogenous distribution of nanoparticles. For example, gold and platinum nanoparticles have the potential to be exploited as catalysts (e.g. use of Pt nanoparticles in fuel cells and in catalytic converters).

Metal nanoparticles can be used for biocide applications. As said before, stable silver nanoparticles can be prepared in a form suitable for effective biocide water-born polymeric coatings, and have also been incorporated into antibacterial ceramics for bathrooms fixtures. Increased protective properties of coatings can be also achieved by adding metal nanoparticles (e.g. Zn, Pb, Mn). Metal particles can be relatively easily functionalised, which could be used to drive self-assembly (e.g. structured materials) or for binding to substrates (e.g. biological sensors, controlled drug delivery mechanisms, etc.).

Doping polymer composites with complex *oxide nanoparticles* dramatically increases service properties of the composites during exposure in strong aggressive media. Again (i.e. as with metals) it's the chemical, especially catalytic, properties of metal oxides that are showing the most interesting potential. Transparency is often an essential co-ingredient, as in photocatalytic self-cleaning windows (and can even be a key property on its own, as in the well-known sunscreen applications).

Rare earth oxides are sensitive to air moisture and other contaminants. The chemical reactivity can therefore strongly influence the surface properties, in particular the light emission from dopants present on the surface. Besides, the high surface to volume ratio enhances this effect and makes the nanometre scale crucial to take advantage of it. *Silicate nanoparticles* undergo ion exchange readily, which allows them to be rendered compatible (improve compatibility) with a wide range of polymers for preparing composites at low cost. Chemical resistance can be used by the building industry. Also suitable for sensor applications.

Mechanical properties

Depending on the chemistry of the nanoparticle, its aspect ratio, dissemination and interfacial interactions with the polymers (regulated through surface coating and compatibilising agents into the polymer formulation), it is possible to obtain different reinforcing levels on mechanical properties of the final composites.

Metal oxide ceramic nanoparticles can be used to increase the mechanical strength in special alloys, resulting also in lower weight materials. Depending on the chemistry of the metal oxide, its morphology and interfacial interactions with the matrix material, different effects on mechanical properties of the final composite can be obtained (e.g. high or low stiffness, strength, toughness, etc.). This can be achieved at relatively low particle volume fractions.

Silicate nanoparticles are also used to improve mechanical strength in composites, allowing for low-weight and still strong materials. Silicates have been proven to increase mechanical properties in a way that larger particles are unable to. Especially a high elastic modulus can be achieved without the proportional loss in impact strength that is observed when larger reinforcing particles are used. As a result, this can widen the use of low-cost thermoplastics to environments where only much more expensive polymers have been used. Thus, nanocomposites from layered silicates can exhibit significantly improved mechanical properties (e.g. modulus, tensile strength and wear resistance) compared to the pure polymers. These properties can be important for packing or injection of moulded parts (e.g. in the automotive industry).

Metal nanoparticles can also be used as mechanical reinforcement (enhanced toughness) in metal-ceramic nanocomposites. *Non-oxide ceramic nanoparticles* also result in an improvement in modulus, fracture toughness and interlaminar shear strength.

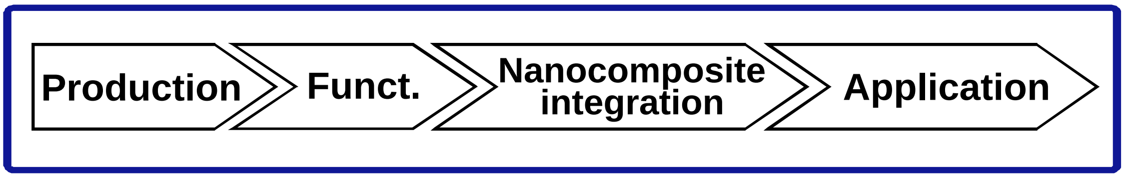
In spite of this, and according to the opinion of some experts, certain nanoparticle-based composites will have a brief heyday and then be overtaken by nanotubes composites. There is no doubt that in terms of mechanical properties, nanotubes are poised to make a very important contribution to this field, as has been already shown by a number of research groups.

Other properties

Other properties of nanoparticles have been mentioned, such as their *high density data storage*. However, this can be considered more an application field than a property itself (stemming mainly from their magnetic behaviour). There is a high potential to increase the data storage density by using special arrangement of high anisotropy magnetic nanoparticles (to avoid super-paramagnetic behaviour). Here, the self-organized nanostructures can be used. Other properties pointed out include *biological properties/bioactivity.* Again, this has not been considered a property itself, but as a combination of the high specific surface area and chemical properties of nanoparticles.

2.3 The nanoparticles / nanocomposites pipeline

This section reviews the different steps in the nanoparticles pipeline: production and functionalisation of nanoparticles, (potential later) incorporation into nanocomposites and final application (including nanocomposites, amongst others). The step of the incorporation of nanoparticles into nanocomposites has been included because of the extreme importance of this issue for the research and industrial communities at the moment.



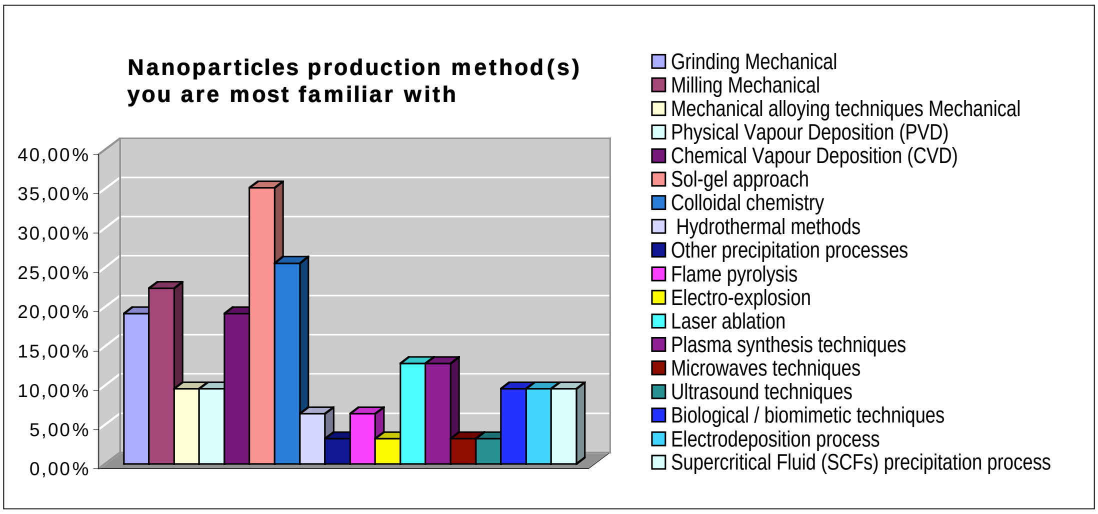
It should be remarked that this is not always a linear approach with sequential independent steps. In many cases each and every different application has one or a few specific production, purification and functionalization processes to obtain the desired properties for the lowest amount of time and money. Also, some processes combine steps; for example sol gel processes combine the creation of particles with their dispersion / integration into a matrix material.

2.3.1 Nanoparticles production

Production of nanoparticles can be achieved through different methods. Most common approaches include Solid state methods, Vapour methods, Chemical synthesis / Solution methods and Gas-phase synthesis methods.

According to the experts in the Delphi panel, the main barriers for the success of nanoparticles production can be considered the high price and certain technical barriers. Lack of appropriate equipment and environmental problems are also a barrier in limited cases. However, this depends very much on the production method followed for the production of nanoparticles.

The following paragraphs give an overview of the main barriers indicated by the experts in the Delphi panel for each of the methods presented below. According to the experts, these are the methods that they are most familiar with:



Solid state methods

These methods are quite well established, and have been used for an amount of years now. Here, certain technical barriers, price and the unavailability of more appropriate equipment have been pointed out by the experts as key barriers.

Grinding

The achievement of homogeneous size distributions can be considered the most important barrier associated to this process. Some environmental barriers also exist, and comprise mainly the generation of high waste volumes.

Milling

Issues related to the final quality of nanoparticles produced and the contamination of nanoparticles by milling media can be considered key barriers. High manufacturing cost as well as heterogeneous size distribution is identified as the main drawbacks of milling techniques.

Mechanical alloying techniques

This section mainly refers to *silicate* nanoparticles in thermoplastic compounds. Here, it is a matter of applying the maximum amount of processing and still keeping the cost down (technical/price barrier). Output, energy and supporting additives must be optimized to get a cost effective manufacturing process. Some experts think that this is an expensive and slow process, which is only possible on bulk for limited materials and applications.

Vapour methods

Vapour techniques are used for the production of metal and metal oxide ceramics. According to the experts price can be considered the key barrier in vapour methods.

Physical Vapour Deposition (PVD)

In general, this method is expensive, generating low volumes of material. Higher throughput at lower cost is required for the success of this production method at the industrial level.

Chemical Vapour Deposition (CVD)

The same arguments can be used for CVD. Thus, price should be seen as the main barrier, with chemical approaches being cheaper and possibly better to control, according to the opinion of some experts. Some other experts have also indicated the lack of appropriate equipment as another important barrier for the success of CVD methods. However, the development of commercial equipment will help to solve this problem, according to the same sources.

Other vapour methods include **Vacuum Evaporation on Running Liquids (VERL)**.

Chemical synthesis / solution methods

According to the participants in the Delphi panel, chemical approaches are the most popular methods for the production of nanoparticles. In general, certain technical barriers (as opposed to e.g. price or environmental barriers) can be pointed out as the main drawback for their success. In general, additional processes need to be carried out to prevent agglomeration. Finding suitable *passivating* groups that are used to also functionalise the particles is an important area of research in itself.

Sol-gel approach

There are difficulties in simultaneously controlling all parameters. For this reason, reproducibility is often an issue. In general, low yields are obtained by using the sol-gel approach. However, upscaling capabilities are expected to resolve the problem. Agglomeration is also a concern when using sol-gel approaches. To finalise, there are minor environmental problems, such as large volumes of contaminated solvent (usually water) to deal with.

Colloidal chemistry

The main problems are reproducibility between batches and producing particles in large quantities. According to the experts, controlled scale-up of commonly used methods can solve both problems today, provided that there is a sufficient market demand to justify the cost. Another important barrier is finding the appropriate *surfactant* that will eliminate agglomeration of the nanoparticles. Environmental problems identified for the sol-gel approach are also applicable to this method.

According to some sources, colloidal chemistry methods will continue to be developed over the next 5-10 years.

Other precipitation processes include **hydrothermal methods.**

Gas-phase synthesis methods

Flame pyrolysis

Flame pyrolysis can be considered a relatively fast method. On the other hand, surface morphology and purity are key problems related to this process.

Electro-explosion

This is an expensive and slow process, according to the experts; only possible on bulk for certain materials and applications.

Laser ablation

This method requires expensive equipment, with very low deposition rate on the other hand (as compared to chemical routes). In general, it is an expensive process due to energy conversion inefficiencies.

Plasma synthesis techniques

Certain environmental problems and price are important issues when using this technique. According to the opinion of some experts, chemical approaches are cheaper and possibly better to control. Nevertheless, other experts think that main barriers are already overcome. In fact, some notable industrial corporations are using it for the production of e.g. metal nanoparticles. Some problems (e.g. upscaling) are being addressed and will be solved within a short timeframe, according to the same source.

Other novel production methods

Microwaves techniques, for example, are expensive processes due to energy conversion inefficiencies. Other methods include **ultrasound techniques** (which can be used in conjunction with some other techniques) and **electrodeposition processes**, which main barriers can be considered of a technical nature. **Biological / *biomimetic* techniques** face also important technical barriers. Better scientific understanding is still needed, but is improving all the time, according to some experts. Some of these techniques promise enormous versatility and are now only in the earliest stages of exploration. Large-scale synthesis would be another major hurdle to be overcome. **Supercritical Fluid (SCFs) precipitation process** is a quite complex process, requiring costly equipment. According to some experts, upscaling problems could be overcome using existing know-how (e.g. from food processing and pigments industries) if market demand for high-purity nanoparticles is sufficient.

Other production processes mentioned include **Combustion synthesis via urea or citric acid processes**, which could be adapted for continuous production, **delamination of layered materials** (e.g. natural clays, synthetic LDH) and **controlled crystallization from amorphous precursors** (e.g. for metal nanoparticles). According to some experts, the latter is a relatively convenient way to prepare nanoparticles embedded in amorphous matrix (no need of further surface *passivation*) but this technique is suitable for the limited system compositions (with high nucleation rates and slow growing rates).

2.3.2 Nanoparticles functionalisation

After nanoparticles are produced and purified to a satisfactory level it can be necessary to *functionalize* them. This is an intermediate process that prepares them to be used for certain applications. Nanoparticles can be functionalised in many different ways. Most commonly used functionalisation methods include coating and chemical modification of nanoparticles.

Functionalization is an extra step that will add cost to the total production chain but can have such marked effects that in some cases it is necessary to use. The main barriers associated to nanoparticles functionalisation methods can be considered technical, but also high costs associated. Additional information about nanoparticles functionalisation methods can be found below.

Coating of nanoparticles (e.g. stabilizers, hydrophilic/-phobic substances)

Many chemical compounds have been identified as materials that could be used as nanoparticles' coatings, including alkanethiols, polymers and proteins. The control of the reactions with the passivating groups and particles is a key issue, because it is difficult to build atomic structures with precise chemical control.

Metallic particles are highly oxidizable; therefore, their stabilization by suitable passive surface layer is normally necessary. A promising technique could be the preparation of core/shell nanoparticles by various gas phase synthesis methods such as arc-discharge, etc. The *passivation* treatment should be completed before exposing the nanoparticles to the ambient air. The coating of the nanoparticles by various hydrophilic/-phobic substances is another important issue, which is, according to the opinion of experts, in rather developed stage.

For sensor and imaging applications, the coatings used are typically bio-molecules (e.g. streptavidin), which are difficult to produce at high purity. The cost is unlikely to fall in the near future, but this is not necessarily a main barrier in high-value applications, as the overall quantities of coating required are small, typically mg. scale for pilot projects.

According to the opinion of the experts, there are no major technical barriers, apart from ensuring an homogeneous coating. Relatively standard chemical processes can be applied for the coating of nanoparticles. For the coating of *silicate nanoparticles*, a key issue to consider is finding the appropriate chemistry to make the silicates compatible with different polymers.

As already said the specific coating process to apply depends very much on the final application; for that reason it is very difficult to give a concrete estimation of final cost added by this functionalisation method. Nevertheless, it could be estimated at some 10-50%, according to the participants in the Delphi panel.

Chemical modification of nanoparticles

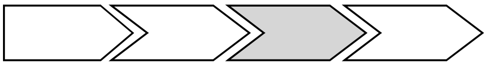
A key issue here is finding the appropriate *surfactant* to modify the nanoparticles in question. In general, the chemical modification of nanoparticles requires an additional step; however, in situ approaches are being currently developed.

Modification step in e.g. *silicate* nanoparticles is still quite expensive due to the requirement to work in a low concentration aqueous solution for most modifications. In addition, there are certain environmental hurdles. Large volumes of solvent are required, which is costly to recycle on industrial scale. However, this barrier could be overcome by using closed-loop processes.

According to the opinion of some experts, there are no major technical barriers, because relatively standard chemical processes are applied. In any case, the modification depends very much on the final application, making it difficult to estimate costs associated.

In spite of this, experts participating in the Delphi panel indicate that the final cost added by this functionalisation method can be again estimated at some 10-50% of the final cost.

2.3.3 Nanocomposites incorporation



Nanoparticles can be incorporated into polymeric nanocomposites, resulting in e.g. improved mechanical, electrical and optical properties, better barrier and flame retardant behaviour, etc. There are several methods for doing this, the most common ones being the incorporation by melt compounding or during polymerisation. The following paragraphs (based on the information given by the participants in the Delphi panel) give a condensed overview of such methods.

Incorporation by melt compounding (mixing into a composite ‘melt’)

The general perception is that for e.g. silicate nanoparticles, price for the functionalized silicates is still too high, considering the cost / performance ratio. According to some experts, the cost of nanoclay and required additives adds generally more cost to thermoplastic nanocomposites than can be motivated by the benefits they provide.

An example of the above is that the smallest available lab scale melt compounding equipment (e.g. *Brabender Plastograph*) requires 40 ml sample volume. Even at 1% loading, the cost of preparing an adequate amount of nanoparticles for compounding trials can be prohibitive if those particles must be functionalised first. The volume cannot be reduced given the quantity needed to prepare test pieces to ISO or ASTM standards. Nanoparticles can be prepared by colloidal methods at multi-gram scale today: the cost of functionalising is unlikely to fall in the near future.

Nevertheless, there are a few examples where the perception expressed above is not always shared by the experts. When using nanocomposites as flame retardant compounds, it is well accepted that silicate nanoparticles must be combined with traditional flame retardants to have sufficient flame retardancy. This means that the total content of fillers can be reduced so that the final price becomes more attractive.

Silicates and melt must be chemically compatible, which requires careful formulation. Finding the appropriate nanoparticle modification to allow nanoparticles to be suitable for compounding with the other material components is a key issue here[3]. Homogenous mixing without agglomeration is also difficult at the moment. It is the opinion of some experts that difficulties will be reduced over the next 5-10 years, as more formulation know-how becomes public.

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[3] When a polar polymer is used, it is well known that nanocomposites are generated quite fast, even if not using the most appropriate compounding machines, such as rolling mills. Polarity can be considered the most important key factor for a fast and efficient nanocomposite formation, according to some experts. The problem to be solved are the commodities, which are non-polar, such as PP and PE.

Incorporation during polymerization

In general, this method is more difficult than the previous due to reactivity issues. Compatibility problems, however, are being solved by intensive research. Estimations given by some experts indicate that it could take around 5 years to fully understand all solutions.

Others methods

The **controlled crystallization from amorphous precursors** (e.g. for metal nanoparticles) is another method. As said before, this is a relatively convenient way to prepare nanoparticles embedded in amorphous matrix (no need of further surface passivation). However, this technique is only appropriate for limited system compositions (with high nucleation rates and slow growing rates).

Additional methods pointed out by the experts include **blending and hot (dry/wet) isostatic pressing**, ***plasma spraying* techniques** and **co-evaporation / co-deposition** methods, which are used for example with metal oxide ceramic nanoparticles. In the latter, the main barrier is the low quantity of materials produced. These methods, however, are mainly dedicated to thin film applications, e.g. nano-electronics, nano-optics or simply for the enhancement of mechanical properties of surfaces.

2.3.4 Nanoparticles applications

Applications involving nanoparticles are almost endless. The following list is an extensive selection of the most common.

Power/Energy

- Dye-sensitized solar cells (e.g. using TiO_2)
- Hydrogen storage (e.g. using metal hydrides)
- Improved anode and cathode materials for solid oxide fuel cells
- Thermal control fluids (e.g. using Cu)
- Environmental catalysts (e.g. ceria in diesel)
- Automotive catalysts
- Miniaturised varistors (e.g. doped ZnO)

Healthcare/medical

- Targeted drug delivery (e.g. insulin)
- Nanospheres for inhaling drugs (currently injected using biocompatible Si)
- Bone growth promoters
- Anticancer treatments
- Coatings for implants such as hydroxyapatite
- Sunscreens (e.g. using ZnO and TiO_2)
- Molecular tagging (e.g. CdSe)
- Carriers for drugs with low water solubility
- Antibacterial wound dressings (e.g. using Ag)
- Fungicides (e.g. using ZnO)
- Biolabeling and detection (e.g. using Au)
- MRI contrast agents (e.g. using superparamagnetic iron oxide)

Engineering

- Cutting tool bits (e.g. WC, TaC, TiC, Co)
- Spark plugs (e.g. using nanoscale metal and ceramic powders)
- Controlled delivery of herbicides and pesticides
- Chemical sensors
- Molecular sieves
- Abrasion-resistant coatings (e.g. using alumina, $Y\text{-}Zr_2O_3$)
- Nanoclay-reinforced polymer composites
- Lubricant / hydraulic additives (e.g. Cu MoS_2)
- Pigments
- Self-cleaning glass (e.g. using TiO_2)
- Propellants (e.g. using Al)
- Structural and physical enhancement of polymers and composites
- Thermal spray coatings (e.g. based on TiO_2, TiC-Co)
- Inks: conducting, magnetic, etc. (using metal powders)
- Flame retardant polymer formulations

Consumer goods

- Anti-counterfeit devices
- Packaging using silicates
- Ski wax
- White goods
- Glass coatings for anti-glare, anti-misting mirrors (e.g. using TiO_2)
- Sports goods: tennis balls, rackets (e.g. using nanoclays)
- Water- and stain-repellent textiles
- Pyrotechnics and explosives (e.g. using Al)
- Additives in paints

Environmental

- Water treatment
- Self-cleaning glass (e.g. using TiO_2 based nanostructured coatings)
- Photo-catalyst water treatments (e.g. using TiO_2)
- Anti-reflection coatings
- Tiles coated (e.g. using alumina)
- Sanitary ware
- Soil remediation (e.g. using Fe)

Electronics

- Nanoscale magnetic particles for high-density data storage
- EMI shielding using conducting and magnetic materials
- Electronic circuits, NRAM. (e.g. using Cu, Al)
- Display technologies including field-emission devices (e.g. using conducting oxides)
- Ferro-fluids (e.g. using magnetic materials)
- Optoelectronics devices such as switches (e.g. using rare-earth-doped ceramics)
- Conductive coatings and fabrics (e.g. using rare-earth-doped ceramics)
- Chemical mechanical planarization - *CMP* (e.g. using alumina, silica, ceria)
- Coatings and joining materials for optical fibres (e.g. based in Si)

It is very difficult to accurately foresee a future in an area that is still developing as rapidly as the nanoparticle sector is. The following paragraphs, however, give an integrated overview of the different stage of development of the applications listed above. They are based on the estimates provided by the experts in the Delphi panel. The following three paragraphs each cover one “snapshot” of the overall nanoparticles roadmap. One for the current state of the art, one for the state of the art as predicted in five years from now (2010) and one in ten years from now (2015). The following distinctions have been made in the next figures:

Basic Research & Development Phase (Basic R&D)

Applications in this phase have received the interest of at least one, or more researchers in the world. Some applications might still be in early development, while other are tough to develop and need a lot of basic research to be fully understood.

The object of basic R&D is to validate the original hypothesis. Various applications are currently in this phase.

Applied Research & Development Phase (Applied R&D)

After the hypothesis is validated, research typically (but not necessarily) moves from pure research labs to more commercial labs and companies.

Applied R&D will eventually result in a proof of concept, a successful demonstration model. While the production issues might not have been solved yet, a successful prototype / model has been validated.

Production Research & Development Phase (First applications)

After first demonstrator models and prototypes, initial, usually prohibitively expensive, small amounts of products may be produced. At the same time, if these prove successful, companies will seek to upscale production processes.

Generally at some point, demand increasing sufficiently to offset the investment needed to start bulk production. This phase ends at that point when is clear and possible to start this bulk production.

Mass production and incremental research (Mass production)

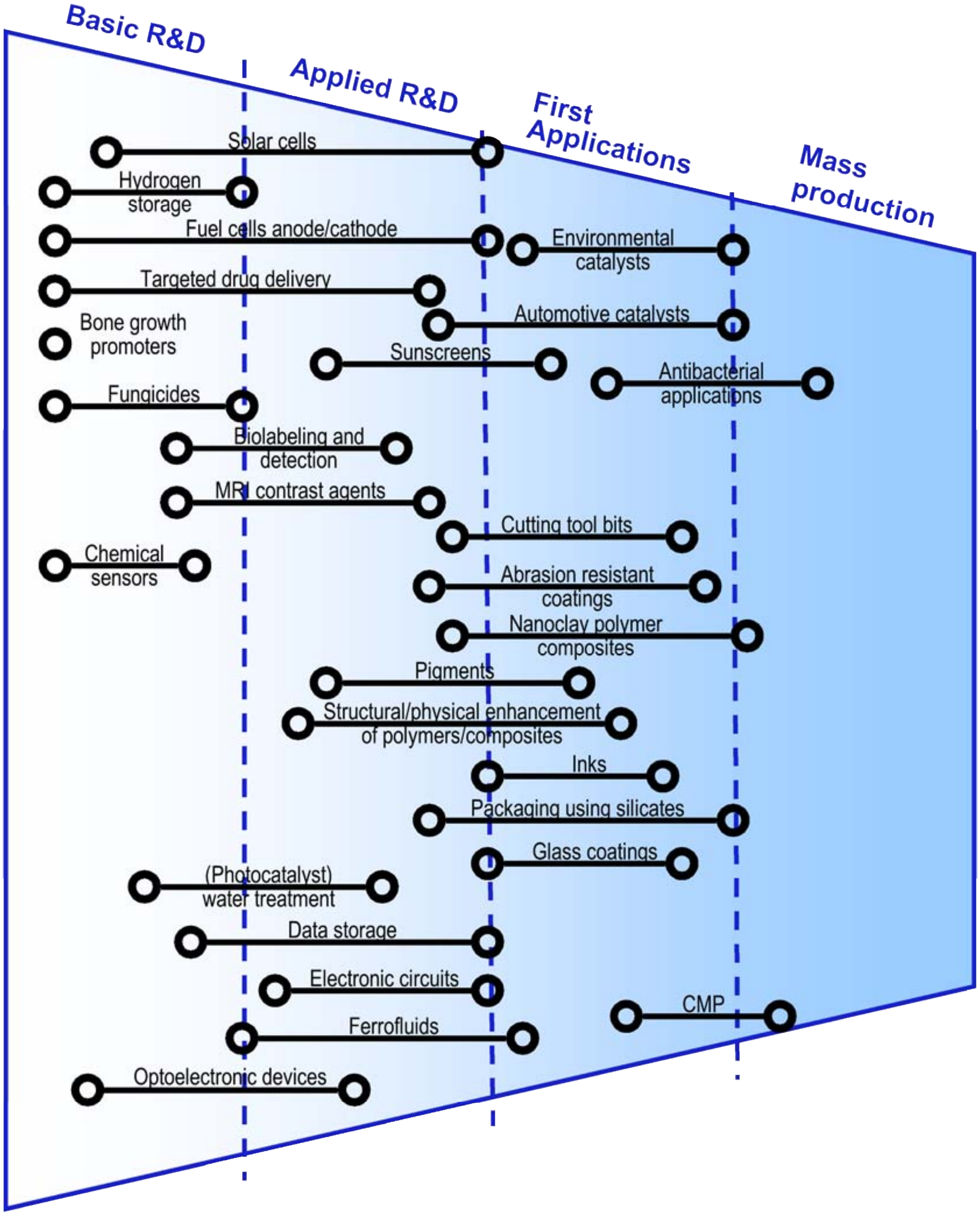
The final development phase, in this phase production has reached bulk amounts and research focuses on incrementally improving the products.

After this phase even more phases can be discerned (market maturity, end of life cycle, etc.) but these have not been taken into account when creating the following figures.

Overview of current applications (2005)

The figure presents an overview of the current state of development of different applications of nanoparticles. The input data for the preparation of the figures in this section has been gathered from the experts participating in the Delphi panel.

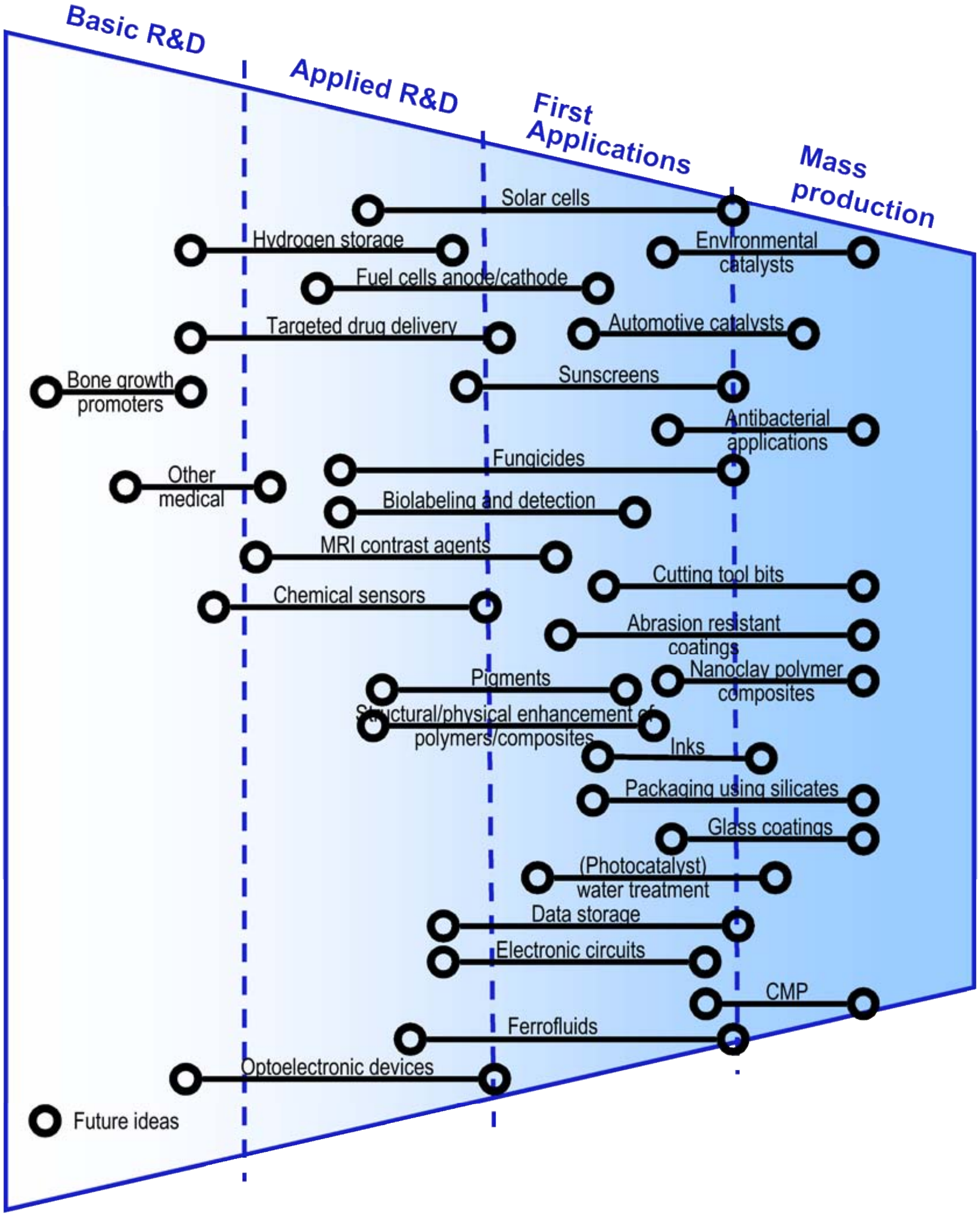
For further information about the added value of nanoparticles for each of these applications together with indications about suitable types of nanoparticles to be used in the respective applications, please refer to Annex III. Overview of applications.



Overview of applications in 2010

The following figure is an overview of the expected state of development of different applications of nanoparticles in year 2010. Data for the preparation of the figures in this section has been gathered from the experts participating in the Delphi panel.

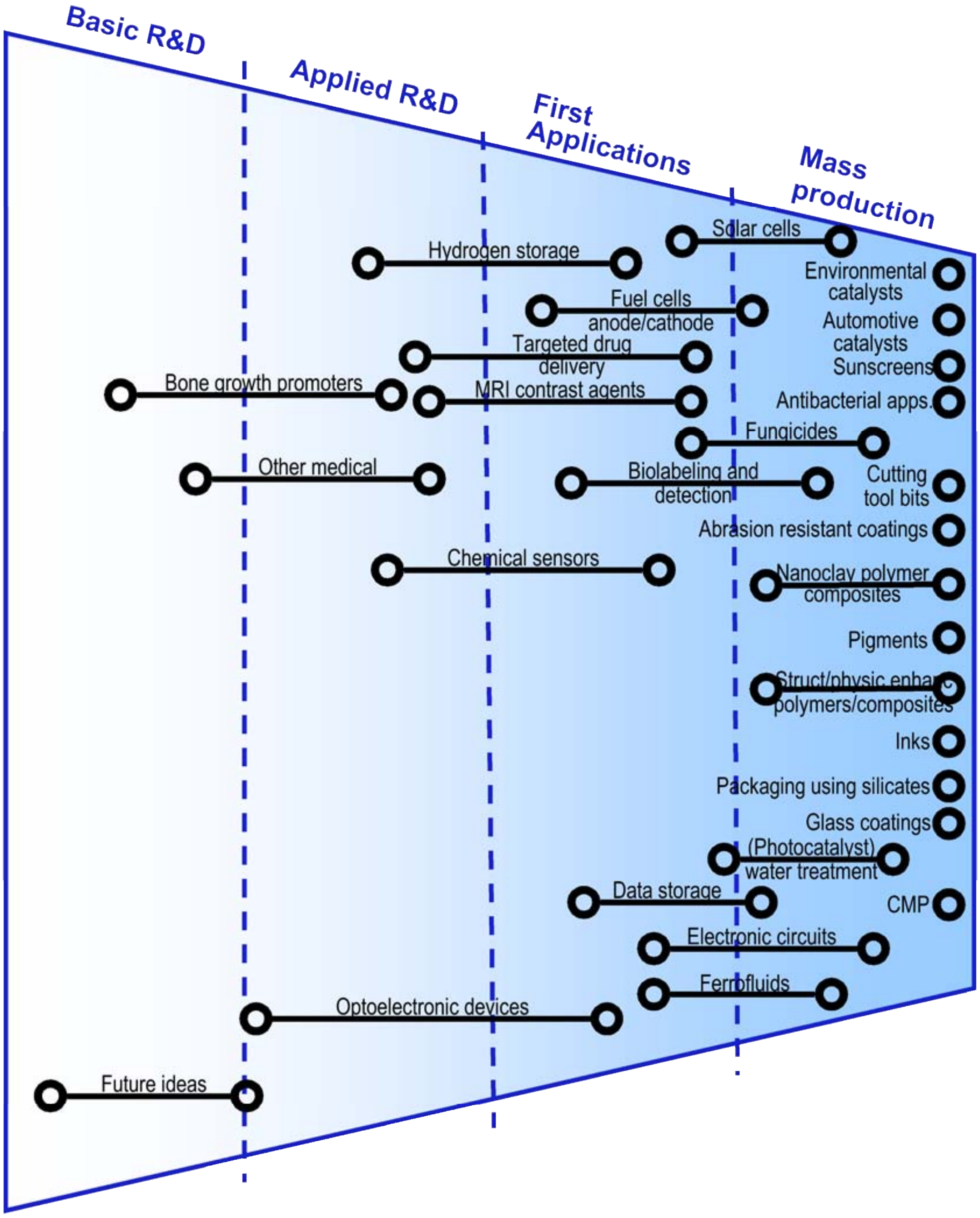
After five years many more applications will have come into fruition. A good number of the potential applications currently considered will be most probably entering into first commercial applications, with some of them already approaching the mass production phase.



Overview of applications in 2015

The following figure is an overview of the expected state of development of different applications of nanoparticles in year 2015. Data for the preparation of the figures in this section has been gathered from the experts participating in the Delphi panel.

By 2015 many applications currently in development will be actual markets and currently still wild ideas may be ready to move to the market.

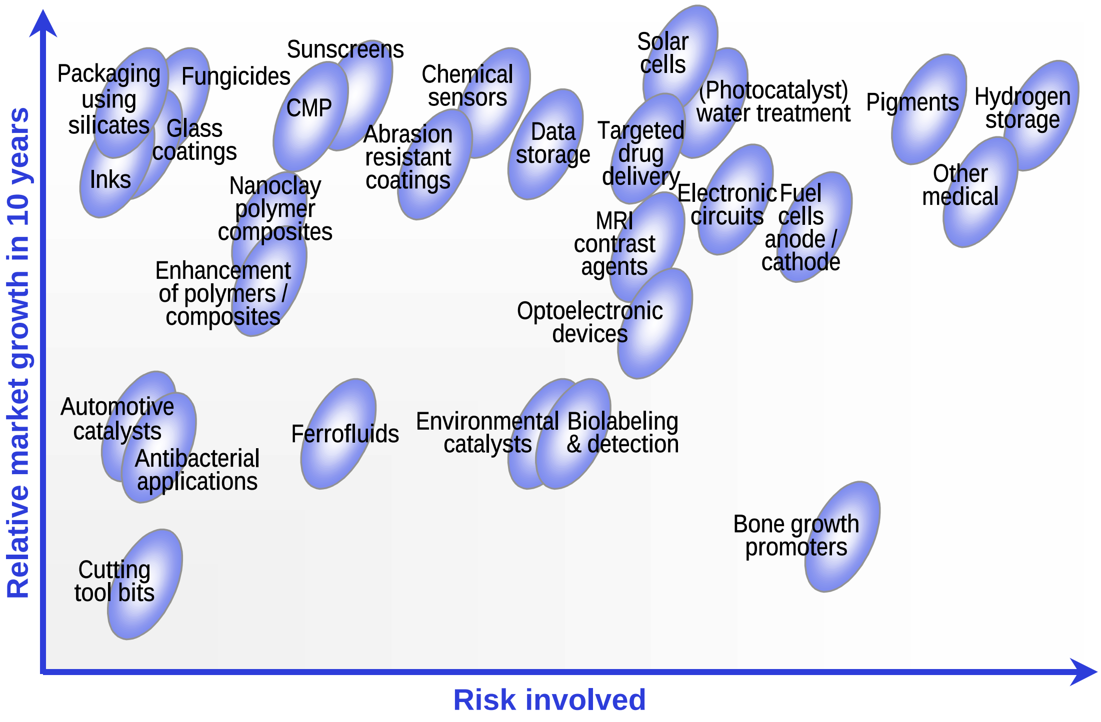


Risk involved vs. expected market growth in the next decade

For selected applications the following figure shows an estimation of (technological plus market) risk involved with the development vs. the estimated market growth of that application in the next decade.

The general purpose of the figure is to compare the relative position of different applications. For some applications, the current market of nanoparticles-related products is zero while for others, a significant market exists today (e.g. *CMP* or certain pigments). Furthermore, the stage of development of different applications has also an impact on the estimated risk (normally, the more advanced the application is, the less risk). However, some applications might face harder restrictions to arrive to the market due to the need to receive approval from regulatory bodies (e.g. for medical applications).

The figure below is based on the input from the experts that have participated in the Delphi panel.



Applications on the lower left of this figure have lower risk but also less potential reward since the related market is not expected to grow so much during the next decade. Applications on the lower right (high risk, low market growth) will need support to be developed. This is the case of, for example, bone growth promoters.

More towards the upper left (low risk, high market growth) we would find the most interesting applications. Packaging, fungicides, inks, glass coatings, sunscreens and reinforcement of composites are good examples. In the upper right we can find applications that combine a high risk with markets that will growth exponentially, if the application develops successfully. This is the case of e.g. hydrogen storage or other medical applications.

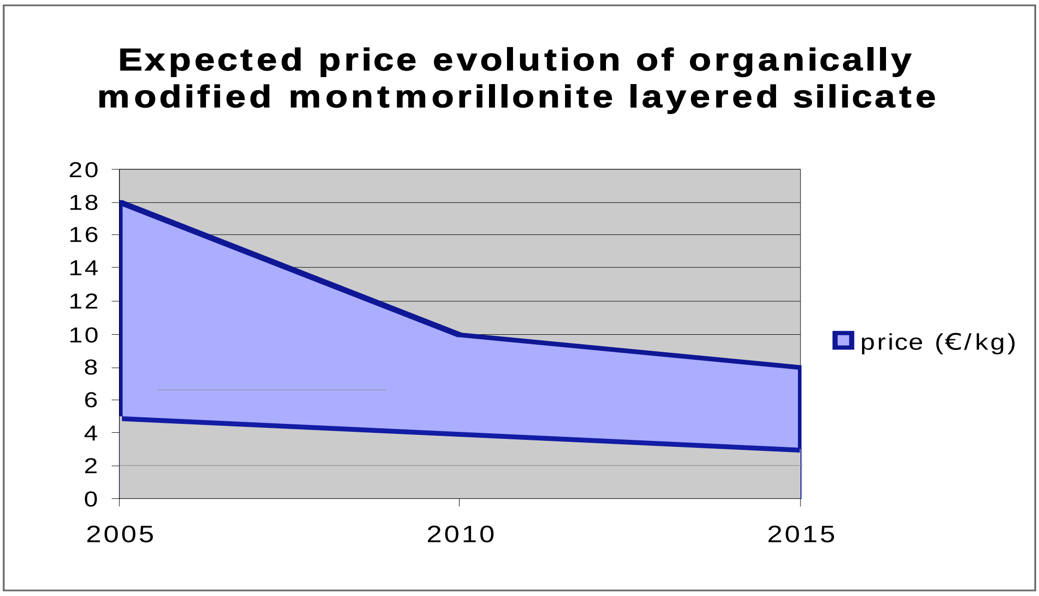
2.4 Estimated evolution of price & worldwide volume production

Although again it is very difficult to accurately foresee a future in a technology area that is still developing as nanoparticles technology is, estimations on price and worldwide volume production of some types of nanoparticles can be quite useful. The following figures have been elaborated based on the indications given by individual participants in the Delphi panel, who have made a laudable effort to provide explicit data.

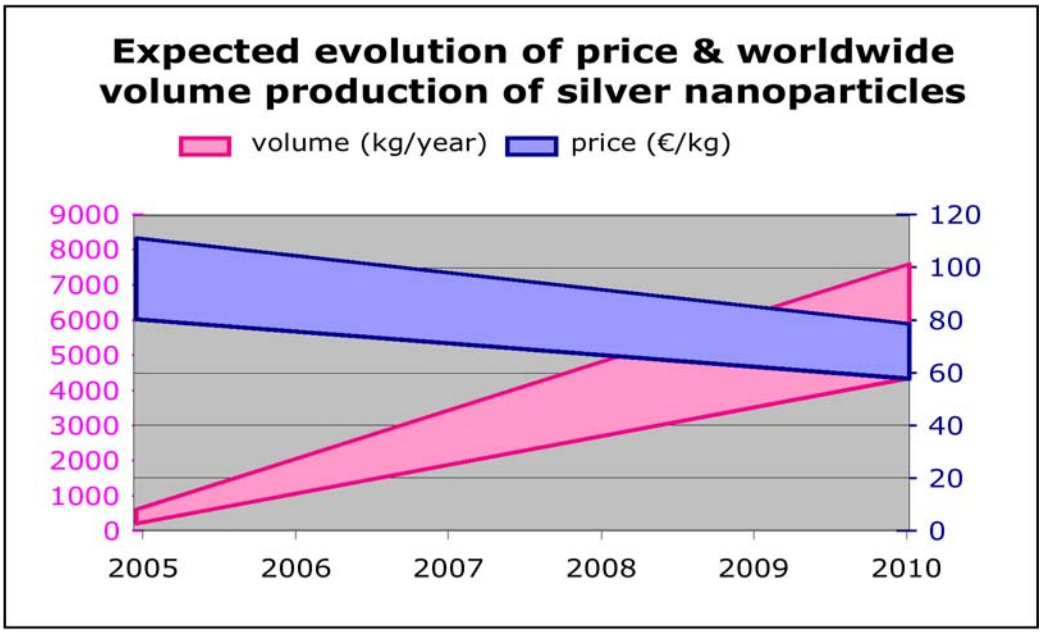
While academic researchers typically do not handle this type of information (estimations), companies are not always eager to show everything they can do (or cannot do), mainly for competitiveness reasons. Furthermore, technological advancements may result in small jumps in the production capability that not even the companies themselves have foreseen yet. On the other hand technological hurdles could make the demand for nanoparticles evolve more slowly than expected, also leading to less reason to expand production capacities.

The following figures are to be used only as an indication of trends in price and volume production curves of these types of nanoparticles. Variations in price exist for the same type of nanoparticle, depending on the quality, functionalisation and final application to be used for. When possible, estimations have been provided as ranges. In any case, figures should be considered only as an average indication.

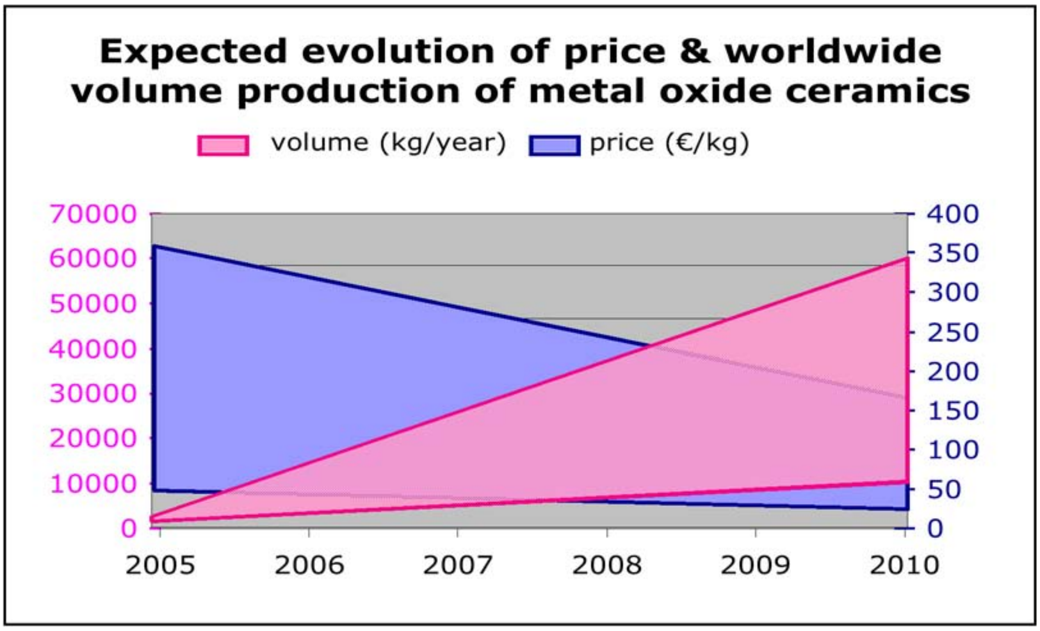
Organically modified ***montmorillonite* layered silicates** are used to reinforce polymer composites. Improvement in e.g. mechanical and/or barrier properties can be achieved by having the clay exfoliated to nano-scale sheets in a thermoplastic compound. Some functional properties (e.g. transparency, crystallinity, gas impermeability, flame resistance, etc.) can be remarkably improved by adding montmorillonite to polymers. Price estimations given by the experts in the Delphi panel are shown in the following figure. The current price for this type of nanoparticles has been estimated at 5-18 €/kg (some experts put the lower limit already at 3 €/kg for some types of functionalized layered silicates). In the next decade, it is expected that the range of prices will get down to 3-8 €/kg.



Silver nanoparticles can be used as pigments. Anticorrosive metallic pigments for waterborne primers and main coatings dramatically increase protective properties of coatings systems. Suitable nanoparticles include silver, lead, zinc or magnesium. Even though silver nanoparticles can reach prices above a hundred euros per gram, they are the preferred type of nanoparticles for this application, according to some experts. The following figure offers an estimation of the evolution in price and volume production in years 2005-2010.



Other pigment-related applications include the use of **metal oxide ceramics** as active fillers. When incorporated into composite polymer materials, they increase their chemical stability 3-5 times, decreasing their permeability by 8-25 times. Some examples of suitable nanoparticles for this application include ViO, AlO and CdO amongst many others.



Other applications of metal nanoparticles include biolabeling and detection. The added value of such nanoparticles is that they provide increased sensitivity and selectivity: metal nanoparticles bind more readily to *analytes* than alternative technologies (e.g. functionalised latex beads) and give more distinctive response (e.g. surface plasmon resonance shift). Silver nanoparticles are suitable for this application, but **colloidal gold** seems to be in a better position, according to some experts. The current price for the later material might reach 1.500 euros per kilogram.

Regarding non-oxide ceramics, 20-120 nm **Hydroxyapatite** (HAp) ceramics are being researched as a bone growth promoter. Their added value relays in the increase of the bioactivity. The minimum price of one kilogram of HAp can be currently estimated at 1.600 – 2.000 euros, according to some experts.

2.5 Non technological aspects

This chapter is devoted to non-technological aspects of nanoparticles and nanocomposites, including issues related to Health, Safety and Environment (HSE), infrastructure/equipment requirements, instrumentation costs and others.

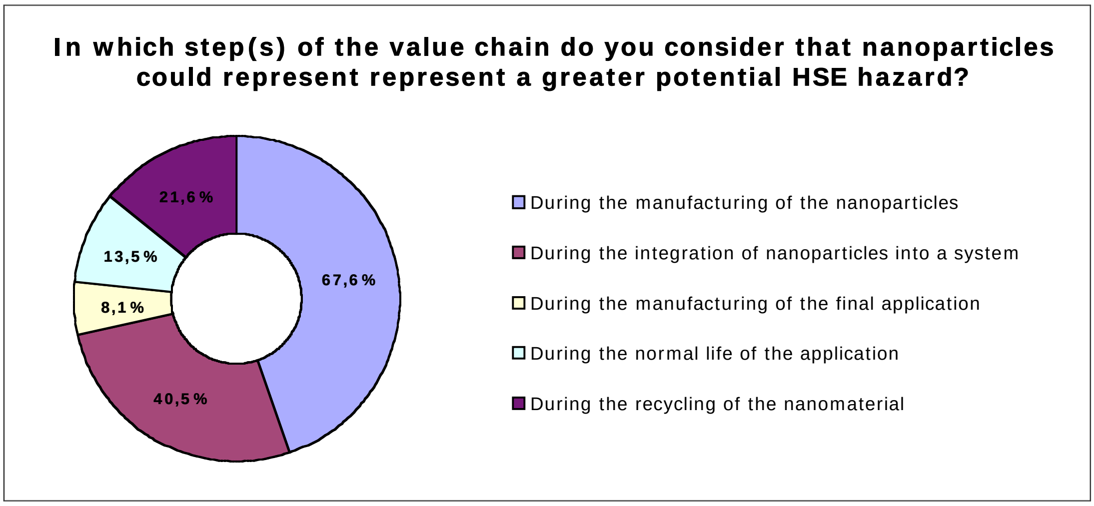
Health, Safety and Environmental (HSE) aspects

A white paper recently published by Cientifica, called *Nanotechnologies: Risks & Rewards* exposed that “many academic establishments and companies have inadequate procedures for monitoring exposure to nanomaterials, leaving them liable for future claims. As a result, some companies working with nanomaterials have seen dramatic increases in their insurance premiums”.

According to the authors, concerns and uncertainties raised, related to health and safety aspects, result in a slower adoption of nanomaterials by the industry. Thus, “companies need to understand and clarify the current trends in both toxicology and regulation in order to ensure that they can reap the rewards of nanotechnologies while avoiding the risks, and this needs to be done immediately”.

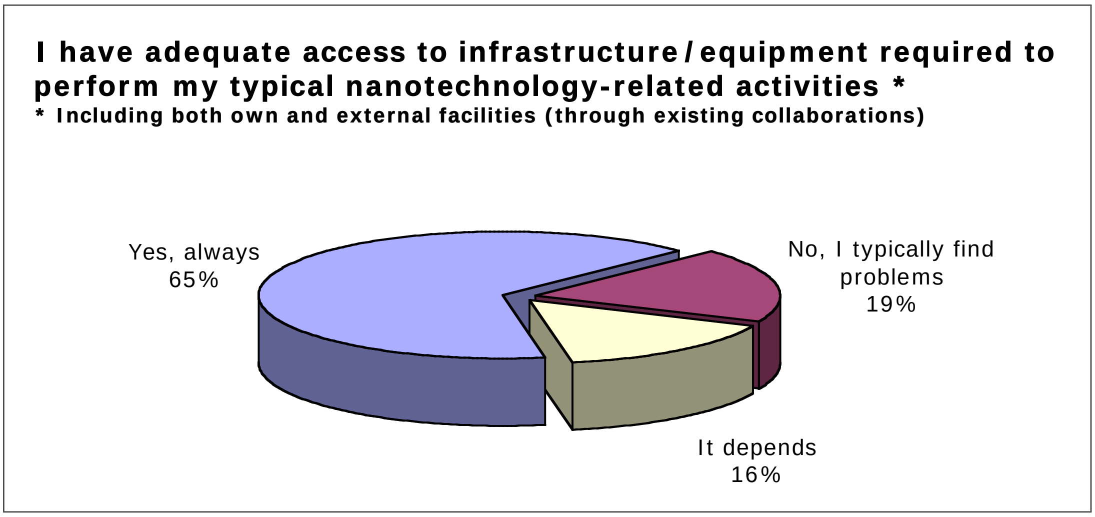
The participants in the Delphi panel have also expressed certain concerns related to the manipulation of nanoparticles. All of them agree in that that special equipment and/or facilities should be adopted in order to protect researchers dealing with nanoparticles from potential (still to be ascertained) related hazards.

The following figure highlights the steps in the value chain of nanoparticles where the participants in the Delphi panel think that a greater potential HSE hazard may occur.
Manufacturing stage has highest concentration of nanoparticles, however, systems and procedures are readily available to effectively minimise HSE hazards during this phase. It does not happen in the same way during the recycling of the nanomaterial. The risks in manufacturing, though there, may be handled adequately through standard industry procedures. Risks during application apply only to some of them - composites are almost certainly low-risk to end users while cosmetics and sunscreens could present potentially serious and as yet not quantified risks. Risks in recycling are probably minimal but the uncertainties are such that the question should be addressed for each product. It requires further research and precautionary measures.



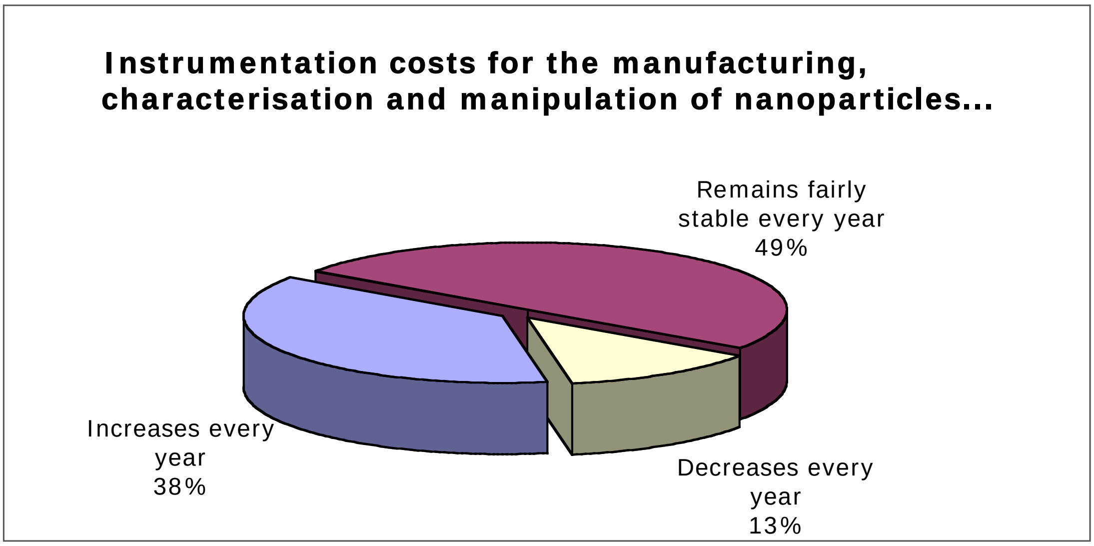
Infrastructure requirements

When asked about infrastructure needs required to perform the nanotechnology day-to-day work, most participants (65%) in the Delphi panel agree that they have adequate access to facilities (either internal or through existing collaborations). Less than 20% finds problems, while the rest says that depends very much on the specific situation.



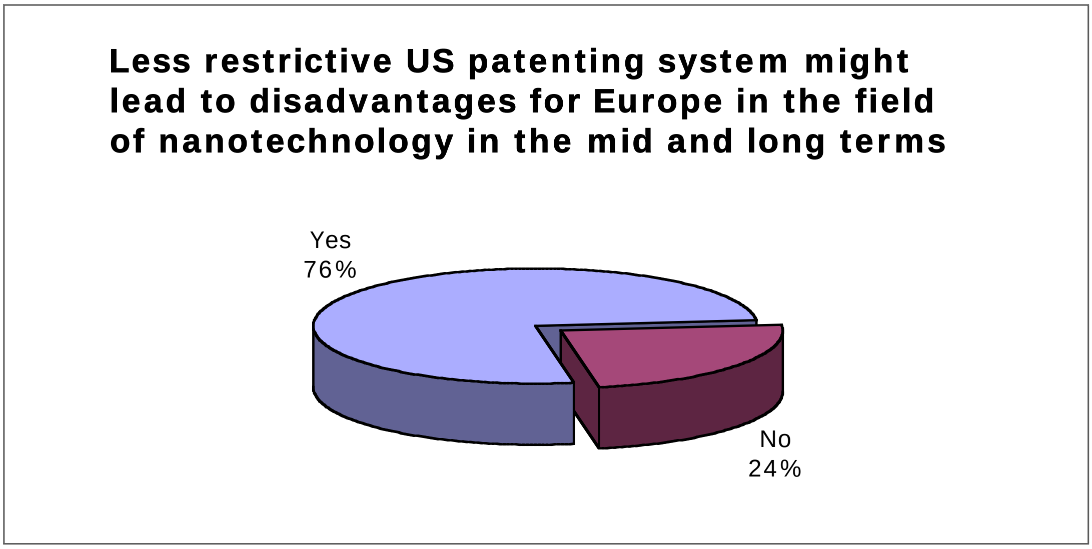
Instrumentation costs

When enquired about price trends of nanoparticle-related equipment, half of the experts in the Delphi panel indicate that they remain fairly stable from year to year. Almost 40% state that they increase, while the rest say that they decrease annually.



Patenting issues

76% of the experts in the Delphi panel think that differences between EU and US patenting systems (with the latter being less restrictive in terms of patent granting) will lead to disadvantages for Europe in the mid/long terms in the field of nanotechnology.



2.6 Conclusions

2.6.1 Most relevant applications

This paragraph can be divided in two different sections: current highest selling applications of nanoparticles, and markets of the future that will most likely generate large benefits. At the moment, the main field in terms of highest revenues is (opto)electronics/ magnetic applications, followed by biotech/pharma and energy/catalysis/mechanical engineering, with the first being about one order of magnitude higher that the others.

Based on the information provided by the experts in the Delphi panel (and going one step below), we find that current top-selling applications pointed out are very much aligned with those indicated in other market reports published in the past. These include *CMP* slurries for Si wafers, several pigments (for magnetic of sunscreen applications), catalysts, biomarkers, etc.

But, what about future applications? Some of them will offer considerable benefits to those that are able to overcome existing barriers. For example, nanoparticles as **reinforcement in polymers** is a tremendous field of research at the moment. Advantages of incorporating nanoparticles into composites have been already discussed earlier in this document. However, drawbacks are still too big to let this application fully enter the commercialisation stage, mainly the insufficient ratio cost/performance and the still-difficult compounding in commodity polymers. Experts in the Delphi panel identify the automotive and packaging industries as the major growth markets of plastic nanocomposites. Some experts think that in order to see a wider implementation of e.g. silicate nanoparticles in thermoplastics, the market must have witnessed a sufficient number of examples where nanocomposites have been successfully applied with clear and obvious benefits owing to the use of that material.

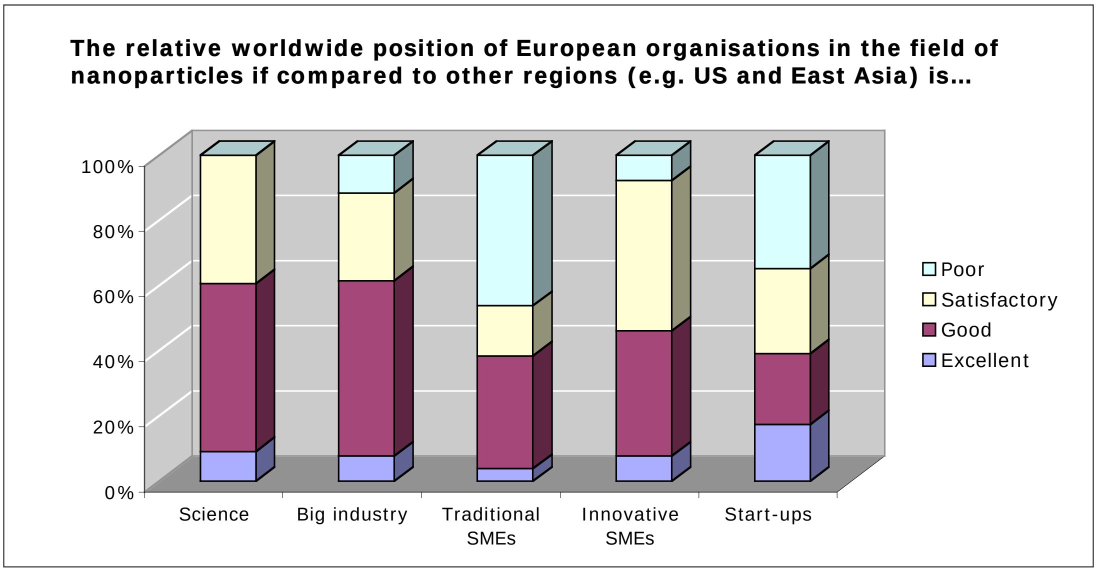
Certain health-related applications are also expected to provide remarkable benefits, if finally developed successfully. Examples of existing/potential applications have been mentioned in this report before. However, there is an application that because of its huge potential impact is worth considering separately. This is the field of **targeted drug delivery**. Nanoparticles can be used as vehicles to deliver drugs orally or inject them into the bloodstream, avoiding (or at least, minimising the negative impact in other areas of the body). A market entry barrier for this application stems from arduous approval process by regulatory bodies (e.g. Food and Drug Administration - FDA). In any case, in the long term *dendrimers* seem to be in a better position than nanoparticles (as classified in this report) for drug delivery applications. Due to their large number of identical surface groups, excellent encapsulation properties and highly controllable chemistry, dendrimers are very suitable for this application. Please refer to the Dendrimers Roadmap for further information.

Coatings using nanoparticles should be also mentioned here. There are currently many of them on the market, offering properties from scratch resistance to optical properties and, of course, self-cleaning. They can be found in eyeglasses, windows, cars, fridges, toilets, taps, etc.

The EU counts with a good position in most of the applications mentioned above (mainly chemicals, medicine and pharma, also materials). The EU has a strong industry and has potential to be revolutionary. The opportunity is there, we should take advantage of it.

2.6.2 EU positioning in the field

The general perception is that European academic research in the field of nanoparticles is of good quality. In fact, over 60% of the participants in the Delphi panel think that it is either excellent or at least good.



The situation with European industry varies considerably depending on the background of the organisation. In this respect, big industry is the best-positioned segment. Results are only comparable to academia, with more than 60% of the experts defining its position as either excellent or good. Some big industrial corporations, but also some medium size companies contribute to this perception.

Examples of big companies include L'Oreal and Arkema Group (both from France), QinetiQ Nanomaterials and Elementis (both from the UK) and Degussa, BASF and Sud-Chemie Group (all Germany-based).

Innovative SMEs are also well positioned, with over 45% of the experts again defining its position as either excellent or good. Examples of notable European SMEs working on the field of nanoparticles are Nanogate (from Germany) or the Irish based NTERA. Traditional SMEs, on the other hand, are poorly evaluated, with more than 45% of the experts defining their position as poor. Finally, responses for start-ups are very distributed, with more than half of the experts defining its position as excellent/good, but on the other hand more than a third defining it as poor. Notable examples include Oxonica and Nanomagnetics (both from the UK) and Nanosolutions (from Germany), again, just to name a few.

2.6.3 Final conclusions and recommendations

Main barriers

Still substantial technological barriers remain, not so much having to do with basic possibility to do something, but much more in translating the principle into a reproducible (industrial) process. In line with this lack of process industry thinking, we find that several experts express concerns about environmental impact of the processes they are working with. Huge amounts of waste can be foreseen, which would contain nanoparticles in a freely dissolved state that can interfere with human and animal life. This aspect is not addressed sufficiently, as many others have pointed out before.

In terms of costs, the barrier cannot be generalized. Applications in nanocoatings or in low loading percentages exploit the idea to use only small volumes in order to get the desired function – even at higher prices per kilo this would still result in an acceptable added cost. On the other hand, it is clear that the lack of industrialisation of processes not only results in variations in quality, but still also in excessive costs (e.g. polymeric nanocomposites).

Improving the production yield of nanoparticles would assist with barriers such as cost. Since size and size distribution is important for the activity of nanoparticles, understanding the optimum ranges of these characteristics is an essential first step. Production yield of specific active sizes and control of the size distribution would reduce waste and costs. An effective and cheap way to achieve this would be post-selection using specialist filter systems. Technologies exist to achieve this. Materials that are not within specification could be recycled. Development of on-line instrumentation capable of measuring size and size distribution would be beneficial in overcoming this barrier. Again technologies exist. On-line instrumentation would improve product consistency and performance. Yields can be increased by preventing agglomeration and preventing unwanted chemical reactions on highly reactive particles during the production process.

What is remarkable is the view of experts on the availability of infrastructure to perform their typical nanotechnology-related activities. Most of them seem content with what they have access to, with only one third stating that they encounter limitations in this area. It is our perception that the lack of pilot plant like facilities does present a limitation to the speed with which science could reach the markets in applications already validated on a small scale.

Scenarios for further development of nanoparticles

As we have seen, most experts foresee a truly remarkable uptake of nanoparticle applications during the next 10-15 years. It is the opinion of W&W that this may be too optimistic. We perceive the need to shift substantial funds towards upscaling and process technologies in order to bring nanoparticles to the final markets. This would not necessarily imply a reduction of the investments made in basic research. According to our opinion and that of most of the experts, what Europe needs is a coherent and very ambitious Nanotechnology Programme at the EU-level covering all aspects: research, application and also upscale. Thus, up-scaling should be well integrated in a nanotechnology programme also covering all the other aspects. If this change takes place, then EU research could make its promise a reality.

The alternative scenario is that of continued focus on lab-scale ‘proof of principle’ work, continued scarcity of upscaling facilities and of start-ups in the nanoparticle area willing (and able) to dedicate serious resources to larger scale production of nanoparticles. In such a scenario (probably with low availability of venture capital), the research would remain of excellent quality, but would probably find its way to the market only through channels presented by a very limited number of specialised SMEs and by big industry (the BASF, Degussa and Arkema of this world). Of course, a viable business case for these companies must meet very stringent demands that many in itself promising applications will not be able to.

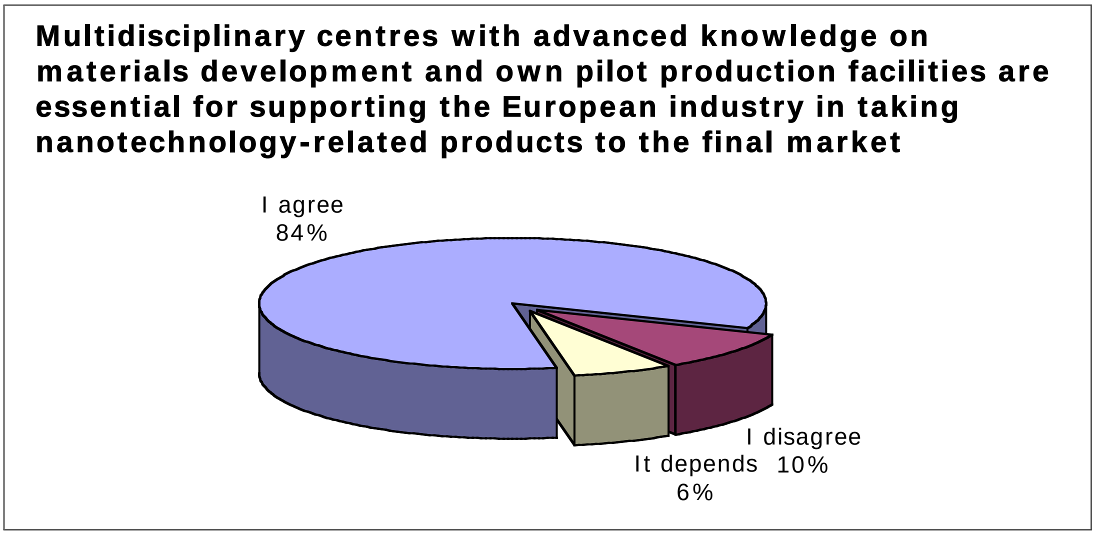
Final recommendations

As already said, the **upscaling** of relevant processes is an issue that needs to be encouraged if Europe wants to bring nanoparticles to final markets. A direct expected consequence would be a reduction in production costs, but also an increased reproducibility between batches, which will help to meet strict standards of most demanding application fields (i.e. pharma and electronics). All of the above is expected to speed up the uptake of nanoparticle-based products by these markets. In any case, the upscaling of different processes will need to be carried out taking into account the most demanding sustainability principles, in order to avoid potential dangers to life and the environment. Large quantities of contaminated solvents can be expected from industrialised process, which could be difficult / uneconomical to recycle. The development of efficient solutions, such as closed-loop processes is needed.

Another focal point would be to increase the **risk capital for production start-ups**, which sell application oriented RTD on the side. The European Investment Bank (EIB) could have a role here, contributing with funds to the creation and consolidation of such star-ups, which would result in a strengthened nanotechnology base in Europe. According to some experts, more funding should be available also for pilot plant and large-scale manufacture. On the other side, if a partnership could be formed between an institution such as the EIB and certain key major corporations it should be possible to devise an efficient scheme to get the benefits of additional funding plus access to mass production and mass marketing capabilities.

A third recommendation would be to have technology research centre(s) identify and pre-develop nanoparticle applications that can benefit **traditional SMEs**. This would not only contribute to the identification (and potential exploitation) of best nanotech-related opportunities by such companies, but to the consolidation of a firm nanotechnology base in Europe, given the amount and relevance of such companies for the European economy. SME sectorial associations could (and should) represent and inform their associates about existing opportunities and how to maximise their exploitation. The opinion from the experts can be visualised in the figure in the next page.

The great majority of applications described in this document are existing conventional applications improved by the application of nanotechnology (e.g. catalysis, polymer composites, packaging and drug delivery). The mass markets for these products are dominated by major multinationals such as oil companies, drug companies, consumer goods suppliers (cosmetics, etc.) and others.


Multidisciplinary centres with advanced knowledge on materials development and own pilot production facilities are essential for supporting the European industry in taking nanotechnology-related products to the final market

The role for start-ups and SMEs in general will most likely be:

- As niche suppliers to end markets.
- As technology providers to major corporations (intellectual property strategies are vital here).
- As intermediate suppliers for incorporation into the final product.

These types of companies typically do not have neither the resources nor the expertise to challenge major corporations in mass production or mass marketing. It is vital therefore to set up opportunities for exchange and dialogue between major corporations, SMEs, start-ups and R+D centres.

We will mention one more recommendation, which is focused on **increasing the awareness** of key players (in several key sectors) about opportunities offered by nanotechnology. The mobilisation of all the actors involved in the value chain of relatively complex sectors (e.g. automotive) is expected to have a substantial impact. Bringing them together in the same room will allow the exchange of ideas, the explanation of nano-products' added value, etc., contributing to the uptake of nanoparticle-based products in such sectors. *Technology Platforms* (both at the European and national level) could be the ideal framework to establish working groups devoted to this activity. It could also be considered the creation of a cross-sectorial working group between different research fields. It could also be the appropriate framework to deal with health and safety issues.

Annex I. List of participants (and statistics)

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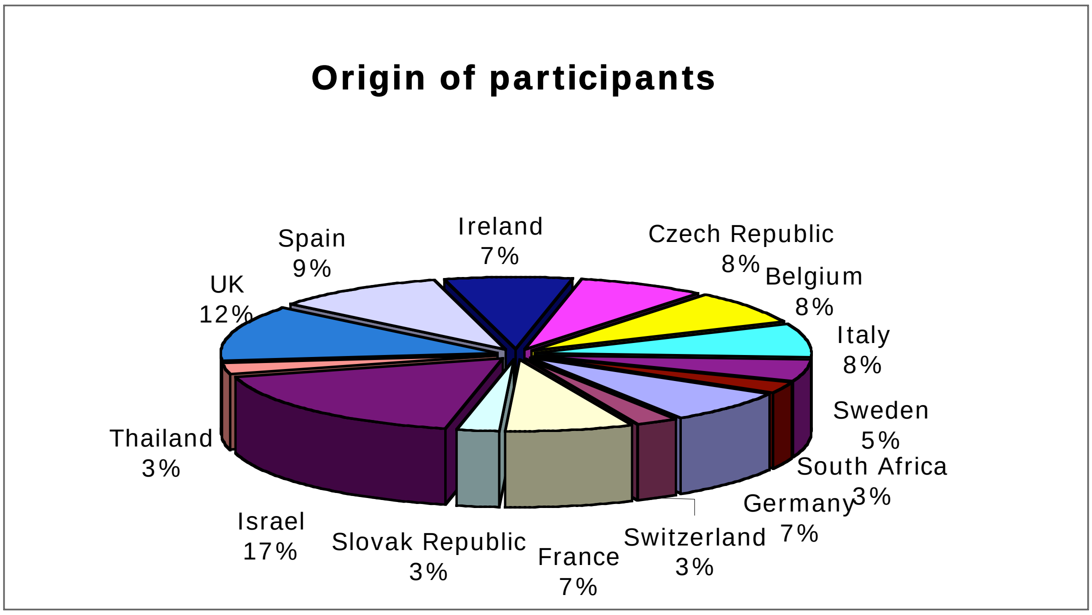
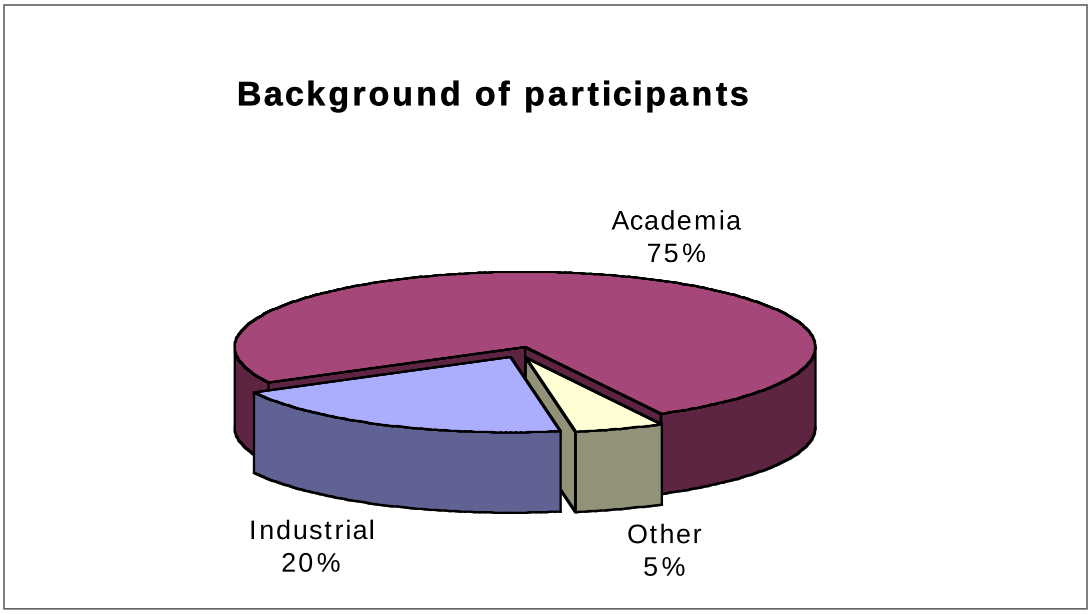

Origin of participants
Ireland 7%
Czech Republic 8%
Belgium 8%
Italy 8%
Sweden 5%
South Africa 3%
Germany 7%
Switzerland 3%
France 7%
Slovak Republic 3%
Israel 17%
Thailand 3%
UK 12%
Spain 9%


Background of participants
Academia 75%
Industrial 20%
Other 5%

Annex II. Glossary of terms

Analyte
The compound being identified and quantified in a diagnostic test.

Anode
A membrane, point or some other object where a feedstock material (such as hydrogen for a typical fuel cell) is oxidised during a chemical reduction. Oxidising means that electrons are stripped and transferred to the *cathode*.

Bentonite
Aluminosilicate clay formed from volcanic ash decomposition and largely composed of *montmorillonite*.

Biomimetic
Imitating, copying, or learning from biological systems.

Brabender plastograph
An instrument which continuously measures the torque exerted in shearing a polymer or composite over a range of shear rates and temperatures. The plastograph records torque, time and temperature on a graph called a plastogram. The results provide information about processability of an experimental composite and the effects of additives and fillers. It also measures other aspects, such as lubricity, plasticity, scorch, cure, shear and heat stability or polymer consistency.

Catalytic converter
An anti-pollution device located between a vehicle's engine and tailpipe. Catalytic converters work by facilitating chemical reactions that convert exhaust pollutants such as carbon monoxide and nitrogen oxides to normal atmospheric gases such as nitrogen, carbon dioxide, and water.

Cathode
A membrane, point or some other object where a feedstock material (such as oxygen for a typical fuel cell) is reduced during a chemical reduction. Reducing means that electrons are added and transferred to the *anode*.

Chemical Mechanical Planarization (CMP)
The use of a compound to polish a wafer's surface to eliminate topological layer effects in the manufacturing of semiconductors and MEMS.

Dendrimer
Macromolecule characterized by its highly branched 3D structure that provides a high degree of surface functionality and versatility. Its structure is always built up around a central multi-functional core molecule, with branches and end-groups. They can be made out of virtually anything that can branch (metal atoms, organometallic groups, or purely organic materials) and they can have a variety of functionalities depending on the application.

Electron affinity (EA)
The electron affinity of an atom is defined as the energy change accompanying the addition of one electron to a neutral gaseous atom. The electron affinity decreases when moving down the periodic table and increases across a row.

Ferrofluid
Specific type of liquid that responds to a magnetic field. Ferrofluids are composed of nanoscale magnetic particles suspended in a carrier fluid. The solid particles are generally stabilized with an attached *surfactant* layer. True ferrofluids are stable, meaning that the solid particles do not agglomerate and phase separate even in extremely strong magnetic fields.

Fuel cell
An electrochemical device that directly transforms the chemical reaction energy from hydrogen (or hydrogen obtained from a hydro-carbonate) and oxygen into electric energy. In the case of pure hydrogen the only other end-result is water or with hydro-carbonates also carbon-containing material.

Fuel cell electrode (Supporting Catalyst Electrode)
The electrode is the part of a *fuel cell* that supports the catalyst that allows for efficient ionization of the fuel with oxygen into electricity and water. In order to raise catalyst efficiency, a porous carbon material with a large surface area is needed.

Functionalization
The term functionalisation is used in this report to refer to the process of preparing a nanomaterial for further applications, such as the coating or the chemical modification of nanoparticles.

Glass transition temperature (Tg)
Temperature point where a polymer experiences a significant change in properties. The polymer structure turns to glassy and visco-elastic states. Below Tg even segmental movement in polymer molecules is restricted, and polymers become rigid and sometimes even brittle bodies. Above Tg polymers are rubber-like.

Heat Deflection Temperature (HDT)
The temperature at which a standard sample of a material will deflect 0,25 mm (0,010 in) under a stated load of either 0,45 Mpa (66 psi) or 1,82 Mpa (264 psi).

Heterojunction
Semiconductor diode junction, which is composed of alternating layers of semiconductor material. Each alternating layer has an alternating band-gap. In such a structure, the implementable diode characteristics can closely approach those of an ideal diode. The diode model parameters that define the diode's current vs. voltage response can be tuned by adjusting the thicknesses and band-gaps of the layers.

Index-matching material
In telecommunication, an index-matching material is a substance, usually a liquid, cement (adhesive), or gel, which has an index of refraction that closely approximates that of an optical fiber.

Ionic potential (IP)
The ionic potential is the charge to radius ratio, which is an important factor in determining the polarizability of an atom. The ionization potential decreases when moving down the periodic table and increases across a row.

IP = valence / radius (nm)

Kaolinite
A layered silicate mineral consisting of one silicon tetrahedral sheet and one aluminum oxide-hydroxide octahedral sheet.

Micrometre (μm)
One millionth part of a metre (10^{-6} m).

Montmorillonite
A hydrous aluminium silicate clay mineral with a 2:1 layer structure composed of two silica tetrahedral sheets and a shared aluminium and magnesium octahedral sheet.

Nanometre (nm)
One billionth part of a metre (10^{-9} m).

Paramagnetism
Tendency of the atomic magnetic dipoles, due to quantum-mechanical spin as well as electron orbital angular momentum, to align with an external magnetic field. Paramagnetic materials attract and repel like normal magnets when subject to a magnetic field.

Passivation
The phenomenon by which a metal, although in conditions of thermodynamic instability, remains indefinitely unattacked because of modified or altered surface conditions.

Plasma spraying
A thermal spraying process in which the heat source is a jet of highly ionized gas (plasma). The coating material is melted in the plasma and propelled onto the substrate.

Polyhedral oligomeric silsesquioxane (POSS)
POSS molecules consist of a core silica cage with a hybrid inorganic-organic composition. In contrast to clay or conventional fillers, POSS nanoparticles have the advantages of being monodisperse molecular weight with well-defined structure, lower density, high-temperature stability, and containing no trace metals. Each POSS compound may contain one or more reactive sites; therefore it can be easily incorporated into common polymers.

Proton Exchange Membrane (PEM)
A polymer sheet that serves as the electrolyte in one type of fuel cell.

Sepiolite
A fibrous clay mineral composed of two silica tetrahedral sheets and one magnesium octahedral sheet that make up the 2:1 layer.

Smectite
A group of clay minerals that includes montmorillonite and saponite. This type of mineral tends to swell when exposed to water.

Specificity
An operating characteristic of a diagnostic test that measures the ability of a test to exclude the presence of a disease (or condition) when it is truly not present.

Superparamagnetism
Phenomenon by which magnetic materials may exhibit a behavior similar to *paramagnetism* at temperatures below the Curie or the Neel temperature.

Surfactant
The term is a compression of *Surface active agent*. They are also known as wetting agents, and lower the surface tension of a liquid (usually water), allowing easier spreading. Surfactants are usually organic compounds that contain both hydrophobic and hydrophilic groups, and are thus semi-soluble in both organic and aqueous solvents.

Annex III. Overview of applications

Power / Energy

Dye-sensitized solar cells

- **Added value of nanoparticles**:

  The use of nanoparticles in photovoltaic cells (instead of organic dyes) has the potential to increase the cells' efficiency (more dye load and improved use of solar spectrum). Nanoparticles add specific optical properties and nanostructuring (especially for electron transport). *Heterojunction* effects are not possible with larger particles

- **Most suitable types of nanoparticles**:

  TiO_2 is the winning category in terms of highest market quota, according to the experts. ZnO and Au are also suitable for this application.

Hydrogen storage

- **Added value of nanoparticles**:

  Optimisation and modification of the process.

- **Most suitable types of nanoparticles**:

  Metal hybrid nanoparticles.

Improved anode and cathode materials for fuel cells

- **Added value of nanoparticles**:

  Improvement in electrical and barrier properties. Highly dispersed nanoparticles might improve anode and cathode efficiency, resulting in new improved fuel cells.

- **Most suitable types of nanoparticles**:

  Suitable nanoparticle categories pointed out include nanoclays, CNTs and metal nanoparticles in nanotubes.

Environmental catalysts

- **Added value of nanoparticles**:

  High surface area of nanoparticles results in an increased catalytic activity (efficiency).

- **Most suitable types of nanoparticles**:

  TiO_2, ceria.

Automotive catalysts

- **Added value of nanoparticles**:

  Nanoparticles exhibit an increased specific surface area that increases reactivity (higher performance) of the catalyst in the *catalytic converter*. Ceria nanoparticles are used in the catalytic converter as a versatile catalyst component, which simultaneously treats the reducing pollutants CO and C_xH_y, and the oxidizing pollutant NO_x. Ceria acts as an oxygen reservoir to stabilize the air/fuel ratio. In general, less metal is required, provided that a proper dissemination is achieved.

- **Most suitable types of nanoparticles**:

  Metal oxide ceramic nanoparticles (e.g. ceria, zirconia) and metals (e.g. Pt, Rh, Pd and Ru) are suitable for this application.

Health care / medical

Bone growth promoters

- **Added value of nanoparticles**:

  The enhancement of the bioactivity.

- **Most suitable types of nanoparticles**:

  Hydroxyapatite (HAp) ceramics.

Sunscreens

- **Added value of nanoparticles**:

  Fast and effective skin protection, resulting in non-irritating sunscreen products (some organic active agents such as avobenzone can cause skin irritation). High UV absorbance and possibility of homogeneous and very fine distribution of low quantities in sunscreens. In addition, nanoparticles can impart antimicrobial activity with minimal effects on colour, clarity, surface gloss, physical properties and melt flow properties.

- **Most suitable types of nanoparticles**:

  ZnO and TiO_2, with the latter being the winning category in terms of highest market quota, according to the experts.

Antibacterial wound dressings

- **Added value of nanoparticles**:

  Mainly, reactivity increase due to high surface area. Silver nanoparticles, for example, have higher surface energy as compared to non-nanoscale silver, providing enhanced protection against bacteria.

- **Most suitable types of nanoparticles**:

  Ag is the most popular type of nanoparticles for this application.

Fungicides

- **Added value of nanoparticles**:

  Used to attack and kill fungus and fungal spores for wood treatments, polymers, agrochemistry, etc.

- **Most suitable types of nanoparticles**:

  Cu_2O nanoparticles.

Biolabeling and detection

- **Added value of nanoparticles**:

  Increased sensitivity and selectivity. Metal nanoparticles bind more readily to *analytes* than alternative technologies (e.g. functionalised latex beads) and give more distinctive response (e.g. surface plasmon resonance shift).

- **Most suitable types of nanoparticles**:

  Silver nanoparticles and colloidal gold, with the latter being the winning category in terms of market quota, according to some experts.

MRI contrast agents

- **Added value of nanoparticles**:

  Specificity of the agent, better resolution and increased potential for early detection.

- **Most suitable types of nanoparticles**:

  Ultra small iron oxides: Fe_3O_4 and Fe_2O_3.

Engineering

Cutting tool bits

- **Added value of nanoparticles**:

  Enhancement of durability, wear resistance.

- **Most suitable types of nanoparticles**:

  ZrO_2 and Al_2O_3, with the later being the winning category in terms of highest market quota. Also, non-oxide ceramics (WC, TaC, TIC) and Co.

Chemical sensors

- **Added value of nanoparticles**:

  New improved and selective sensing functions.

- **Most suitable types of nanoparticles**:

  Several nanoparticles are suitable for this purpose, depends very much on the application (typically based on metal or metal oxide nanoparticles).

Abrasion-resistant coatings

- **Added value of nanoparticles**:

  Thinner and longer life coatings.

- **Most suitable types of nanoparticles**:

  Alumina and Y-Zr_2O_3 nanoparticles.

Nanoclay-reinforced polymer composites

- **Added value of nanoparticles**:

  Compared to many other fillers, higher aspect ratio of nanoparticles gives very good reinforcement at low loadings. This allows optimum thermal (e.g. heat resistance) and mechanical performance (e.g. lightweight, improved mechanical strength, etc.) with no loss of polymer matrix's properties. They can be used to reinforce mechanical stiffness (Young's modulus) and strength (maximum stress) of both commodities and technical polymers, with low clay concentration by weight (typically below 5 wt%). Nanoclays also add improved barrier properties (e.g. flame retardancy).

- **Most suitable types of nanoparticles**:

  Organoclays, including *sepiolite*, *laponite* and *smectite* (e.g. organically modified *montmorillonite* layered silicate). Silicagels and *POSS* nanoparticles have been also pointed out by the experts.

Pigments

- **Added value of nanoparticles**:

  Metal nanoparticles are used as anticorrosive pigments for waterborne primers and main coatings, dramatically increasing the protective properties of coatings systems. Metal oxides nanoparticles are used as active fillers in composite polymer materials, increasing their chemical stability (some 3-5 times) and decreasing their permeability (some 8-25 times).

- **Most suitable types of nanoparticles**:

  Suitable metal nanoparticles include Pb, Zn, Mg and Ag, with the latter being the winning category in terms of highest market quota. Adequate metal oxide nanoparticles include ViO, AlO, CdO and many others.

Inks: conducting, magnetic, etc. (using metal powders)

- **Added value of nanoparticles**:

  The added value of nanoparticles relies in the molecular scale mixing of components, plus the potential for very small ‘writing’ dimensions (e.g. in dip-pen nanolithography or plastic electronics). Size distribution and particle agglomeration are critical in this application.

- **Most suitable types of nanoparticles:**

  Still a broad field: standard good conductors such as silver.

Structural & physical enhancement of polymers and composites

- **Added value of nanoparticles**:

  Mechanical properties enhanced by the incorporation of nanoparticles into polymers and composites include improvement in modulus, fracture toughness and bending and interlaminar shear strength. Additional functional properties can be also remarkably improved by adding nanoparticles to polymers (e.g. transparency, crystallinity, gas impermeability, flame resistance, modification of the electrical properties, etc.).

- **Most suitable types of nanoparticles**:

  The type of nanoparticles to incorporate depends very much on the final properties desired. Some suitable nanoparticles for this application include nanoclays, nanooxides and nanohydroxides of metals. Organically modified montmorillonite, TiO_2, Y_2O_3 or SiO_2 are good examples.

Consumer goods

Packaging using silicates

- **Added value of nanoparticles**:

  Morphology and proper distribution of nanoparticles creates extra long path for gas molecules to get through plastics, reducing their permeability.

- **Most suitable types of nanoparticles**:

  Nanoclays, in particular bentonite (largely composed of the mineral montmorillonite) and kaolinite have been suggested as very suitable materials for this purpose.

Self-cleaning glass

- **Added value of nanoparticles**:

  The very high surface area of nanoparticles allow an increased catalytic activity, but also transparency.

- **Most suitable types of nanoparticles**:

  TiO_2 is the most popular type of nanoparticles for this application.

Environmental

Water treatment

- **Added value of nanoparticles**:

  Higher activity and performance.

- **Most suitable types of nanoparticles**:

  Depends on the application (typically metal oxide ceramics).

Photo-catalyst water treatments

- **Added value of nanoparticles**:

  Higher activity.

- **Most suitable types of nanoparticles**:

  TiO_2 and TiO_2 nanotubes (ordered arrays).

Electronics

Nanoscale magnetic particles for high-density data storage

- **Added value of nanoparticles**:

  Size alone is the benefit but shape is important because of the superparamagnetic limit. Very small nanoparticles exhibiting high magnetic anisotropy are expected to be able to reach very high density data storage.

- **Most suitable types of nanoparticles**:

  Fe alone or in combination with other metals (or even non-metals), CoPt. According to some experts, FePt will be the winning category in terms of highest market quota.

Electronic circuits

- **Added value of nanoparticles**:

  Metal nanoparticles, as opposed to non-metal ones, present more point-to-point contacts, allowing for thinner layers and more reliable electrical path.

- **Most suitable types of nanoparticles**:

  Silver, copper and aluminium nanoparticles.

Ferro-fluids (using magnetic materials)

- **Added value of nanoparticles**:

  The use of *superparamagnetic* nanoparticles coated with a suitable *surfactant* (preventing their agglomeration and subsequent sedimentation) is a basic method for the production of ferrofluids. Isolated Fe-particles show superparamagnetic properties of great use for addressing magnetic storage problems. If in solution (fluids), these systems could be easily coated on a substrate for the production of magnetic storage devices.

- **Most suitable types of nanoparticles**:

  Suitable nanoparticles include Fe (possibly coated with a carbon layer), Co, FeCo and Fe_3O_4. According to some experts, Fe_3O_4 will be the winning category in terms of highest market quota.

Optoelectronics devices such as switches (e.g. using rare-earth-doped ceramics)

- **Added value of nanoparticles**:

  Possibility to control the energetic levels (gap) through the control of the pparticle size. Possibility to create new luminescent materials by choosing the adequate couple (oxide matrix/rare earth emitter). In addition, there is an increase in the emission rate.

- **Most suitable types of nanoparticles**:

  Gd_2O_3 or Y_2O_3 matrix doped with Eu, Tb, Er, Ce. According to the experts, the winning category in terms of highest market quota can be considered Y_2O_3 doped with Er or Ce.

Chemical mechanical planarization - CMP

- **Added value of nanoparticles**:

  Reduced scratching of the surface being polished.

- **Most suitable types of nanoparticles**:

  Alumina, silica and ceria nanoparticles (typically below the 100 nm range).

NanoRoadMap is a project co-funded by the 6th Framework Programme of the EC

Roadmap Report on Dendrimers

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The present document is a roadmap report prepared by Willems & van den Wildenberg (W&W) in the framework of the NanoRoadMap (NRM) project, co-funded by the 6th Framework Programme (FP6) of the European Commission.

This roadmap report is mainly based on the input received by experts participating in the Delphi-like panel. It is one of the key deliverables of the NRM project and is issued for discussion and information purposes. The views expressed do not necessarily reflect those of the European Commission.

Table of contents

1 Introduction

1.1 Background

The NanoRoadMap (NRM) project, co-funded by the European Commission (EC), is aimed at roadmapping nanotechnology related applications in three different areas:

- Materials
- Health & Medical Systems
- Energy

Within the project, an international consortium consisting of eight partners covering seven European countries and Israel, has joined forces to cover the timeframe for technological development in this field up to 2015. The results of the NRM project are to be used by any European entity interested in planning an R&D strategy taking into account nanotechnology. An important potential user is of course the EC itself in the preparation of the 7th Framework Programme (FP7) for research and technology development.

For additional information on the NRM project, please refer to www.nanoroadmap.it

1.2 Goals

The primary objective of NRM is to provide coherent scenarios and technology roadmaps that could help the European players to optimise the positive impact of nanotechnology on society, giving the necessary knowledge on its future development and when technologies and applications will come into full fruition.

The key users of the reports are mainly European SMEs, research organisations, public bodies in general and the EC in particular. Even though a special focus is put on SMEs, these roadmaps are also meant to be useful for larger corporations.

This report is one of the three final deliverables of the NRM project (together with the reports on the field of Health & Medical Systems and Energy) and it is aimed at providing a thorough overview of specific topics selected for roadmapping within the field.

1.3 Methodology

1.3.1 Collection and synthesis of relevant existing information

A report was published in October 2004, as the most important deliverable of the first stage of the project. It was based on the collection and synthesis of existing public sources in 31 countries and was published as key input for the celebration of the First NRM International Conference held in Rome the 4th – 5th of November 2004. The full report can be downloaded for free on the project web site.

The report focused on reviewing the different types of nanomaterials, describing the topic, its most remarkable properties, current and future markets & applications, and leading countries & highlighted R&D activities in the field. A general review of non-technological aspects (social, legal, ethical and health and safety aspects, but also economical aspects and infrastructures requirements) was also performed.

The 12 topics identified, even not being completely homogenous in terms of scope or materials classification, were intended to adequately cover the field of nanomaterials. The following list was agreed upon the different partners of the NRM project (similar classifications can be found in the existing bibliography):

- Nanostructured materials
- Nanoparticles / nanocomposites
- Nanocapsules
- Nanoporous materials
- Nanofibres
- Fullerenes
- Nanowires
- Single-Walled & Multi-Walled (Carbon) Nanotubes
- Dendrimers
- Molecular Electronics
- Quantum Dots
- Thin Films

1.3.2 Selection of topics

Another major goal of that report was to set the basis for discussion and selection for roadmapping of 4 out of the 12 topics identified above. A preliminary selection of topics was presented during the First International Conference in November 2004.

After a thorough discussion, which involved international experts in the field of nanotechnology, four topics were selected (and validated in dialogue with the European Commission). The topics chosen are:

- Nanoporous materials
- Nanoparticles / nanocomposites
- Dendrimers
- Thin Films & coatings

1.3.3 Roadmaps elaboration

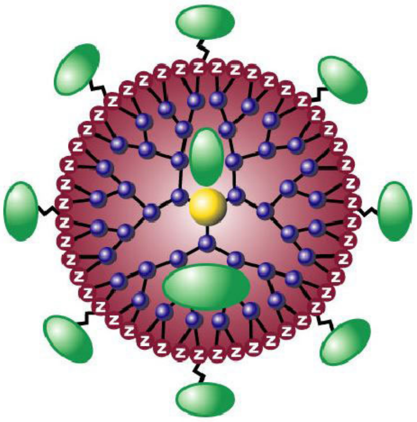
One roadmap has been prepared for each of the four aforementioned topics. The present report gathers all the work executed during this phase, and can be considered as the key deliverable for this activity. The results of these roadmaps will be presented in 8 National Conferences and one International Conference to be held in October – November 2005.

A Delphi-like approach (referred to as Delphi panel in the future) has been used for the preparation and execution of the roadmaps. The methodology followed consisted of 2 cycles, and it was the same for the four topics. The Delphi exercise consisted in:

1. Selecting top-international experts in the field (see the annexes for more information)
2. Preparing a dedicated on-line questionnaire for each topic to be roadmapped
3. Circulating the questionnaire and gathering experts' responses (1st cycle)
4. Preparing a first draft roadmap document based on the input gathered from the experts and personal interviews with some experts
5. Circulating the draft roadmap document, asking for feedback (2nd cycle)
6. Elaborating the final version of the roadmap

2 'Dendrimers' Roadmap

2.1 Definition of dendrimers



Courtesy of Dendritic NanoTechnologies, Inc

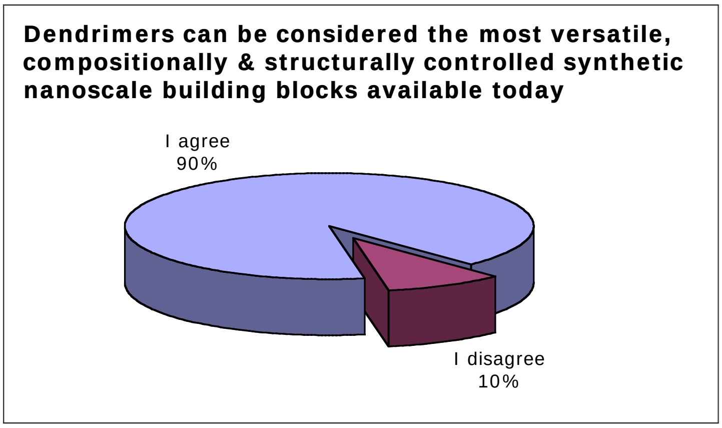
A dendrimer is generally described as a macromolecule, which is characterized by its highly branched 3D structure that provides a high degree of surface functionality and versatility. Its structure is always built up around a central multi-functional *core molecule*, with *branches* and *end-groups*.

Dendrimers can be made out of virtually anything that can branch (metal atoms, organometallic groups, or purely organic materials) and they can have a variety of functionalities depending on their application. Dendrimers are synthesised in a stepwise manner through a hierarchical self-assembly process, in which additional iterations lead to higher generation dendrimers. The molecule becomes more sphere-like, when the number of generations increases.

Dendritic polymers are recognized as the fourth major class of macromolecular architecture (together with linear, cross-linked and branched architectures), consisting of four sub-categories: random hyperbranched, dendigrafts, dendrons and dendrimers. This roadmap deals primarily with the field of dendrimers.

The principal difference between a dendrimer and other hyperbranched polymers is that each of the monomer units in the dendrimer has at least one functional unit that allows further branching. Some hyperbranched structures have a similar structure to that of dendrimers (apart from the centre of their architecture), but with parameters not as easy to control as in *real* dendrimers. Synthesis of this type of structures requires less effort, on the other hand, leading to derivatives with certain useful *defects*.

2.2 Most remarkable properties of dendrimers

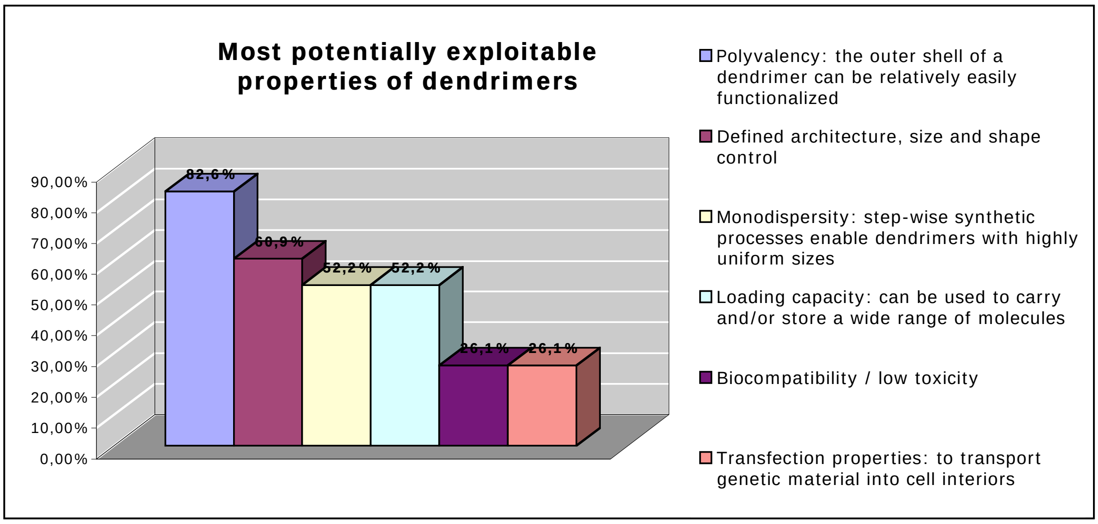


Dendrimers can be considered the most versatile, compositionally & structurally controlled synthetic nanoscale building blocks available today

Dendrimers can be considered, according to most (90%) experts consulted, the most versatile, compositionally and structurally controlled synthetic nanoscale building blocks available today. In itself perhaps not too surprising given the fact that all experts are working on dendrimers, the argument used is the following. When comparing dendrimers with other nanoscale synthetic structures (e.g. traditional polymers, buckyballs or carbon nanotubes), these are either highly non-defined or have limited structural diversity.

As a result of their architecture and construction, dendrimers possess inherently valuable physical, chemical and biological properties, opening up a whole range of applications that cannot be accessed using normal linear macromolecules. This allows selective functionalisation and the tailoring of size dependent properties.

According to the experts in the Delphi panel, the most remarkable properties of dendrimers are (in order of expert-rated importance):



Polyvalency

The outer shell of a dendrimer admits functionalisation fairly easily, allowing multiple functionalities to be added. Polyvalency is useful as it provides for versatile functionalization; it is also extremely important to produce multiple interactions with biological receptor sites, for example, in the design of antiviral therapeutic agents. Using dendrimers as a scaffold to present multiple copies of a surface group or groups, new biological activities are uncovered with unique pharmacokinetics. Different ligands can be coupled to dendrimers to use them as transfection reagent, e.g., ligands recognising only the surface of a certain cell type combined with ligands that facilitate the escape from the *endosome*.

Functionalisation of the periphery can also result in copolymers with interesting properties, such as viscosity, stability, etc. Dendrimer properties can be easily tuned by modifying the end groups (e.g. changing the end groups on a same skeleton induces solubility in organic solvents, in CFC or in water). Metal functionalization of the periphery has applications, for example, in catalysis. Other applications include sensing, nanoscale templates, ionic conductivity and photonic or electronic applications (e.g., enhancement of the electronic transfer: amplification effect). Easy functionalisation is also key to enabling compatibility with other materials (e.g., within an opto-electronic device), which is perceived by the experts as a key differentiator from competing materials / technologies.

Defined architecture, size and shape control

Dendrimers branch out in a highly predictable fashion to form amplified three-dimensional structures with highly ordered architectures. This property is relevant for applications such as protein modelling or catalysis. Size control is also important in therapeutic applications, as different molecular sizes exhibit different pharmacokinetics (other dendritic polymers such as *dendronised* polymers or hybrid linear-dendritic structures have even more potential than pure dendrimers for certain medical applications).

The shape persistence of dendrimers is very important, as it allows the defined placement of functions not only on the dendrimer surface but also inside the dendritic scaffold. This is of crucial importance for several applications, e.g. in sensing. Here, the shape persistent dendritic scaffold prevents self-aggregation of peripherally attached *chromophores*, resulting in high fluorescence intensity of the particles. Furthermore, stiff dendritic architectures possess defined pores or voids. This is a prerequisite for defined interactions between the dendrimer and incorporated guest molecules.

In the context of liquid crystal systems, this property allows the design of Liquid Quasi Crystals (QC). Inorganic QCs are interesting because of their particular (e.g. mechanical, optical) properties. According to some experts, dendrimers are the only organic material that has these properties. Furthermore, dendrimers have potential for the design of flexible displays. Soft self-assembly of dendrimers allows the tailoring of electronic properties in complex systems (multiple functionalities) with a precision approaching that of biological systems. According to the same source, the design of macromolecular devices (machines, motors, etc.) will be quite likely associated with dendrimers, which represent a significant step towards the creation of nanostructured complex systems.

Monodispersity

Step-wise synthetic processes enable the production of dendrimers with highly uniform sizes with defined surface functionality. Monodispersity offer researchers the possibility to work with a *tool* for well-defined scalable sizes. Judiciously performed assembly of components results in dendrimers of desired size and shape, for varying transport and penetration ability. This property is useful for applications such as the synthesis of container molecules, use as templates or in electronic applications.

Monodispersity is, according to some experts, one of the most important differences between dendrimers and polymers. Well-defined structures are particularly important for biological and medical applications.

Loading capacity (molecular container property)

Internal cavities of dendritic structures can be used to carry and/or store a wide range of metals, organic, or inorganic molecules by encapsulation and absorption. The appropriate type (and degree) of functionalization results in the desired loading capacity. This property makes dendrimers very suitable as drug delivery vehicles and also appropriate for obtaining electro-optic or magnetic devices. It also allows the use of dendrimers to store, for example, nanoparticles of metal and to prevent precipitation, allowing for the creation of dispersions of what some have called 'nanoreactors'. The possibility of loading dyes could lead to novel ways of labelling. The possibility of transporting materials makes dendrimers an attractive potential carrier in biosubstrates or an additive for special materials.

Biocompatibility / low toxicity

Some dendrimer systems display very low toxicity levels, with dendrimers carrying anionic groups being less toxic than those carrying cationic groups. Dendrimers commonly show also negligible or very low immunogenic response when injected or used topically. These properties make them highly suitable for drug delivery and biolabeling. In this sense, high biocompatibility is crucial both for preventing toxic reaction and for seeking biodegradability options.

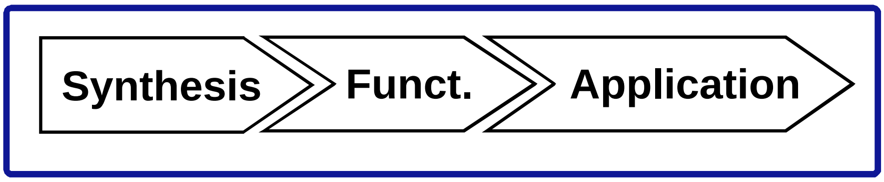
Dendritic polymers have great potential in various kinds of therapies, especially given their ability to be designed for biological specificity, therefore their biocompatibility and lack of toxicity is important. However, not all dendrimers are biocompatible nor show low toxicities. Only some dendrimers have these properties. As said, dendrimers carrying cationic groups can have significant toxicities.

Transfection properties: to transport genetic material into cell interiors

The high diversity of chemical structures possible in dendritic architectures enables the design of selected macromolecules that are able to pass through membranes. Dendrimers have been applied in existing products, for example, to transfect eukaryotic cells in vitro (e.g., SuperFect, PolyFect). Feasibility of these products has already been demonstrated, while benefits have been generated with these dendrimer-based products.

2.3 The dendrimers' pipeline

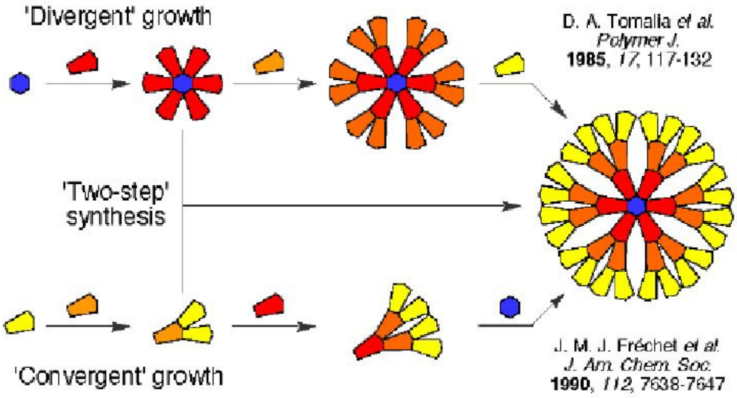
This section reviews the different steps in the dendrimers' pipeline: synthesis, functionalisation and application. Following their synthesis, dendrimers are typically functionalised accordingly to the features the researcher wants them to display and the final application they will fulfil. Finally, dendrimers are incorporated into the final product (application):



However, it should be noted that this is not always a linear approach with sequential independent steps. In many cases each and every different application has one or a few specific production, purification and functionalization processes to obtain the desired properties for the lowest amount of time and money. It is therefore not possible to optimise all these steps independently and the best approach is an integral one.

2.3.1 Dendrimer synthesis

Dendrimer synthesis can be achieved through different methods. However, divergent and convergent synthesis are the most common and extended methods. According to the experts in the Delphi panel, the main barriers for the success of dendrimer synthesis methods can be considered the elevated price and some technical barriers. The main technical challenges for dendrimer synthesis, be that convergent or divergent, are found in establishing process control methods, specifications and final product analytical methods so that the synthesis gives reproducible, high purity and well defined products. It is difficult to anticipate when these barriers could be overcome, as the technical issues mentioned above are faced anew for each type of dendrimer. Thus, it depends very much on when each application of a new dendrimer architecture is pursued. In limited cases, the lack of improved equipment can also be considered a significant barrier.



Courtesy of Andy Shipway

Divergent synthesis

In the divergent approach, the synthesis starts at the core and works its way out to the outer part of the dendrimer. The core, which contains multiple reaction sites, is treated with an excess of the first monomer reacting with all the core's reaction sites. This monomer also has additional reactive groups. An excess of a second monomer is reacted with the half generation (core and monomer), giving rise to the first generation. A continuation of this iterative process leads to higher generations. It is with these higher generations that most types of dendrimers become rather globular and some of their unique properties show.

It needs to be said that there are two main divergent routes that have been reported in different papers (Tomalia–Vögtle and Denkewalter–Newkome). The picture and the text above refers to the Tomalia (PAMAM) structure, which is based on this commercial, readily available material. There is a subtle but important difference between Tomalia and Newkome divergent processes: in the initial Vögtle–Tomalia routes branching occurs at the surface substituent(s), whereas the Denkewalter–Newkome approaches involved a single surface attachment and the monomer possesses the 2- or 3-branching centre, respectively. According to the experts following the latter approach, this could eventually lead to higher yield (no reversibility, higher monodisperse products, greater purity for eventual drug encapsulation) and more thermally stable materials. According to the same sources, this route could have greater commercial possibilities and ease in synthesis.

In divergent synthesis, the efficiency of each reaction cycle is very important. After each generation, there is a need to eliminate the excess of reagents (due to similar polarity, the purification from precursor molecules and partially reacted products is difficult). High generation dendrimers typically show defects on the surface (defects at early generations lead to highly defect structures). Nevertheless, divergent synthesis strategies remain the preferred methods for commercial production of dendrimers.

Cost effective & selective purification can be considered the key technical barrier in most high-generation dendrimers synthetised using the divergent synthesis approach.

Price is always an issue in multi-step syntheses. Some dendrimers can already be prepared with minimal excess of reagents and simple purification techniques. The solution is to limit the size of the molecule (therefore, limiting the number of generations of growth); often this is enough in terms of numbers of reactive end groups. If size is needed, they can be conjugated with (natural or synthetic) macromolecular components.

But, is there really a need for high generations dendrimers? According to some experts, the highest generation having practical applications (except for calibration applications) is the 6th generation (G6) dendrimers (for transfection applications). Furthermore, and still according to the same sources, even though phosphorus dendrimers have been synthesised up to G12, the highest generation of these showing interesting properties (both for materials science and for biology) is G4. From a medical perspective, some experts agree with the previous argument in that it is unlikely that dendrimers of a generation beyond G4 or G5 will be needed. According to the same source, this is unlikely to be a major issue in the context of new pharmaceuticals given existing developments. Certainly, progress to date has been sufficient for the initial human clinical trials to proceed to the proof of principle stage relatively rapidly.

For high purity dendrimers with a high control of polydispersity key aspects can be considered the purification of individual generations and additionally the yield of functionalisation reactions.

Convergent synthesis

Convergent synthesis starts at the periphery and finishes at the core. The convergent synthesis involves the creation of dendrons and their assembly around the core. A limited number of reactions is required at each step of the growth process. Convergent synthesis makes it easier to yield the desired dendrimer and have further control over all molecular design parameters.

There are no major technical barriers in convergent synthesis. Only in the case of large dendrons, the coupling to the central core represents substantial difficulties.

This approach leads to very fast build-up of larger structures, on the other hand requiring efficient coupling procedures of large molecular fragments, which can be difficult, in some cases. Purification (the amount of reagents needed and the intermediate purification is substantially reduced) and characterisation methods are easier. In addition, since dendrons can be attached to other molecules, this approach gives access to numerous novel architectures.

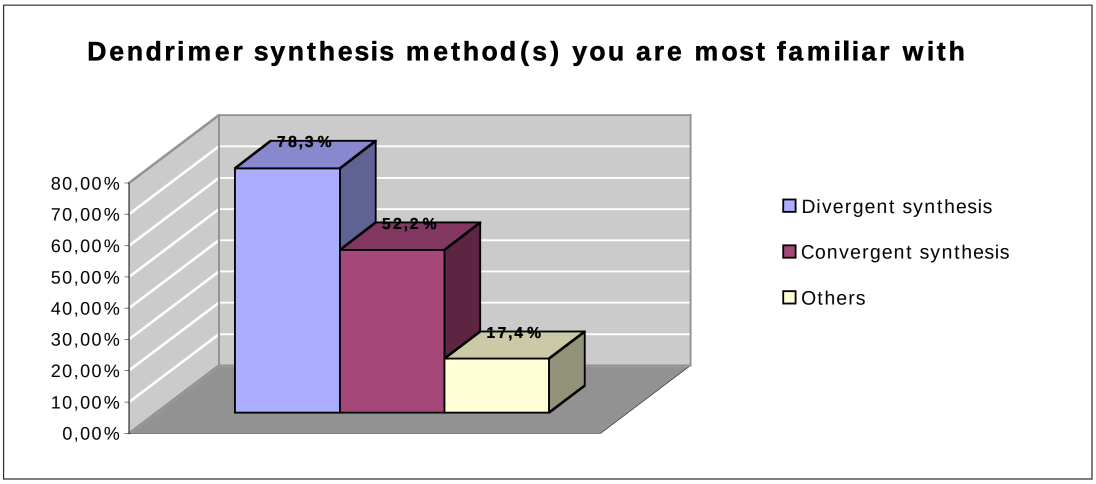
As said, price is always an issue in multi-step syntheses. However, by using convergent methods, low generation dendrimers might be created that can then easily be attached to other macromolecules, if size is desired. For large dendrons, the coupling to a central core is the main issue. This is to be overcome by improved organic synthesis, computer simulation of the behaviour of large systems and their reactivity, which might be of great use in the design of better systems.

In general, it could be said that the convergent approach is appropriate for obtaining small dendrimers while the divergent approach is good for obtaining large dendrimers (which typically show defects). It should be kept in mind, however, that in the convergent paths, dendrons are usually synthesised by divergent paths, so the barriers associated to the latter do usually also apply to the former.

Other synthesis methods

Other synthesis approaches mentioned by the experts in the Delphi panel include combined synthesis (divergent-convergent), dynamic synthesis and double exponential synthesis. According to some experts, the combined synthesis might play a major role in the future reduction of dendrimer costs, since a G4 might be setup from a G2 core and a convergent attachment of a G2 shell (without the need of a G3 intermediate). The conjugation of dendritic fragments to linear macromolecules is also an option to be considered.

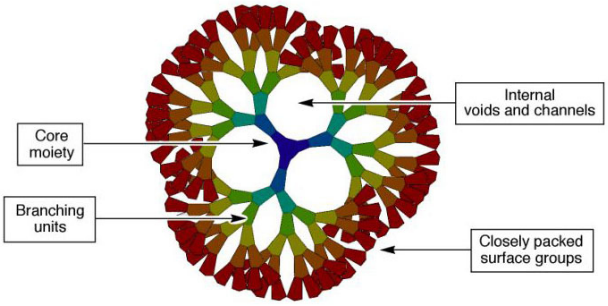
According to the experts in the Delphi panel, these are the synthesis methods that they are most familiar with:



2.3.2 Dendrimer functionalisation

Dendrimers can be (relatively easily) functionalised to display features that are useful for the application they will fulfil. Most commonly used functionalisation methods are filling dendrimer cavities, modification of the dendrimer core and modification of the dendrimer surface.

According to the experts, the main barriers associated to dendrimer functionalisation methods can be considered the cost added by the functionalisation, followed by certain technical barriers. Additional information about dendrimer functionalisation methods can be found below.



Courtesy of Andy Shipway

Filling dendrimer cavities

Due to their tree-like structure, dendrimers have internal cavities that can be used to trap small molecules. Customising interior spaces and reactivity allows experts to add extenders or new functionalities to the interior of dendrimers. Dendrimers functionalised this way display customisable encapsulation properties that allow for extended functionalities, depending of the final use that the dendrimers will fulfil.

Modification of the dendrimer core

The overall challenges in the modification of the core or the dendrimer surface can be considered the same: making sure you have control of the synthesis, which can only be assessed with sound analytical methods. A key barrier to success in the modification of the dendrimer core is the limited number of reactive handles at the core of most dendrimers. Once again, this challenge needs to be addressed for each dendrimer application, so no definitive timeline can be given to overcome these barriers.

Although the percentage of final cost added by this functionalisation method depends very much on the dendrimer framework available, the experts in the Delphi panel have estimated it at 20% - 50%.

Modification of the dendrimer surface

Surface properties can be functionalised making use of *capping* reagents on the outermost generation. By doing this, dendrimers may display a novel range of functional properties, including:

- Polyvalency: the outer shell of a dendrimer can be functionalised to attach reactive groups. Each of these reactive sites has the potential to interact with a target entity, often resulting in polyvalent interactions.
- Flexible charge and solubility properties: through use of appropriate capping groups on the dendrimer exterior, the charge and solubility of dendrimers can be readily manipulated.

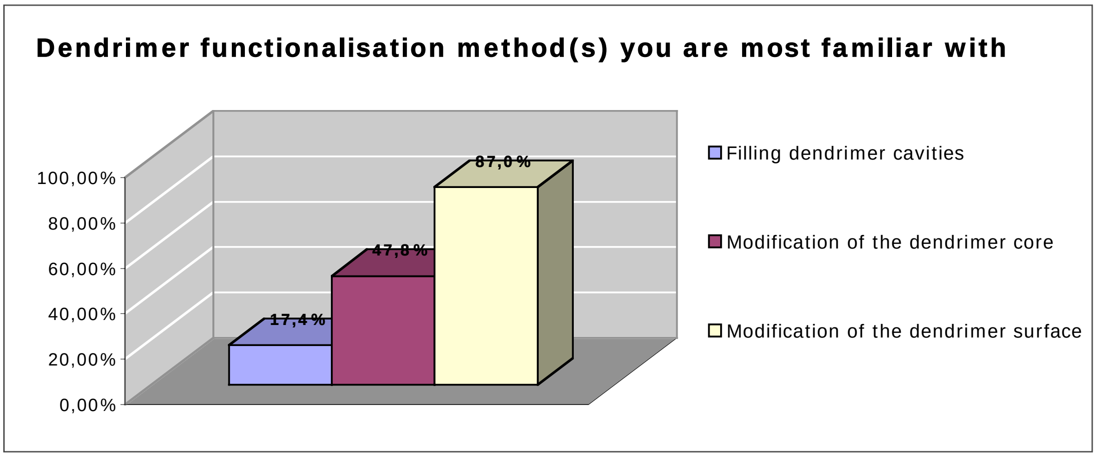
- Flexible binding properties: through the use of appropriate capping groups on the dendrimer exterior, dendrimers can be designed to exhibit strong affinity for specific targets.
- Transfection: dendrimers can be designed to move through cell boundaries and transport genetic material into cell interiors.

The controlled functionalisation of the surface can be considered a matter of synthetic methodology and equipment. Modification of the dendrimer surface is relatively easily achieved (according to the experts, the easiest of all modification processes) and is straightforward in most cases, depending on the structural features of the dendrimer and the degree of functionalization desired. If full functionalization is required (sometimes not necessary) and if the molecule to be attached at the chain ends is large, steric issues may arise and the problem becomes technical.

The functionalisation of dendrimers can be considered relatively easy to perform, when compared to most other nanomaterial categories. In addition, it is possible to verify their degree of functionalisation to a higher degree of accuracy than it is possible with most other nanomaterial categories, in which this is determined based on statistical methods. The functionalisation is usually the key to giving dendrimers the final properties required for the application they will fulfil.

The percentage of final cost added by this functionalisation method depends very much on the cost of the capping molecules and the desired degree of functionalisation. As a result, there is a very big variation in the estimations given by the participants in the Delphi panel. Answers given range from few percent to almost hundred percent.

Based on the responses given by the participants in the Delphi panel, these are the functionalisation methods that they are most familiar with:


Dendrimer functionalisation method(s) you are most familiar with

2.3.3 Dendrimer applications

Countless applications involving dendrimers are being researched worldwide. The following is an extensive list of the most common dendrimer applications:

Power/Energy

- Catalytic agent

Healthcare/medical

- Cellular Transport
- Artificial cells
- Diagnostics
- Targeted drug delivery (e.g. protein, antibody and anti-inflammatory)
- MRI contrast agents (e.g. organ, vascular and tumour imaging)
- Transfection reagents, DNA-carriers
- Protein / enzyme mimics or modelling
- Manufacture of artificial bones
- Development of topical microbicide creams
- Biomedical coatings (e.g. for artificial joints)
- Novel polyvalent dendrimer-based drugs

Engineering

- Molecular weight and size standards
- Chemical / biological sensors & detectors
- Carbon fibre coatings and ultra thin films
- Polymer and plastics additives (i.e. for lowering viscosity)
- Creation of foams (i.e. synthetic zeolites or insulating material)
- Building blocks for nanostructured materials

Consumer goods

- Ink / laser-printing toners
- Industrial adhesives
- Manufacture of nanoscale batteries and lubricants

Environmental

- Decontamination agents (trapping metal ions)

Electronics / optoelectronics

- Molecular electronics for data storage
- 3-D optical materials
- Light-harvesting systems
- OLEDs (i.e. flat panel displays and other light emission applications)
- Quantum dots
- Liquid crystals

Others

It is very difficult to accurately foresee a future in an area that is still developing so much. The following paragraphs, however, give an integrated overview of the different stage of development of the applications listed above. The following three paragraphs each cover one “snapshot” of the overall dendrimer roadmap. One for the current state of the art, one for the state of the art as predicted in five years from now (2010) and one in ten years from now (2015). The following distinctions have been made in the next figures:

Basic Research & Development Phase (Basic R&D)

Applications in this phase have received the interest of at least one or more researchers in the world. Some applications might still be in early development, while others are tough to develop and need a lot of basic research to be fully understood.

The object of basic R&D is to validate the original hypothesis. Many applications are currently in this phase as researchers are still struggling to understand basic properties of dendrimers.

Applied Research & Development Phase (Applied R&D)

After the hypothesis is validated, research typically (but not necessarily) moves from pure research labs to more commercial labs and companies.

Applied R&D will eventually result in a proof of concept, a successful demonstration model. While the production issues might not have been solved yet, a successful prototype / model has been validated.

Production Research & Development Phase (First applications)

After first demonstrator models and prototypes, initial, usually prohibitively expensive, small amounts of products may be produced. At the same time, if these prove successful, companies will seek to upscale production processes.

Generally at some point, demand increasing sufficiently to offset the investment needed to start bulk production. This phase ends at that point when is clear and possible to start this bulk production.

Mass production and incremental research (Mass production)

The final development phase, in this phase production has reached bulk amounts and research focuses on incrementally improving the products.

After this phase even more phases can be discerned (market maturity, end of life cycle, etc.) but these have not been taken into account when creating the following figures.

Overview of current applications (2005)

The figure in the following page is an overview of the current state of development of different dendrimer applications. The text and the figures presented in this section are mostly based on the input given by the participants in the Delphi panel.

Due to their organized structure, ease of modification, and strong adsorption behaviour to a variety of substrates, dendrimers can be used in the manufacturing of sensors to detect e.g. hazardous chemical vapours. Some types of dendrimer-based **sensors and detectors** are already commercial.

The exceptionally uniform molecular size of the various generations of PAMAM dendrimers makes them excellent **molecular weight and size standards** for calibration of analytical instruments. The US administration is already using them for this purpose.

Current applications include also **inkjet inks and toners**. At low levels, certain types of dendrimers dramatically improve water resistance and adhesion of inks to a variety of substrates (e.g., paper, glass, metal or plastic). In toners, they impart good admix and flow characteristics, stable properties, and high image quality. In the field of *in vitro* **diagnostics**, dendrimer-antibody conjugates are used in an immunoassay for rapid and sensitive detection of markers indicative of heart attacks.

Some health-related applications are already approaching the first stages of commercialisation. These include, for example, the use of dendrimers as **MRI contrast agents** and **transfection reagents** (DNA carriers). PAMAM dendrimer conjugates with paramagnetic ions, for example, are being studied for their use as magnetic resonance imaging (MRI) contrast agents.

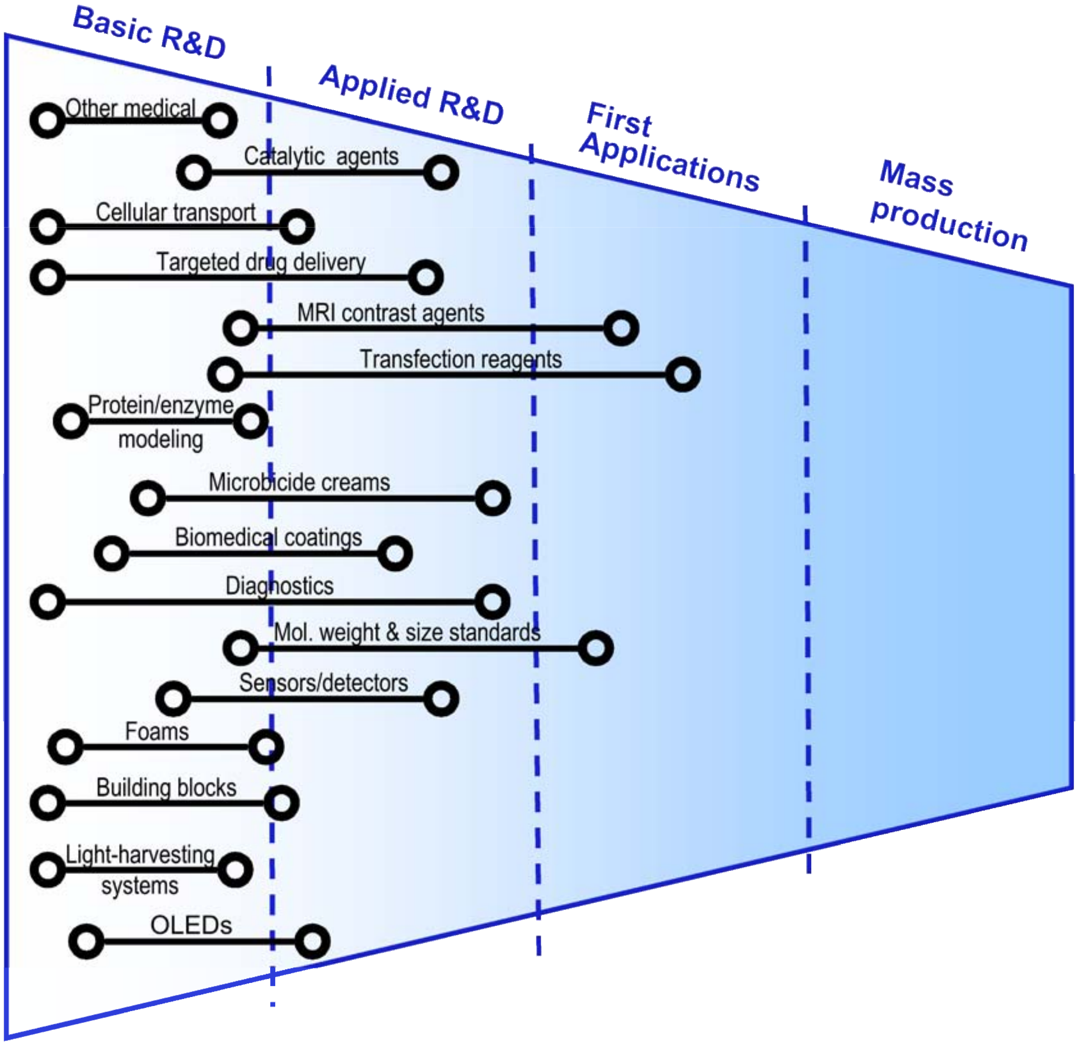
Other uses of dendrimers approaching the first commercialisation stages include, for example, their use as **catalytic agents** (giving homogeneous catalysts that are easily removed, e.g. by centrifugation or ultrafiltration) or into **microbicide creams.**

A lot of applications are, however, in the basic and applied R&D phases. Many of the applications in the medical field still remain in the (pre-)R&D phase. This is the case for certain **targeted drug delivery** applications, **cellular transport** or protein / enzyme **mimicking or modelling**. The use of dendrimers in the creation of **foams**, as **building blocks** for nanostructured materials or in **light-harvesting systems** is also in its earlier stages.

Some promising areas of research include the use of dendrimers in **gene therapy** or in **nanocomposites**. Dendrimers are also being used as the basis for **coating technologies**. Dendrimer-based coatings can display many of the same attributes of dendrimers in coating form. They are currently being investigated for applications in nano/microelectronics.

Dendrimer research is very much application-oriented. Development timeframes of different applications are difficult to estimate, because barriers are not so much linked to the synthesis or the functionalisation, but to the final application being researched and the cost for a given volume.

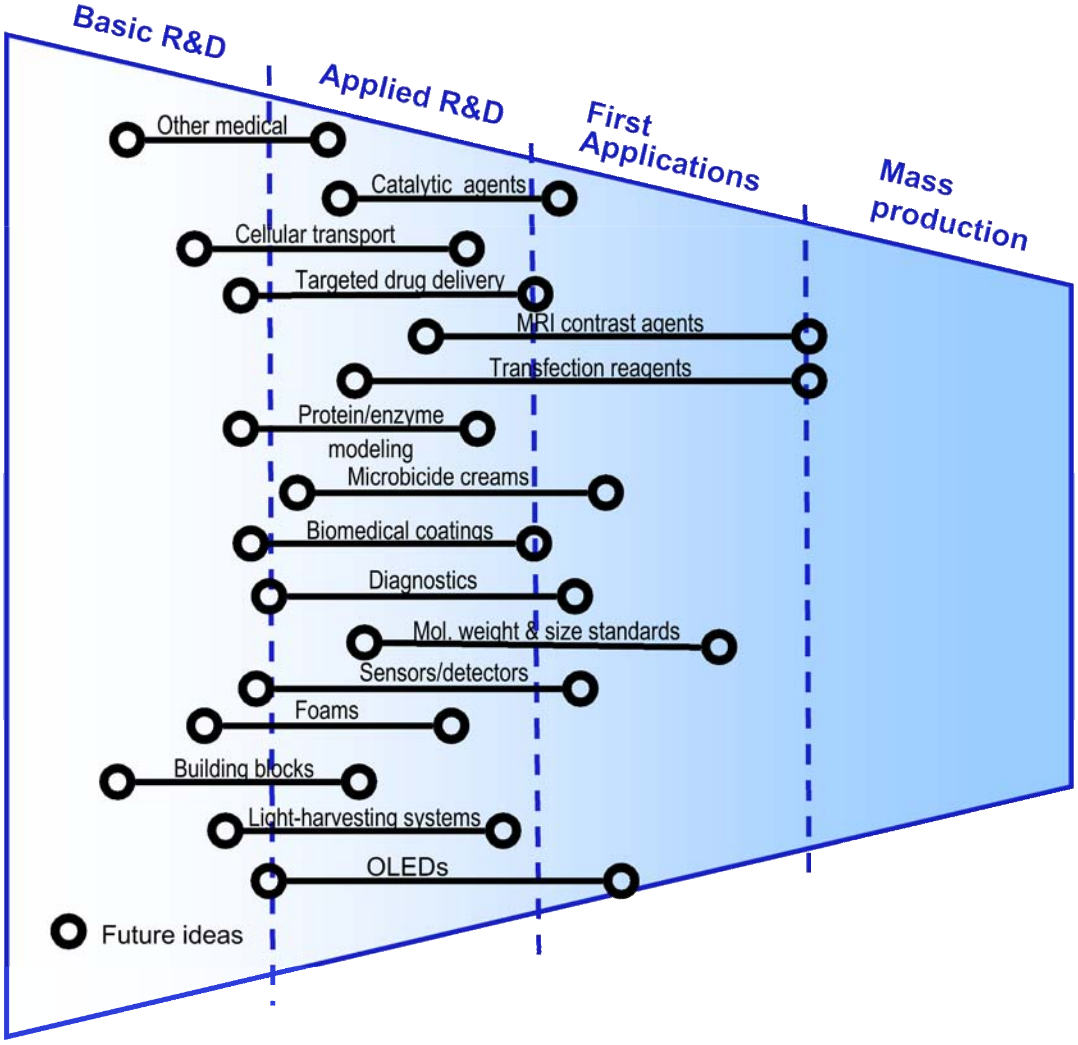
There are certainly many dendrimer-related applications possible. In spite of this, only a small number of them (up to a third, according to some experts) may reach the final market. One example is the field of coatings, where hyperbranched polymers will most probably take over due to their low production costs, as well as to their potential use as fillers or stabilizers. OLEDs are another example, facing tremendous competence from other materials such as conjugated polymers.



Overview of applications in 2010

The following figure is an overview of the expected state of development of different applications of dendrimers in year 2010. After five years many more applications will have come into fruition. The text and the figures presented in this section are mainly based on the input given by the participants in the Delphi panel.

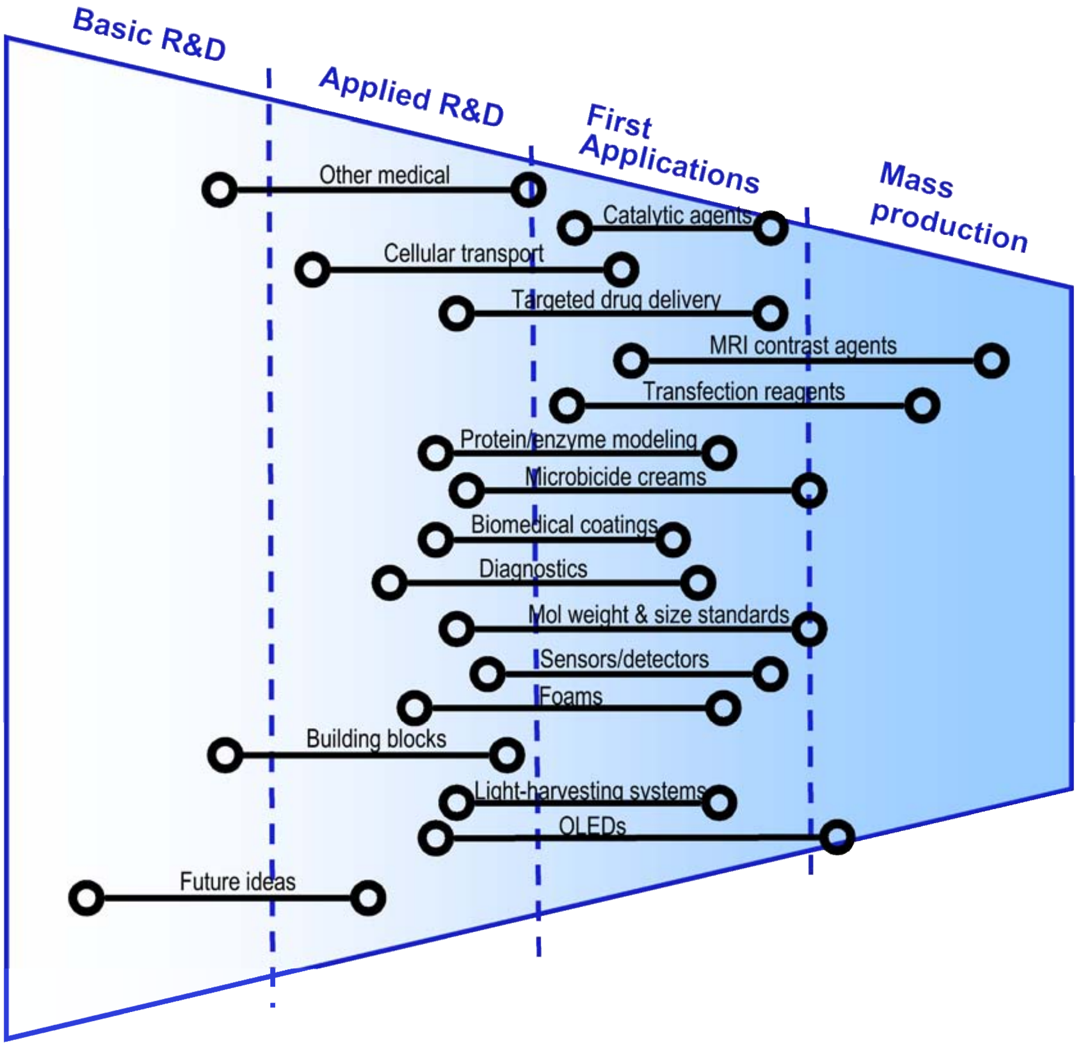
A good number of the potential applications currently considered will most probably be either in the applied R&D phase or already approaching the first commercial applications.



Overview of applications in 2015

The following figure is an overview of the expected state of development of different applications of dendrimers in year 2015. The text and the figures presented in this section are mainly based on the input given by the participants in the Delphi panel.

By 2015 many applications currently in development will be actual markets and currently still wild ideas may be ready to move to the market. Certain specific electronic and medical applications, however, might take even further time to develop. In the case of health-related applications, this might be due to the need to carry out lengthy clinical trials and the need for relevant administration approval.

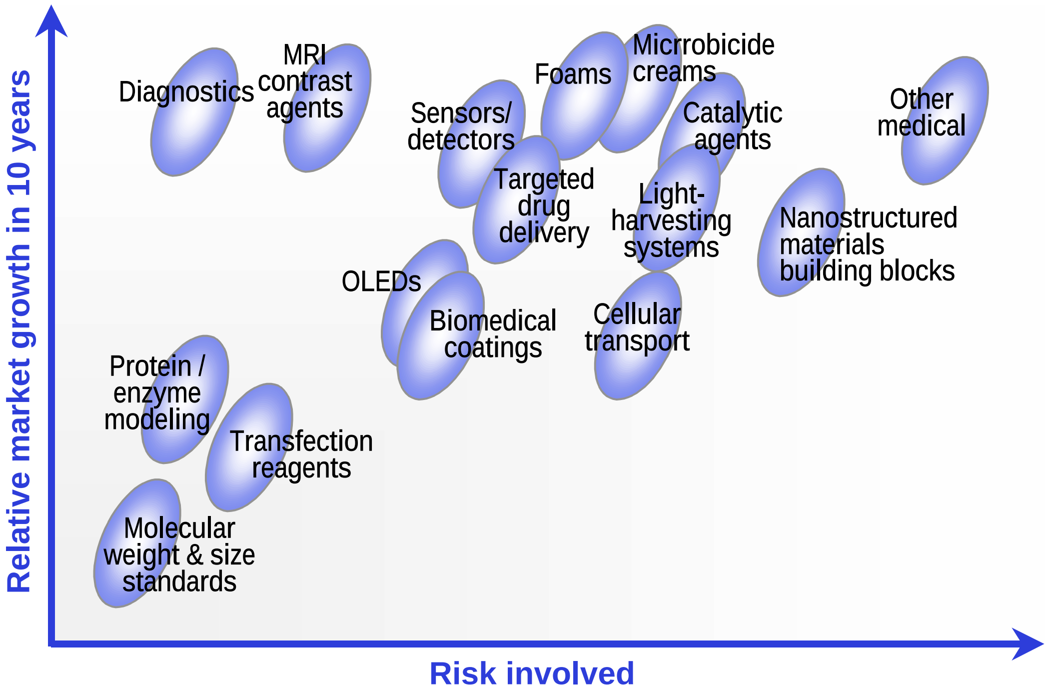


Risk involved vs. expected market growth in the next decade

For selected applications the following figure shows an estimation of (technological plus market) risk involved with the development vs. the estimated market growth of that application in the next decade.

The general purpose of the figure is to compare the relative position of different applications. For some applications, the current market of dendrimer-related products is zero while for others, a significant market exists today. Furthermore, the stage of development of different applications has also an impact on the estimated risk (normally, the more advanced the application is, the less risk). However, some applications might face harder restrictions to arrive to the market (e.g. FDA approval for medical applications).

The figure below is based on the input from the experts that have participated in the Delphi panel.



Applications on the lower left of this figure have lower risk but also less potential reward since the related market is not expected to grow so much during the next decade. Applications on the lower right (high risk, low market growth) will need support to be developed. More towards the upper left (low risk, high market growth) we would find the most interesting applications. In the upper right we can find applications that combine a high risk with markets that will growth exponentially, if the application develops successfully.

However, it can be appreciated that there are no applications clearly positioned neither in the lower right end (clearly unattractive applications) nor in the upper left end (highly attractive applications, probably with the only exception of MRI contrast agents and diagnostics). A common trend observed in the previous figure is that applications with higher expected market growth in the next decade do also have higher risks associated.

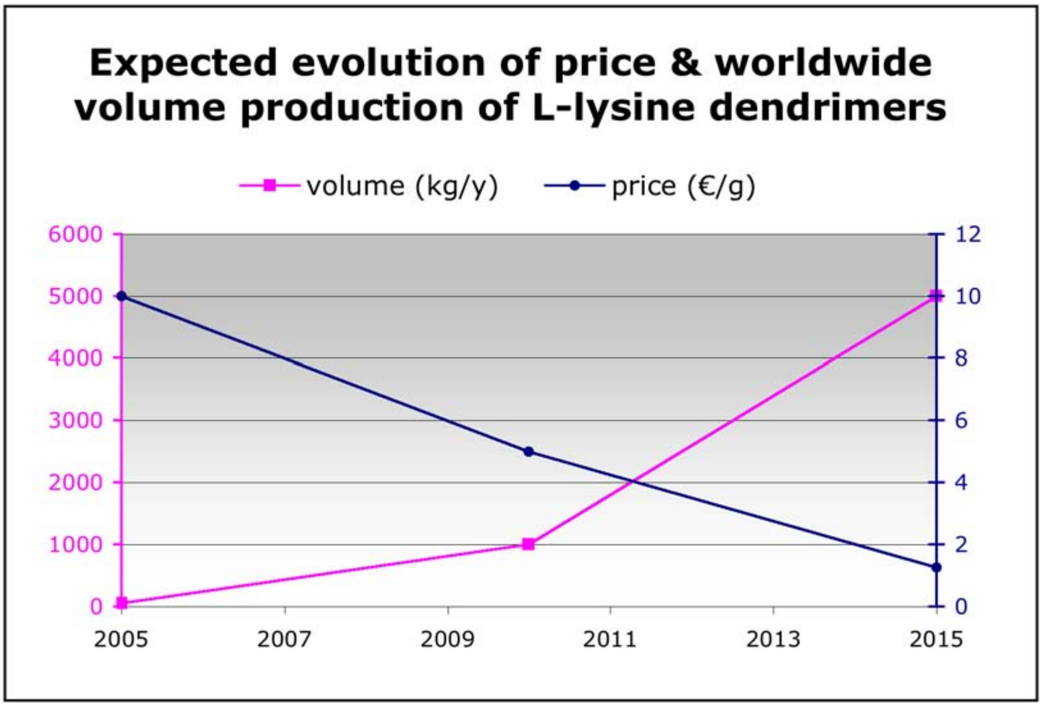
2.4 Estimated evolution of price & worldwide volume production

Although again it is very difficult to accurately foresee a future in a technology area that is still so much developing as dendrimer technology is, estimations on price and worldwide volume production of some types of dendrimers can be quite useful. The following figures have been elaborated based on the indications given by individual participants in the Delphi panel, who have made a laudable effort to provide explicit data for this chapter.

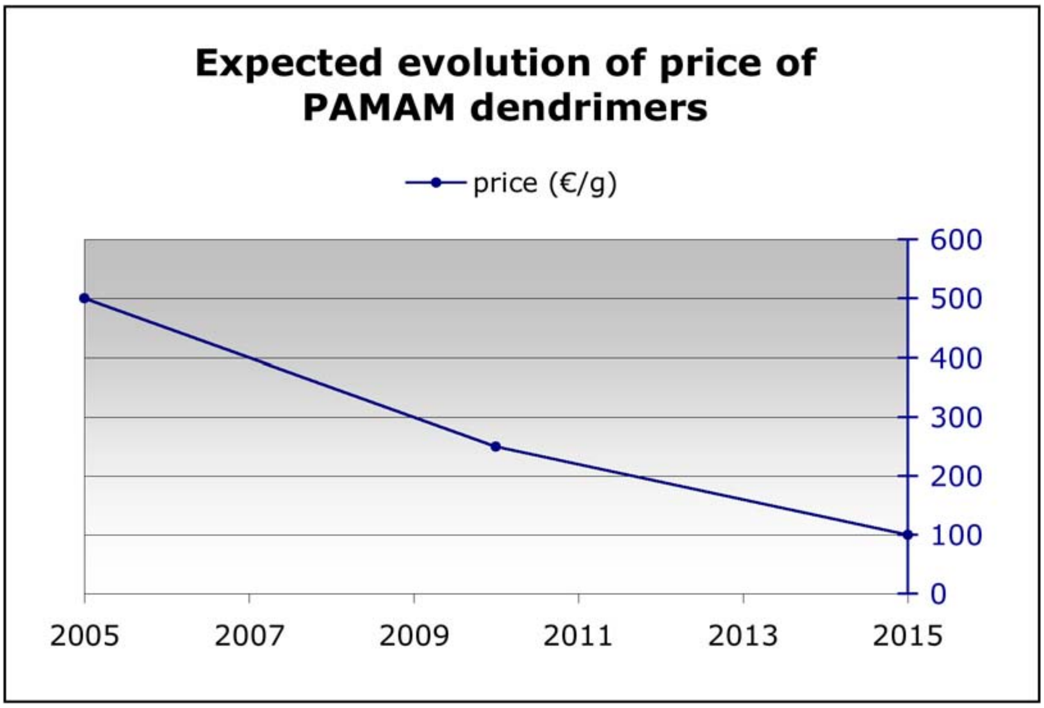
While academic researchers typically do not handle this type of information (estimations), companies are not eager to show everything they can do (or cannot do), mainly for competitive reasons. Furthermore, technological advancements may result in small jumps in production capability that not even the companies themselves have foreseen yet. On the other hand technological hurdles could make the demand for dendrimers evolve more slowly than expected, also leading to less reason to expand production capacities.

Additionally, in almost all the areas in which dendrimers show promise there are competing technologies that could stop dendrimer-based solutions ever being widely commercialised. According to some experts, the areas where dendrimers will most likely achieve sustained commercial success will be those where the application strongly depends on the unique characteristics of dendrimers, such as polivalency.

The following figures are to be used only as an indication of trends in price and volume production curves of these types of dendrimers. For the same dendrimer family, variations exist in price (depending on the generation, quality, etc.). For this reason, data should be only considered as an average indication.



L-lysine dendrimers have use in targeted drug delivery applications. They are also used in the development of topical microbicide creams, due to their superior manufacturability, stability and biological compatibility when compared to other types of dendrimers. The binding of viruses and bacteria to their human host or environment is a polyvalent binding event. This type of dendrimer is an ideal platform from which to develop a polyvalent antiviral or antibacterial to interfere with these processes.



PAMAM dendrimers have countless applications. They have use as catalytic agents and as templates for ‘nanoreactors’ in foams. They are also being used in targeted drug delivery, where the dendrimer acts as precise synthetic nano-containers and nano-scaffolding with non-immunogenic properties, if appropriately designed. They also provide for high loading capacities.

PAMAM dendrimers also have applications as MRI contrast agents. Here, the added value of dendrimers is that they offer increased resolution and better contrast for a lower concentration. PAMAM-based dendrimers with certain functionalisation can bind to / store high amounts of contrast-providing groups.

PAMAM dendrimers also have use as transfection reagents, where nanosized complexes are needed to be taken up by a cell. Partially degraded PAMAM dendrimers are very suitable for this application. According to some sources, the volume of PAMAM dendrimers required for this application can be estimated to be in the lower kg range. This type of dendrimer also has use in diagnostics or as protein / enzyme mimics and in modelling.

2.5 Non technological aspects

This chapter is devoted to Non-technological aspects of dendrimers, including issues related to Health, Safety and Environment (HSE), infrastructure/equipment requirements, instrumentation costs, etc.

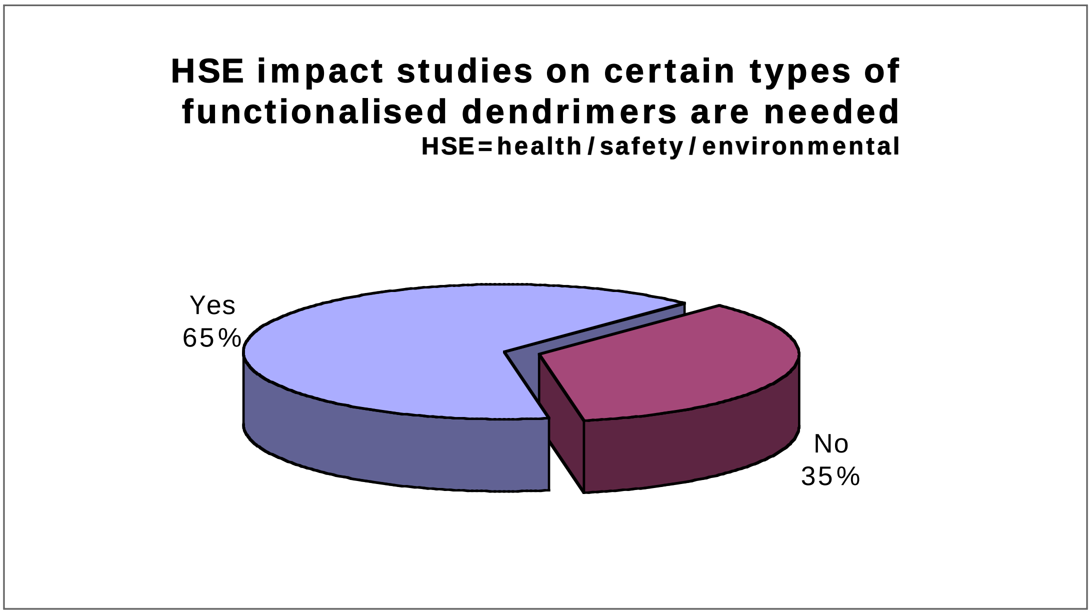
Health, Safety and Environmental (HSE) aspects

A white paper recently published by Cientifica, called *Nanotechnologies: Risks & Rewards* exposed that "many academic establishments and companies have inadequate procedures for monitoring exposure to nanomaterials, leaving them liable for future claims. As a result, some companies working with nanomaterials have seen dramatic increases in their insurance premiums".

According to the authors, concerns and uncertainties raised, related to health and safety aspects, result in a slower adoption of nanomaterials by the industry. Thus, "companies need to understand and clarify the current trends in both toxicology and regulation in order to ensure that they can reap the rewards of nanotechnologies while avoiding the risks, and this needs to be done immediately".

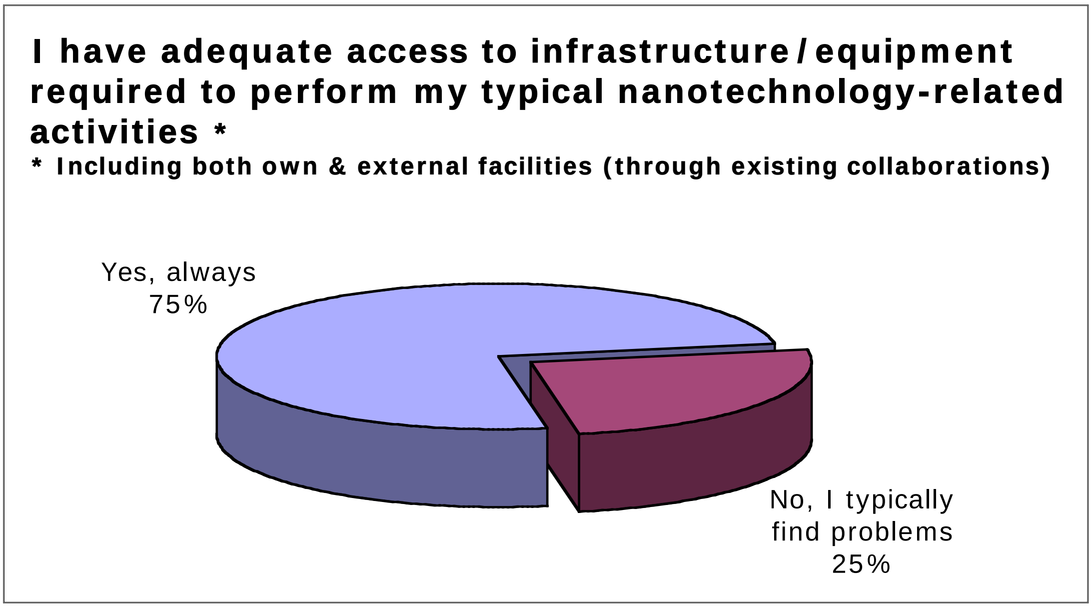
When enquired about whether HSE impact studies of certain types of functionalised dendrimers are required, 65% of the experts participating in the Delphi panel agree that these types of studies should be performed.

A key consideration here is, according to the experts, who is working with the nanomaterial and how novel this is. Dendrimers are often likely to be developed by companies with good experience of bringing novel chemicals to market and their synthesis lends itself to established methods of risk evaluation. Other nanomaterials that might present dangers, such as nanoparticles, nanotubes, buckyballs etc. often involve realms and groups with much less of a history. Dendrimers are thus less likely to present surprises in the HSE realm.



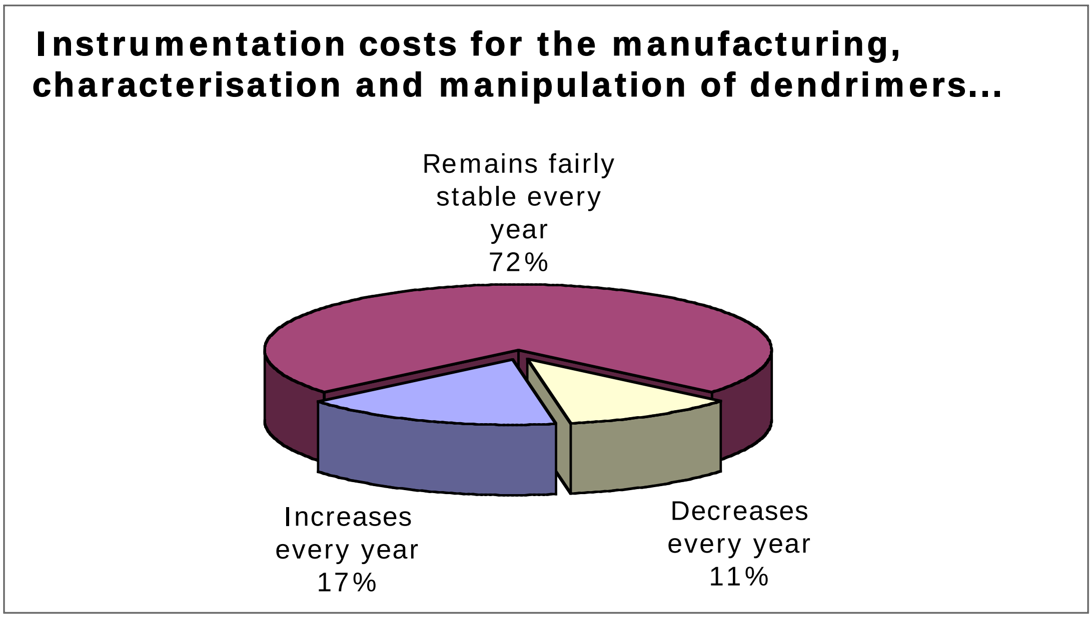
Infrastructure requirements

When asked about infrastructure needs required to perform the nanotechnology day-to-day work, most participants (75%) in the Delphi panel agree that they have adequate access to facilities (either internal or through existing collaborations). Only 25% finds problems.



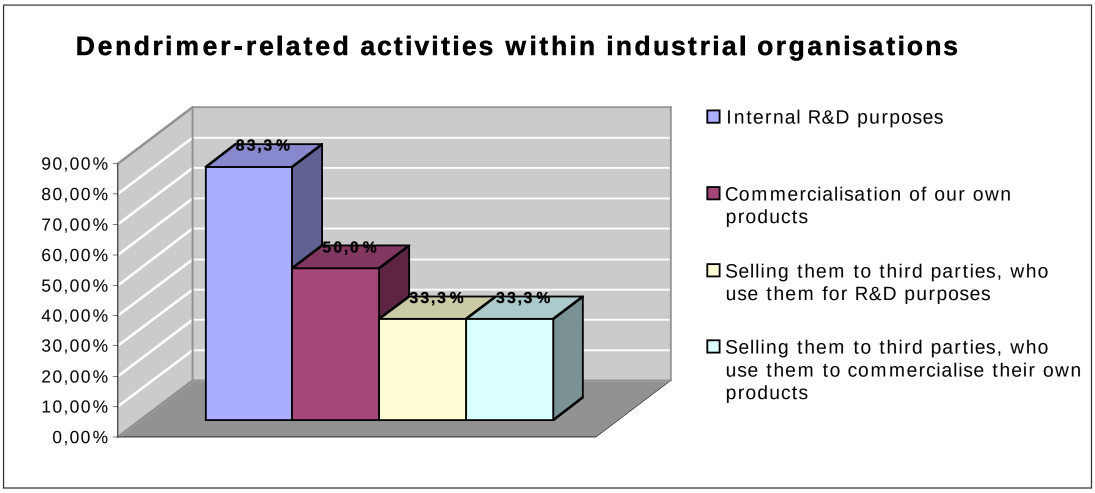
Instrumentation costs

When enquired about price trends of dendrimer-related equipment, 72% of the experts in the Delphi panel indicate that they remain fairly stable from year to year. The other answers are divided between the experts that think that the price increases annually (17%) and those that think it is the opposite way (11%).



Dendrimer-related activities within industrial organisations

In the last years, dendrimers have generated a very high interest throughout the scientific (and increasingly also the industrial) community. The following figure (responses gathered from participants in the Delphi panel) shows the current activities of industrial organisations in the field of dendrimers. It can be observed that companies combine internal research tasks with the commercialisation of its own products and / or the selling of dendrimers to third parties.



2.6 Conclusions

2.6.1 Most relevant applications

The potential applications of dendrimers are almost endless, as already discussed earlier in this document. However, the field of medical applications can be considered a step above the others, which is probably not surprising given that dendrimers essentially represent engineering at biological size scales. Applications such as transfection reagents, MRI contrast agents, or microbicide creams are in full development, with several companies and research groups pursuing them worldwide. In addition, elevated costs associated can be considered a less limiting factor in medical-related applications than in some others fields. This has led to an explosion of dendrimer-related patents in this field over the last several years (much more in the US than in Europe, however).

Investigations of dendrimers as carriers for imaging contrast agents (a very early application of dendrimers) have demonstrated excellent potential. The use of dendrimers in this application allows for enhanced organ, vascular or tumour imaging and diagnostics. For example, the superior ability to visualize vascular permeability and renal function allows early diagnosis of acute renal failure.

Dendrimers have also been used as transfection reagents. PAMAM dendrimers chemically synthesised with positively charged amino surface groups, have been used to deliver nucleic acids. Currently, cationic lipids are the most popular reagent for siRNA transfection, providing a positively charged vehicle to carry the negatively charged nucleic acids into cells. Compared to cationic lipids, these polymer-based reagents display greater transfection efficiency and less toxicity in many cell types. Dendrimer-based reagents are being researched in order to create a more efficient and versatile delivery reagent with low toxicity levels.

Other life sciences applications are also receiving a lot of attention. Targeted drug delivery is one of the most attractive potential applications of dendrimers. The high level of control over the dendrimer architecture makes them ideal carriers for the delivery of active pharmaceutical ingredients. Drugs that have been encapsulated into or attached onto dendrimers include cisplatin, doxorubicin, adriamycin, methotrexate, 5-fluorouracil, ibuprofen, and nifedipine. If successfully developed, the potential reward associated to this application will be huge. Dendrimers may take the place of polymeric agents, but with advantages such as the large number of identical surface groups, excellent encapsulation properties and highly controllable chemistry. On top of this, factors such as the high availability of research funding and the hard commercial push by dedicated companies such as Dendritech also contribute to the development of this application.

On the other hand, medical applications will require official approval by relevant administrations (e.g. the FDA – Food and Drug Administration in the US) before being commercially implemented. In July 2003 the FDA allowed the first clinical trials of a dendrimer based pharmaceutical: Vivagel™, a topical microbicide for the prevention of HIV infection in women developed by the Australian company Starpharma. Phase I clinical trials of Vivagel™ are currently underway.

Another area receiving a lot of attention is electronics, with sensing applications being a bit more advanced than others. Some very good work is also being performed in light-harvesting and light-emitting macromolecules. IBM has a strong interest (and lots of patents) on the application of dendrimers in micro- and molecular electronics. Another area where attempts are being made to exploit the three-dimensional shape of dendrimers is in generating porosity in dielectric materials.

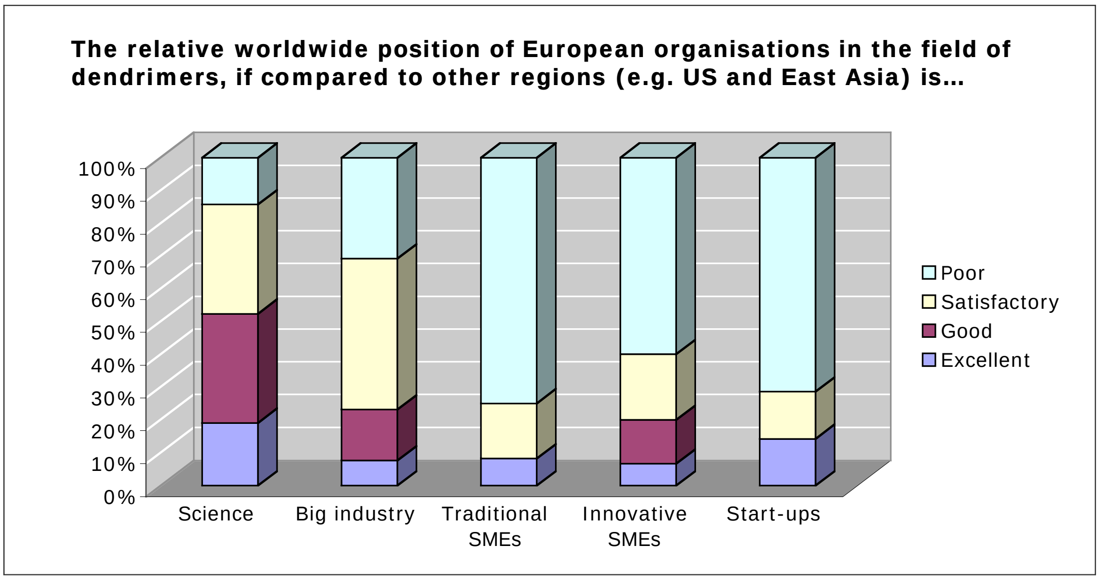
There are a number of commercial dendrimer-based products that are just starting to appear. The Swedish company Perstorp sells dendrimer-like materials for a variety of applications, high performance varnish for boats being only one example. DSM, in the Netherlands, has a new type of dendritic-based material that promises to reduce the number of steps in the papermaking process, making it much more efficient and environmentally friendly.

2.6.2 EU positioning in the field

Here, a clear distinction should be made between the academic and the industrial communities. The general perception is that European academic research in the field of dendrimers is of good quality. In fact, more than 60% of the participants in the Delphi panel think that it is either excellent or at least good.

The situation with European industry is considerably different. In this sense, only big industry has a satisfactory position, with less than 20% of the experts defining its situation as poor. Companies like DSM and Akzo Nobel (both from The Netherlands), Qiagen, Schering and Bayer (all three from Germany) and Perstorp (from Sweden) contribute to this perception.

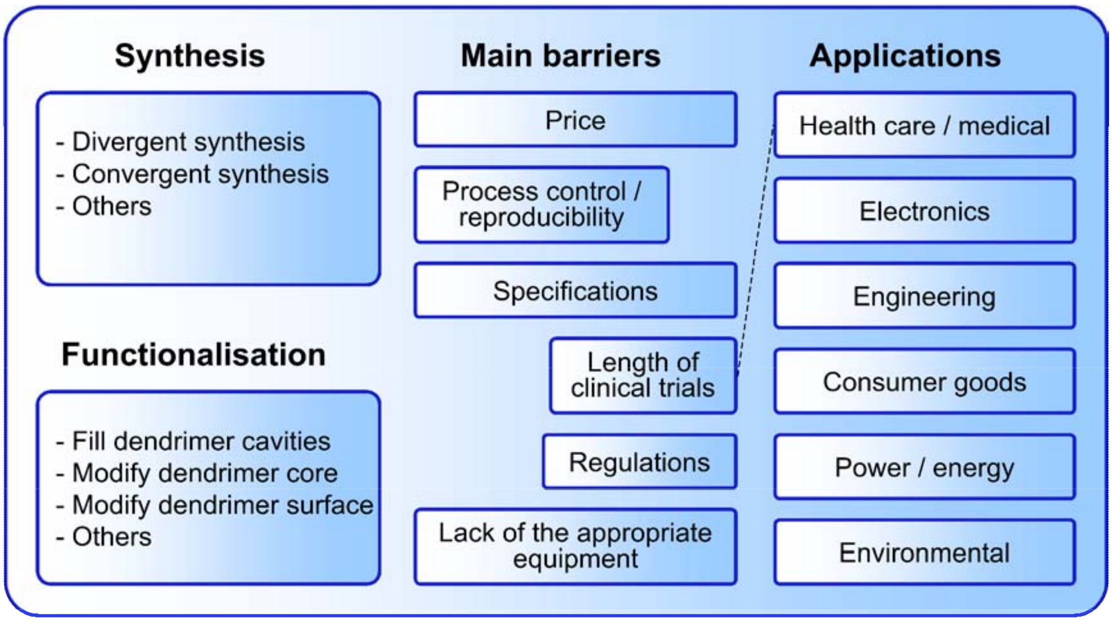
Both traditional and innovative SMEs and start-ups are poorly evaluated, with more than 40% of the experts defining their position as poor.



From a EU RTD policy point of view, this diagnosis by the experts leads to clear suggestion to focus RTD policy instruments above all on the link between academic excellence and industrial competitiveness. Putting this assessment alongside the earlier statements regarding barriers to market (which highlighted above all the price of dendrimers) it becomes all the more clear that industrialization is the key missing ingredient in EU dendrimer research and development.

2.6.3 Final conclusions and recommendations

The following figure summarises the most important barriers in the production and commercialisation of dendrimer related products.



<u>Price</u> is, according to the experts, the most important barrier in dendrimer synthesis and functionalisation approaches. Considering this, substantial efforts should be put to reduce their price, possibly through research on novel synthesis methods or through the reduction of steps in existing ones. If dendrimers are to be competitive against other materials / technologies in various applications such as those reviewed in this document, an important reduction of costs will be required, except in cases where dendrimers (or very similar macromolecular entities and methods) offer unique capabilities. Some of the biomedical applications (not including MRI and targeted delivery) fall into this category. Upscaling of production is a key field of research for driving down costs in many applications. It seems that now is an appropriate time for the production of dendrimers for many applications to come out of the labs and move into the pilot plants.

Another major potential barrier in the commercialisation of dendrimers for certain applications is problems with <u>reproducibility</u>. For some applications (e.g., medical, electronics), it is key to work with high purity and well-defined products with reproducible properties. Only in limited cases, the <u>lack of more appropriate equipment</u> can be considered a barrier to the success of dendrimers.

According to most experts, opportunities for dendrimers-related applications in the field of new therapeutic molecules are very broad. Targeted research, however, will require substantial investment from national and EU governments. This would be justified because, as the figure in page 22 (*Risk involved vs. expected market growth*) shows, risks associated with these developments will, in the short term, be very high. Once it becomes clear that there are a number of key medical uses for these drugs, the pharmaceutical industry will be ready to take the next step and invest the necessary resources on its own.

Other barriers are application-specific. The medical field, for example, will have to face lengthy clinical trials in order to be able to commercialise dendrimer-based products. Other aspects that might influence broader application fields might be regulation and application-related specifications. Even though it could be tempting to ask for a global regulation involving all types of dendrimers, their chemical diversity and related properties are so broad that this would be unfeasibly complex. According to some sources, it would be easier to just use regulations classically applied to small molecules.

Annex I. List of participants (and statistics)

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BASF Aktiengesellschaft
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Rosario Núñez
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Ezequiel Pérez
University of Malaga
Professor
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QIAGEN GmbH
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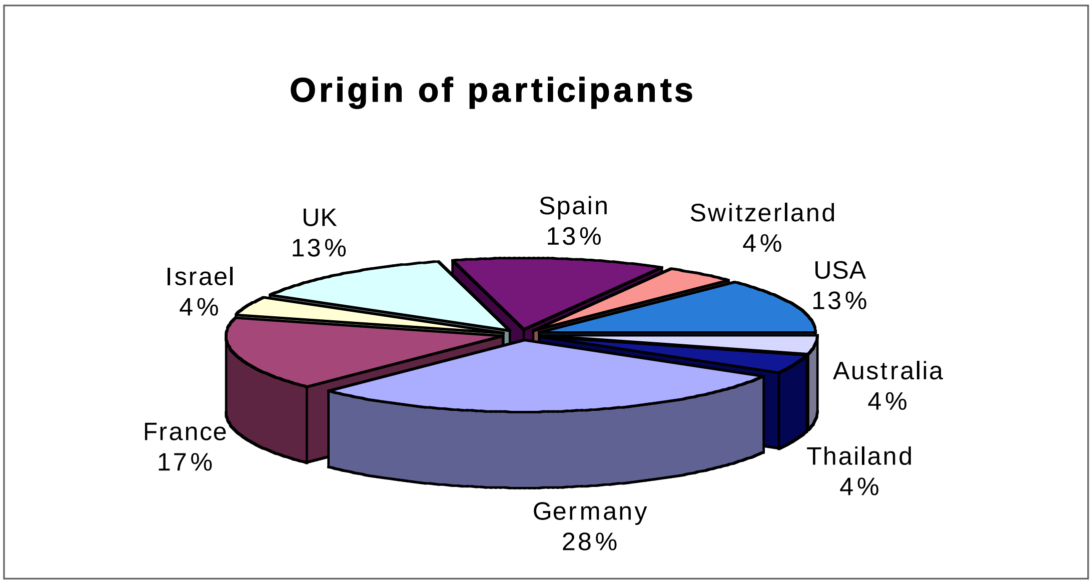
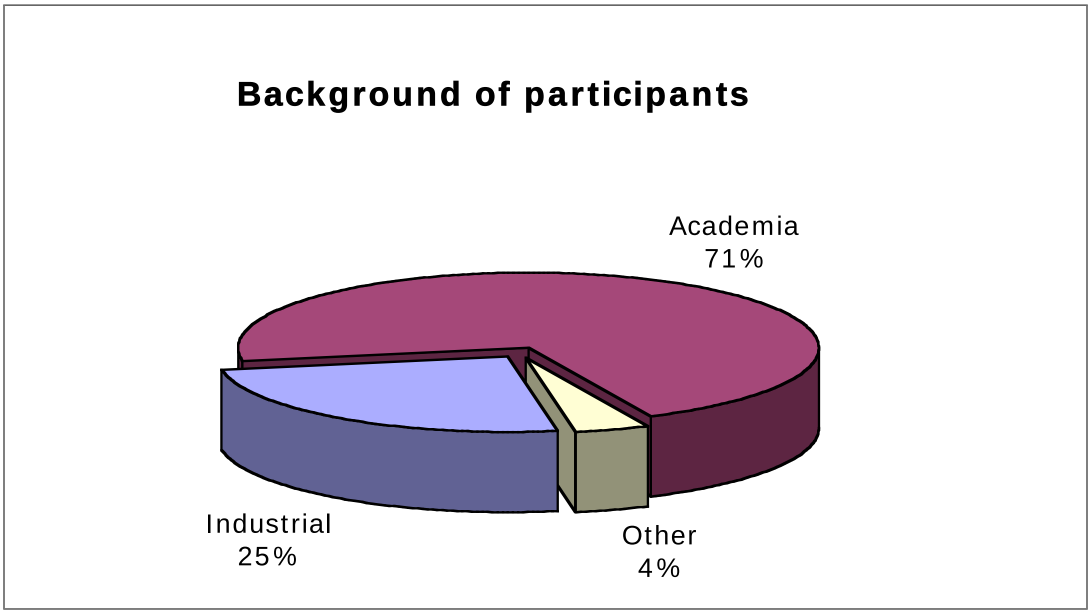
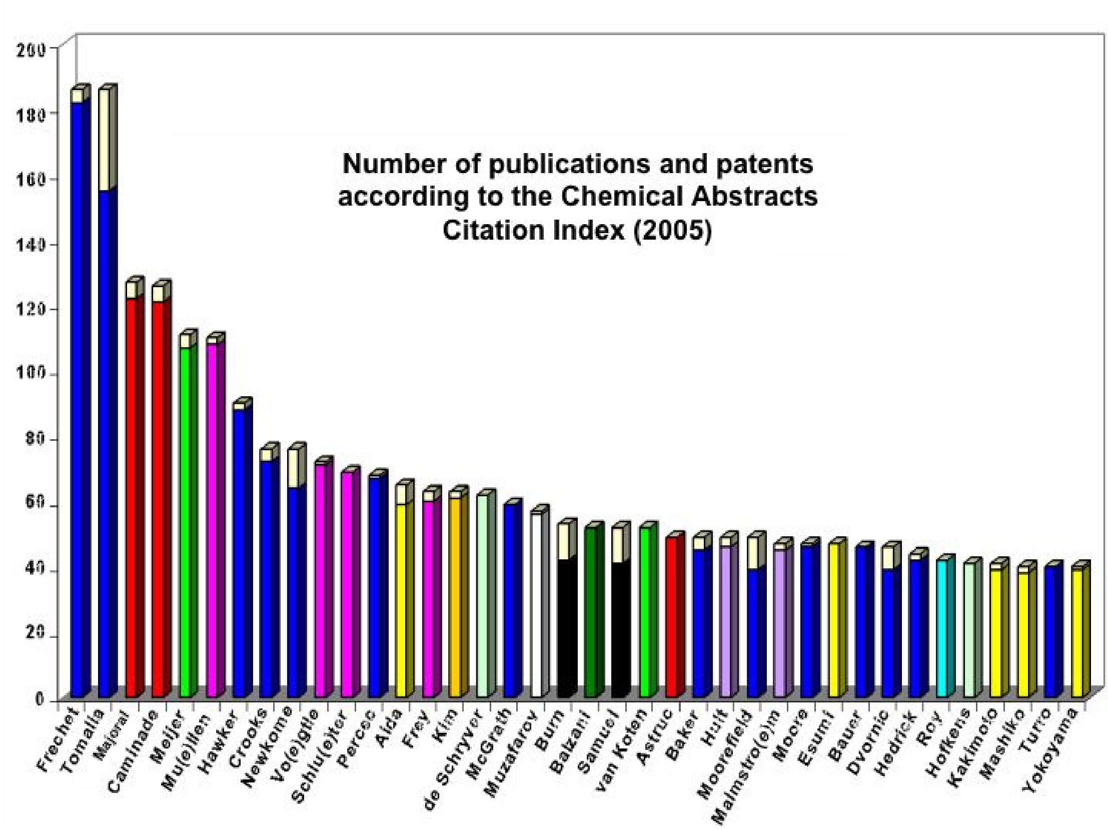
Germany


Origin of participants
UK 13%
Spain 13%
Switzerland 4%
USA 13%
Israel 4%
Australia 4%
France 17%
Thailand 4%
Germany 28%


Background of participants
Academia 71%
Industrial 25%
Other 4%

Annex II. Number of publications and patents



NRM
nanoroadmap project

NanoRoadMap is a project co-funded by the 6th Framework Programme of the EC

Draft Roadmap Report on Thin films & coatings

This version is circulated within the Delphi Panel to clarify open issues
Please read carefully and provide feedback wherever you see fit

Statements are preliminary – pending Expert panel approval
Responses are not linked to individuals participating in the Delphi panel

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31st July 2005

Table of contents

1 Introduction

1.1 Background

The NanoRoadMap (NRM) project, co-funded by the European Commission (EC), is aimed at roadmapping nanotechnology related applications in three different areas:

- Materials
- Health & Medical Systems
- Energy

Within the project, an international consortium consisting of eight partners covering seven European countries and Israel, has joined forces to cover the time-frame for technological development in this field up to 2015. The results of the NRM project are to be used by any European entity interested in planning an R&D strategy taking into account nanotechnology. An important potential user is of course the EC itself in the preparation of the 7th Framework Programme (FP7) for research and technology development.

For additional information on the NRM project, please refer to www.nanoroadmap.it

1.2 Goals

The primary objective of NRM is to provide coherent scenarios and technology roadmaps that could help the European players to optimise the positive impact of nanotechnology on society, giving the necessary knowledge on its future development and when technologies and applications will come into full fruition.

The key users of the reports are mainly European SMEs, research organisations, public bodies in general and the EC in particular. Even though a special focus is put on SMEs, these roadmaps are also meant to be useful for larger corporations.

This report is one of the three final deliverables of the NRM project (together with the reports on the field of Health & Medical Systems and Energy) and it is aimed at providing a thorough overview of specific topics selected for roadmapping within the field.

1.3 Methodology

1.3.1 Collection and synthesis of relevant existing information

A report was published in October 2004, as the most important deliverable of the first stage of the project. It was based on the collection and synthesis of existing public sources in 31 countries and was published as key input for the celebration of the First NRM International Conference held in Rome the 4th – 5th of November 2004. The full report can be downloaded for free on the project web site.

The report focused on reviewing the different types of nanomaterials, describing the topic, its most remarkable properties, current and future markets & applications, and leading countries & highlighted R&D activities in the field. A general review of non technological aspects (social, legal, ethical and health and safety aspects, but also economical aspects and infrastructures requirements) was also performed.

The 12 topics identified, even not being completely homogenous in terms of scope or materials classification, were intended to adequately cover the field of nanomaterials. The following list was agreed upon the different partners of the NRM project (similar classifications can be found in the existing bibliography):

- Nanostructured materials
- Nanoparticles / nanocomposites
- Nanocapsules
- Nanoporous materials
- Nanofibres
- Fullerenes
- Nanowires
- Single-Walled & Multi-Walled (Carbon) Nanotubes
- Dendrimers
- Molecular Electronics
- Quantum Dots
- Thin Films

1.3.2 *Selection of topics*

Another major goal of that report was to set the basis for discussion and selection for roadmapping of 4 out of the 12 topics identified above. A preliminary selection of topics was presented during the First International Conference in November, 2004.

After a thorough discussion, which involved international experts in the field of nanotechnology, four topics were selected (and validated in dialogue with the European Commission). The topics chosen are:

- Nanoporous materials
- Nanoparticles / nanocomposites
- Dendrimers
- Thin Films & coatings

1.3.3 *Roadmaps elaboration*

One draft roadmap has been prepared for each of the four aforementioned topics. The present report gathers all the work executed during this phase, and can be considered as the deliverable for this activity till now. The results of these roadmaps will be presented in 8 National Conferences and one International Conference to be held in September – November, 2005.

A Delphi-like approach (referred to as Delphi panel in the future) has been used for the preparation and execution of the roadmaps. The methodology followed consisted of 2 cycles, and it was the same for the four topics. The Delphi exercise consisted in:

1. Selecting top-international experts on the field
2. Preparing a dedicated on-line questionnaire for each topic to be roadmapped
3. Circulating the questionnaire and gathering experts' responses (1st cycle)
4. Preparing a first draft roadmap document based on the input gathered from the experts and personal interviews with some experts
5. Circulating the draft roadmap document, asking for feedback (2nd cycle)
6. Elaborating the final version of the roadmap

2 ‘Thin films & coatings’ Roadmap

2.1 Definition of thin films

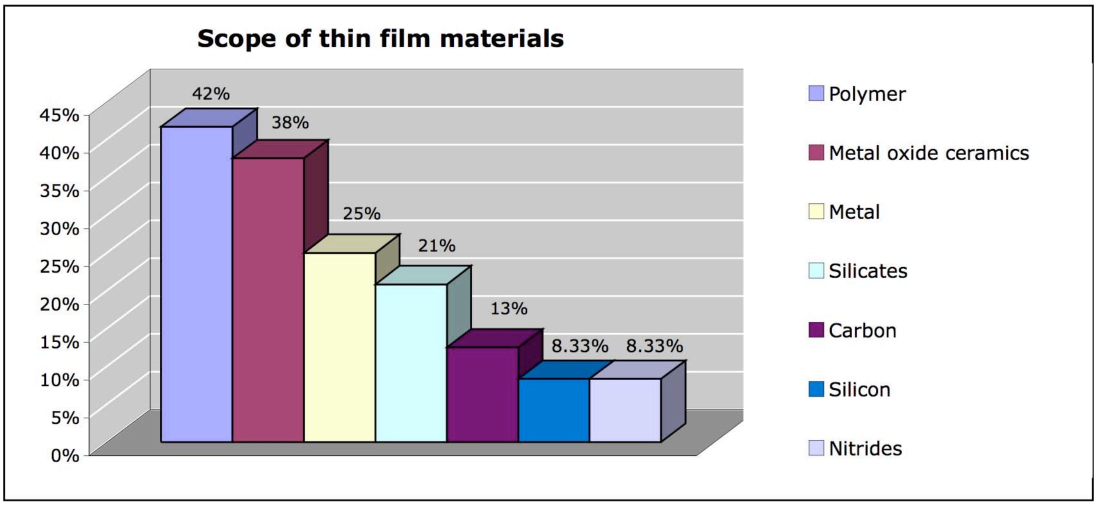
PICTURE

Would you like one of your pictures to be published, please contact us.

This chapter focuses materials’ structures resulting from the deposition of one or more materials’ layers onto a surface. The thickness of the thin films considered is below the order of 100 nm.

Typical production processes are physical vapour deposition (PVD), chemical vapour deposition (CVD) or sol-gel. Lately, many research groups are looking at the possibilities for printing technologies to create functional (patterned) thin films.

Materials used include Si films (amorphous, crystalline or polycrystalline), 57Fe3O4 (magnetite) and other metal/metal-oxides (for magnetism-related applications), YBCO (superconductivity), diamond (scratch resistance), selenides or metal sulfides (applications exploiting luminescence properties). Finally, there’s a wide range of (nano) particles formerly used in (nano)coatings that are being reconsidered; for instance, Tungsten Oxide may be replaced by ZnO thin films.



Not surprisingly, polymer thin films are very much investigated. There are some important reasons behind this fact. They are applicable in a huge variety of applications, ranging from the electronic sector as photo-resist in semiconductor wafer’s production process, right through organic light emitting displays (OLEDs) up to simple anti-corrosion coatings. Moreover, organic thin films can be applied at low temperature (as compared to ceramic/inorganic materials) and therefore can be handled by less sophisticated processes (e.g. sol-gel).

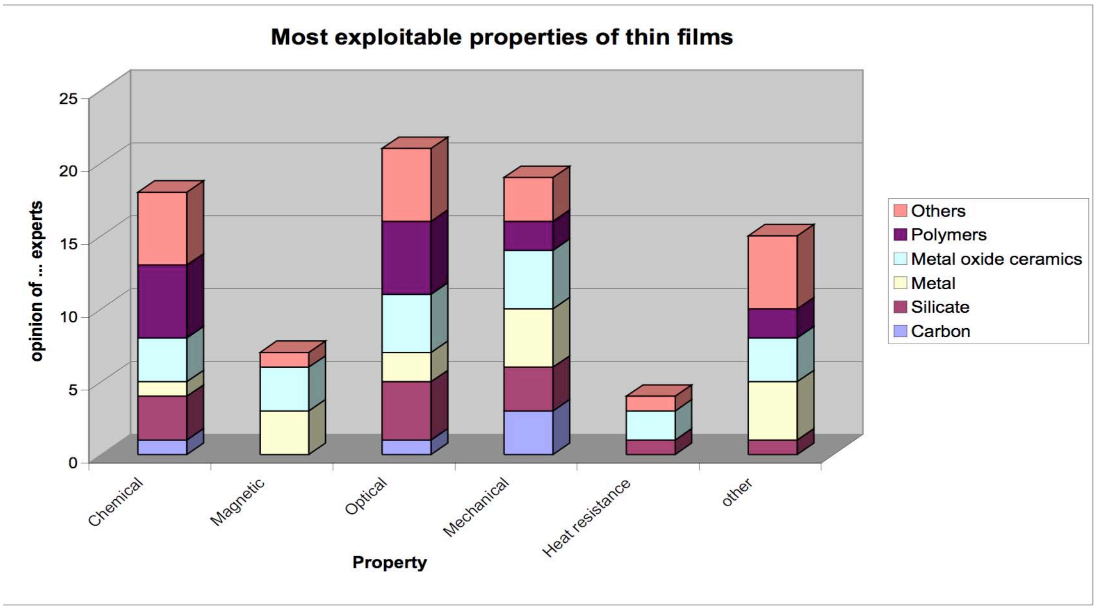
By adding inorganic fillers to organic thin films, mechanical properties can be improved. Normally this would mean sacrificing flexibility and transparency properties of organic materials; however, nanotechnology allows keeping these properties, with regard to transparency mainly because the particles are smaller than the wavelengths of visible light.

2.2 Most remarkable properties of thin films

The main advantage of thin films (or any other coating) is that materials properties can be transferred to the surface (thus enabling the use of not specialised substrates). The substrate and the thin film are a material system where each of them provides the required functionality.

In general, nanotechnology provides the tools for controlling 3 key parameters for thin films performance: chemical composition (and crystalline structure at nano-sized domains), thickness and topology (including nano-scale patterning of thin films' surface).

According to the experts, most remarkable thin film properties are: optical, mechanical and chemical properties. Monolayer thin films could, most of the times, provide these properties, although multi-layer thin films are sometimes required. Of course, in many applications, it is exactly the combination of properties (often the transparency combined with chemical or mechanical properties) that exploits the nanoscale most.



Chemical properties

Thin films could be designed to have properties like water repellence, anti-fogging, chemical barriers and chemical inertness, oxygen or moisture barriers over polymers or antimicrobial surfaces. The functionalisation of polar/apolar surfaces is crucial for sensors' applications and together with hidrophilic/hydrophobic balances is essential in hard coatings. By increasing the inorganic content, thin film stability could also be improved. The appropriate chemical composition (e.g. hybrid coatings) also provides good etch barrier characteristics (e.g. for plastics on automotive bodies) or has also a great impact on electrical properties (e.g. in SiOxNy) and especially on insulation properties (relevant for semiconductor circuit structures).

Optical properties

These include a.o. light emission, trapping, transmission, opaqueness, fluorescence, waveguides, anti reflection, etc. Some thin films have the ability to emit light without the need for a backlight; these are applied in displays. Thin films can be designed to be transparent or opaque (or both depending on the applied voltage or incident light) and applied, a.o. in windows, displays or solar cells. In some cases multi-layered thin films are required for achieving the desired properties (e.g. OLEDs use small molecules in multi-layers for up to full colour displays). Thin films of high refractive materials could be designed to be planar waveguides for photonics' applications. Dielectric thin films could also be used to generate surface plasmons resonance that's exploitable in optical modulators or chemical sensors. Nanotechnology enables a precise knowledge on the exact thickness required for desired optical and/or electrical properties. The interface between the thin film/layer and the substrate is crucial for understanding the optical (but also) electrical behaviour at ever decreasing thicknesses and for optimising the layer thickness.

Mechanical properties

These include a.o. wear/ abrasion resistance, hardness, scratch resistance, dry lubrication, reduced Strain-to-failure, etc. Surface heterogeneities of either chemical or morphological origin drastically affect interface phenomena (wetting-adhesion-friction). Nanotechnology enables the design and production of thin films with the required thickness and topology.

Electrical (conductivity, insulation, etc.) **and magnetic properties**:

Highly dependent on the chemical composition, some thin films' high conductivity properties are of great importance for CMOS' wiring materials or for OLEDs. The dielectric characteristic of some thin films' material is exploited together with magnetic properties in high-density storage and Non-volatile memory applications. Nanotechnology in this area enables the preparation of thinner films as well as a better dispersion of magnetic particles.

Thermal properties

Thin film coatings are applied in windows or more sophisticated applications like aircraft engines (e.g. Thermal Barrier Coatings based on Zirconia). Nanotechnology enables the optimisation of thin film thickness and density (incl. pores, if any) to specific requirements. Application of multi-layered thin films allows, for instance, blocking the travel of atomic vibrations that produces heat flow whilst still letting the electrons flow as a current (application in thermoelectric devices).

2.3 The Thin films & coatings' pipeline

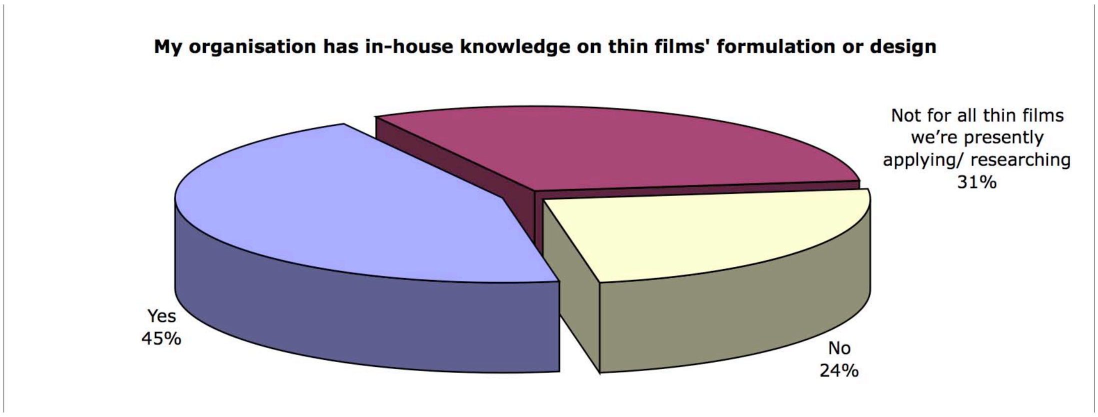
This section deals with each of the steps in the thin films pipeline, from their production to their application.

The following table summarises the production techniques considered within this chapter. For each of them a brief description is given and main bottlenecks outlined.

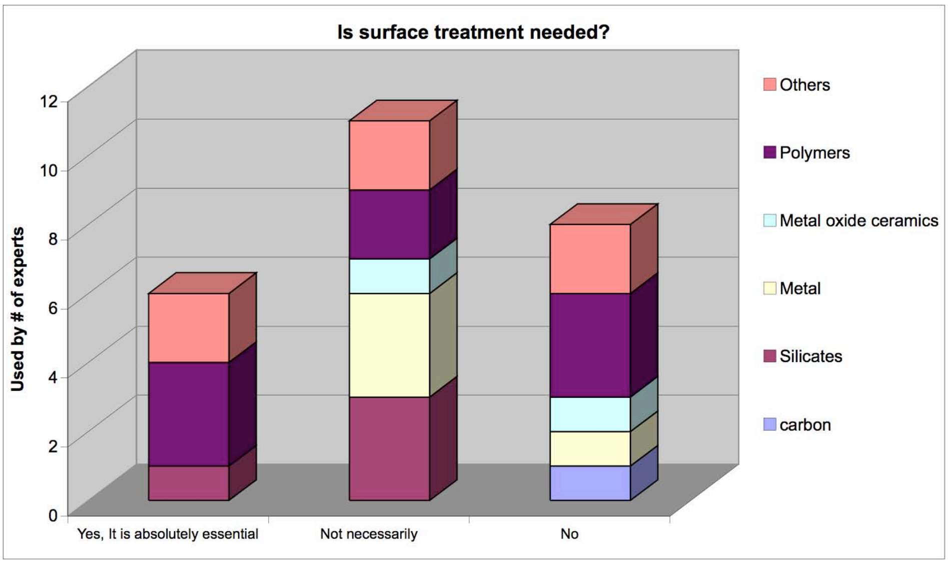
Thin film production	Thin film post-treatment	Patterning methods	Surface Treatment
• Chemical Vapour Deposition (CVD) • Physical Vapour Deposition (PVD) • Sol-gel • Electrodeposition / Electroplating • Spin coating • Spray coating • Self-assembly • Positional assembly	• Annealing • Thermal oxidation • Ultra Violet (UV)	• Electron beam nanolithography • X-Ray Lithography • UV-Lithography • Scanning probe lithography • Heated AFM • DipPen nanolithography • Soft lithography • Nanoimprint lithography (NIL) • Inkjet	• Plasma etching • Sputter etching • Ion milling

However, it should be underlined that thin films production does not always follow this linear approach. In fact, for many applications only the first 2 steps are normally implemented whereas for applications in the semiconductors' industry thin films undergo the complete process.

In general, most of the experts having participated in this roadmapping exercise do have in-house knowledge for designing (or formulating) the thin films they're presently researching or applying.

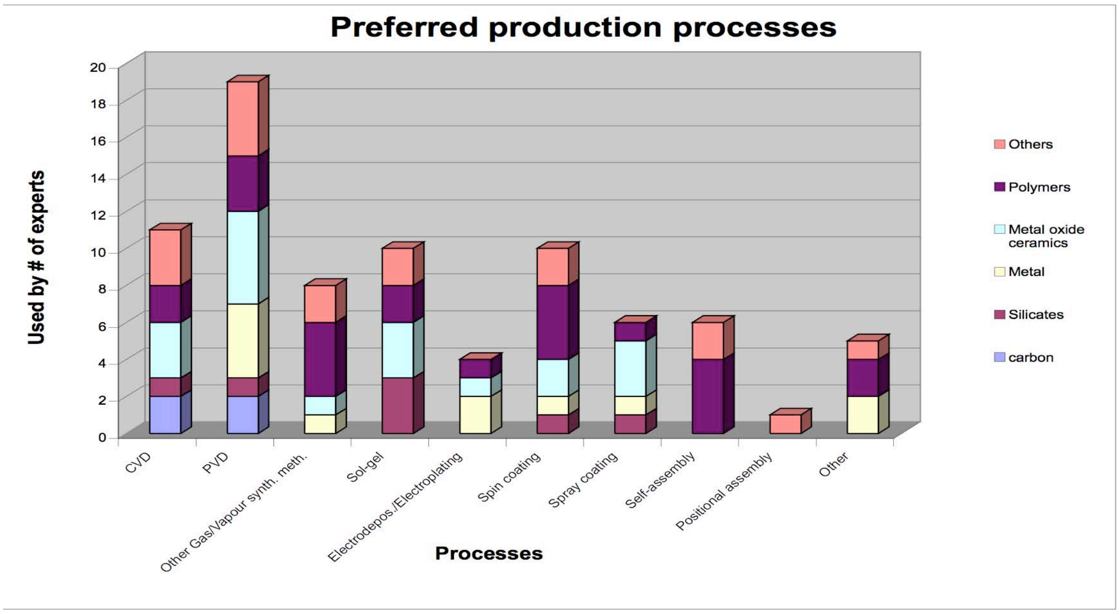


This roadmap does not cover the substrate pre-treatment step (before thin film deposition/production). According to the experts, substrate pre-treatment is not essential for many of the materials considered (e.g. carbon, metals). When it's unavoidable, this is most of the times due to specific application requirements.


Is surface treatment needed?
Used by # of experts
0
2
4
6
8
10
12
Yes, It is absolutely essential
Not necessarily
No
Others
Polymers
Metal oxide ceramics
Metal
Silicates
carbon

2.3.1 Thin films' production

As shown in the graph below, there are many processes presently considered for thin films production and there are huge differences in their stage of technological development. According to the experts, nanotechnology's added value in these processes lies in its provision of new tools to better understand the final material properties resulting from these processes as well as new production tools and approaches.



2.3.1.1 Chemical Vapour Deposition (CVD):

This method consists on heating the material (converting it into the gas phase) and then depositing it onto the surface. The use of chemical reactants triggers the deposition process.

<u>Main barriers to success, ideas to solve problems, comments</u>:
According to the experts there are still some scientific and technical barriers to be addressed. The correlation of the preparation condition with the resulting properties is not yet fully understood and blocks the functionalisation of the coatings to specific applications. Also the adhesion to the surface and process' reproducibility (highly dependent on the quality of the precursor material) are still to be improved. Common to most of thin film production methods is the difficulty to precisely coat 3-D geometries.

Regarding price/cost factors, the deposition rate (throughput) is considered low and the process requires high operating temperatures. Very often vacuum chambers are also required. According to the experts the CVD method is too costly for large area coatings.

Feedback solicited:

- What could nanotechnology bring here to overcome the barriers?
- Which research paths are feasible using nanotechnology?

2.3.1.2 Physical Vapour Deposition (PVD):

This method consists on converting the precursor material into the gas phase (e.g. resistive heating, electron beam, etc.) and then depositing it onto the surface. Several techniques are available for depositing the thin film material. Thermal evaporation, magnetron sputtering and pulsed laser deposition are probably the most widely used.

Main barriers to success, ideas to solve problems, comments:
As for most of the coating processes, experts highlight difficulties to coat 3-D geometries as well as to get a good adhesion coating-substrate. A better understanding on the relation of the process parameters and final properties is also required.

According to the experts, the control at the nano level is still limited and getting the required properties probably requires expensive substrates (e.g. non conventional single crystal substrates) that favour thin film growth in the desired direction and with the desired structure. With regard to material precursors, for some materials the process is considered to perform well (e.g. parylene) whilst for some others the materials are still in their development phase to achieve the required performance.

According to the experts, this is a capital-intensive process that requires expensive equipment to coat large areas (e.g. wafers in semiconductors’ industry). The fact that this process requires vacuum chambers also limits the size of the areas to be coated.

Feedback solicited:

- What could nanotechnology bring here to overcome the barriers?
- Which research paths are feasible using nanotechnology?

2.3.1.3 Other Gas/Vapour synthesis methods

According to the experts, several scientific and technical barriers persist. There’s still basic research needed mainly on the chemical synthesis onto surfaces and to get the proper crystal orientation required for many en-user applications.

With regard to the process itself, according to the experts there’s the need to improve the process reproducibility and uniformity (ultimately leading to improved material quality) as well as the process throughput (deposition rate). With respect to specific materials, the variety of materials that could be processed is rather limited and there are difficulties to model polymer thin film properties.

According to some experts, there isn't a major barrier and there are a lot of opportunities for exploitation. The dissemination of process capabilities to industrial end-users would speed up this process development and probably new research needs will come up.

2.3.1.4 Sol-gel

In the sol-gel process the precursor is dissolved in a solution and precipitates due to chemical reactions. The sol-gel process consists on 4 basic steps: hydrolysis, condensation and polymerisation of particles, growth of particles and agglomeration and formation of networks. The outcome of the process depends on several factors that influence the hydrolysis and condensation rates. Among them, there are few that are considered to have a greater impact: ph, nature and concentration of catalysts, H_20/precursor molar ratio and temperature.

This production method could be used to produce different nanostructures such as nanoparticles, nanoporous materials or nano-fibres. Some of the bottlenecks highlighted herein are common to all these nanostructures production.

Main barriers to success, ideas to solve problems, comments:
Although for some experts this is a well-established process (e.g. for paint material applications), there are still some technical barriers to be addressed: cracking and shrinkage are an intrinsic part of this process and are often difficult to control (especially for low-density materials).

Besides that, there are many parameters simultaneously influencing the final result and, according to the experts, there are a large number of non-controllable variables.

No price/cost barriers have been identified.

Feedback solicited:

- What could nanotechnology bring here to have a better control of production parameters?
- What could be done to control cracking and shrinkage?
- Which research paths could be followed?

2.3.1.5 Electrodeposition

Electrodeposition is a coating process based on the action of electric current and is normally used to produce metallic coatings. The deposition is achieved by negatively charging the substrate to be coated and by immersing it into a solution containing a salt of the metal to be deposited. The metallic ions of the salt carry a positive charge and are attracted to the substrate. When they reach the negatively charged substrate, it provides the electrons for reducing the positively charged ions and, thus, a metallic (chemically stable) coat is obtained.

Main barriers to success, ideas to solve problems, comments:
According to the experts, although this production method has some applications (e.g. Cu damascene); the solvents used are environmentally unfriendly and often toxic/irritating to skin.

2.3.1.6 Spin coating

In the spin-coating method substrates are spun at very high speeds while fluid is poured onto the centre, using centrifugal force to cover the substrate. Close to 100% of the fluid is forced off the surface.

Main barriers to success, ideas to solve problems, comments:
According to the experts, as substrate sizes (e.g. wafers) continue to grow, the spin process faces significant technical obstacles: impractical to spin very large substrates/chambers, substrate stress/breakage, corner defects. Besides that, the de-wetting phenomenon represents one of the main problems to form homogeneous thin films and no solutions have been found to fix this problem.

Although this production process has reached mass-production levels, for most applications it implies high purity for solvents and starting materials. In addition to these limitations, this process wastes a large amount material (very expensive in the case of materials used in display production). Because of that, some experts consider that this process will mostly be used as a research tool.

2.3.1.7 Spray coating

There are two main methods: plasma spray coating and thermal spray coating. The plasma spray coating (also known as plasma arc plating, plasma arc spraying, plasma coating), powders are introduced in a cavity that contains the gas stream of a plasma gun. After being melted, the powders are projected onto the surface being coated. With regard to the Thermal spraying coating, it consists on heating a feed stock material (powder or wire) and accelerating it to a high velocity by a gas stream. Then the particles strike the substrate surface and the particles deform and freeze onto the substrate. The collision speed is an essential element, which directly influences the coating properties.

Main barriers to success, ideas to solve problems, comments:
According to the experts, process reliability is the main bottleneck. The control of 3 variables (material, heat and speed) is essential to get a reliable and reproducible coating matching the expected requirements

***Feedback solicited**:*

- What could nanotechnology bring here to increase the process reproducibility?
- Which research paths are feasible using nanotechnology?

2.3.1.8 Self-assembly

Self-assembling consist on designing atoms and molecules that undergo chemical, physical and biological processes ending up with the atoms and molecules in the desired place with the desired structure. Self-assembling occurs over a certain substrate that facilitates molecules alignment and growth based on the fact that molecules always look for lower energy states.

Main barriers to success, ideas to solve problems, comments:
As one of the few bottom-up techniques, according to the experts, it's still in its infancy and a lot of basic science has to be developed prior to its transfer to industrial environments.

Problems that seem to be common to many other production techniques (fundamental understanding or lack of suitable equipment) have also a higher impact on the development of this technique.

One of the technical barriers specifically highlighted by the experts is related to reactivity of molecules that can polymerize quite easily due to humidity rate in the lab and form aggregates onto the substrates (thus reducing thin films' performance).

The fact that self-assembled layers have a substrate-specific chemical formulation and substrate pattern, according to the experts makes their development application specific and, therefore, expensive.

The availability of patterned substrates for directing thin films nucleation or growth has been pointed out as one of the barriers that will arise as soon as the process move to close-to-industrial environments.

2.3.1.9 Positional assembly

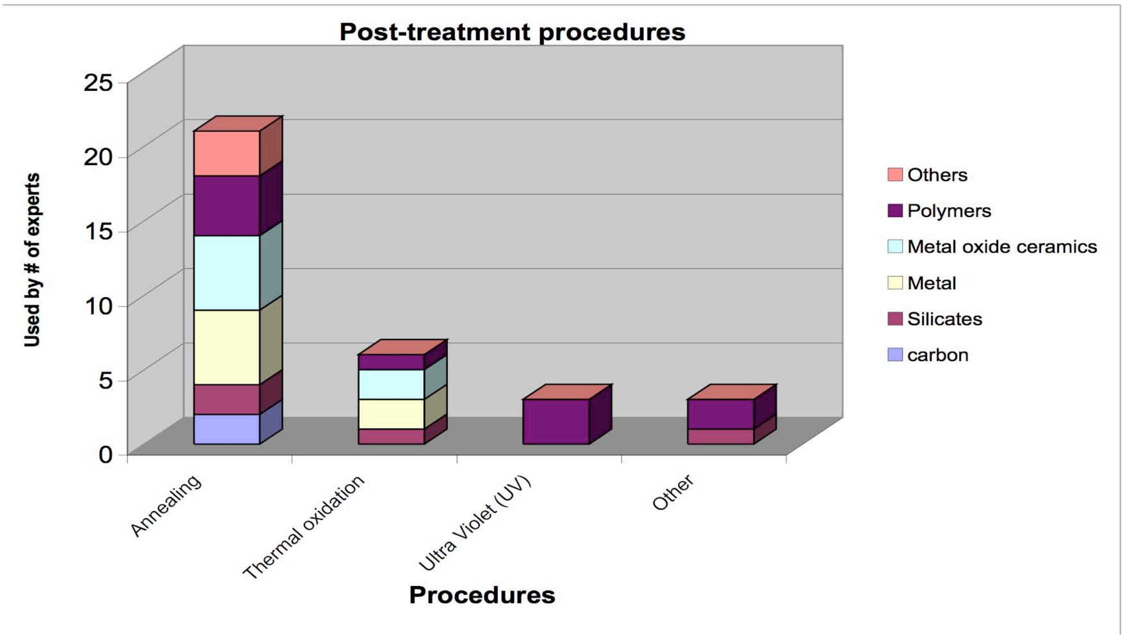
Based on the idea of using molecular machines to assemble molecular parts, positional assembly still requires a lot of basic research. The fact that the development of this technique requires many scientific and engineering disciplines to come together will lead to development timelines far beyond the scope of this roadmap.

2.3.2 Thin films' post-treatment

Post-treatment processes are sometimes required for consolidating the thin film obtained by other (wet) methods like sol-gel or spin-coating. In other cases, thin film post-treatment is used as a subsequent production step (e.g. thermal oxidation to obtain SiO_2 thin film or UV curing to improve thin film adhesion by creating cross-links).

Many post-treatment processes considered have been used for many years by many industries; nanotechnology is now offering room for incremental process innovation thanks to a better fundamental understanding.

***Feedback solicited**:* Do you as expert agree with this statement?



2.3.2.1 Annealing

Annealing is a heat treatment wherein the structure of a material is altered, causing changes in its properties such as strength and hardness. The process consists on two steps: heating and slow cooling. The heat treatment normally results in substantial changes in atoms' position within the crystal lattice structure; this includes removal of crystal defects resulting in substantial changes in a.o. the electrical properties of the material.

Two main processes are considered: gas annealing and vacuum annealing. Vacuum annealing results in improved adhesion, tensile strength and electrolytic performance as well as fewer pores.

Main barriers to success, ideas to solve problems, comments:
Although annealing is a well-established process (e.g. semiconductors' industry) and according to the experts it's an effective process in OLED, OTFT and OLET[1], it is still required to understand the growth mechanism and consequently the control of structural and morphological relaxation. According to the experts, in polymer thin films, it's especially important to understand the impact of the annealing process on the thin film properties.

The temperature required and the long processing time (due to the slow cooling required) hinders the cost-effectiveness of this process. Some experts highlighted that research should perhaps focus on avoiding the need for annealing process. Experts have also pointed out the incompatibility of the annealing process with certain types of substrates as well as the difficulties to ensure process reproducibility.

2.3.2.2 Thermal oxidation

Thermal oxidation is a technique that uses very high temperatures (approximately. 700-1300 ºC) to increase the growth rate of oxide layers. This high temperature is used to speed up the oxidation process (that for most of the materials used – e.g. Si - would naturally occur at a lower pace). The process consists of exposing the raw material substrate to an oxidizing environment (O_2 – dry oxidation – or H_2O – wet oxidation) and occurs at the surface of the substrate where the raw material is progressively replaced by the correspondent oxide. The oxide growth rate is positively affected by time, temperature, and pressure.

Main barriers to success, ideas to solve problems, comments:
According to the experts, two main barriers still exist: the difficulties to ensure process reproducibility and the need for in-situ observation of the process.

Feedback solicited:

- What could nanotechnology bring to improve process' reproducibility or reduce/eliminate the need for in-situ observation?
- Which research path could be explored?

2.3.2.3 Ultra Violet (UV) curing

Ultraviolet (UV) curing could be used both to dry the coating (from liquid to solid) and to cross-link thin film and substrate. A wide range of substrates is suitable for UV curing, from metal sheets to thin polymeric films. There are two crucial parameters: UV-light intensity and exposure duration. Some applications may require several curing steps involving different intensities of light and duration of exposure.

When used for cross-linking, the UV-curing adhesive consists of 2 components: adhesive resin and photo-initiator (already mixed up with the resin). The photo-

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[1] Organic Light-Emitting Display (OLED); Organic Thin Film Transistor (OTFT) and Organic Light Emitting Transistor (OLET)

initiator only reacts with the resin after having absorbed suitable UV light (wavelength and intensity).

Main barriers to success, ideas to solve problems, comments:
According to the experts, when used for cross-linking purposes, a key issue is the stress induced in the film during the cross-linking process. Suitable solutions would require low/no-shrinkage cross-linking agents and the appropriate experimentation.

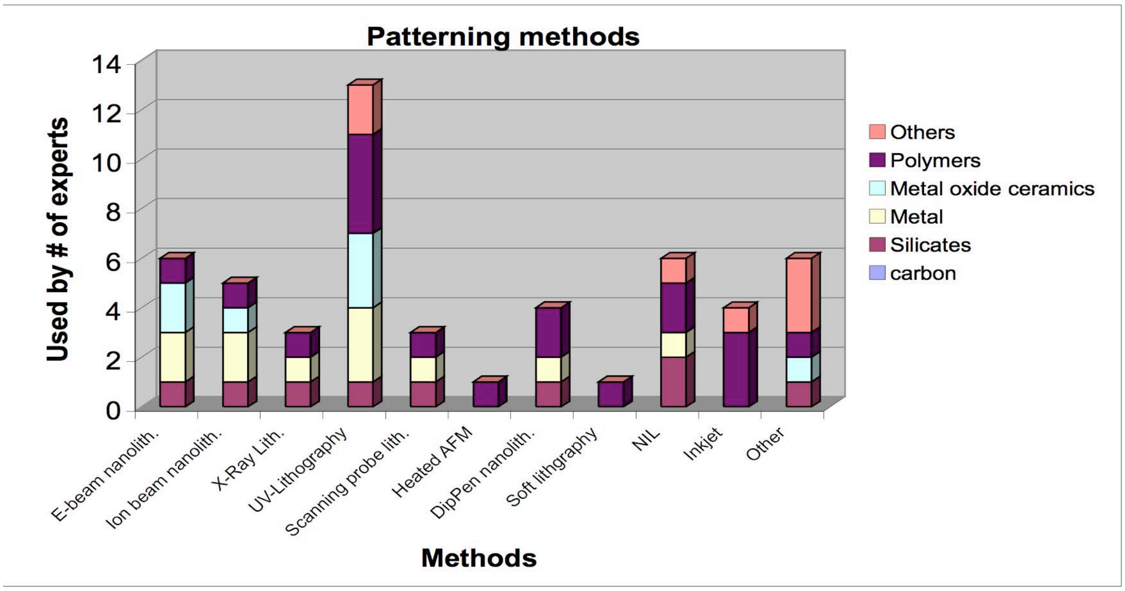
Other bottlenecks are the difficulties to cure complex 3D dimensional bodies by UV curing; it’s very difficult to avoid (not irradiated) shadow zones. According to the experts, this is a standardised process that works well within its resolution limits but the equipment required becomes expensive for features under 100nm. In-situ observation of the process has been pointed out as a possible means to overcome these barriers

Feedback solicited:

- What could nanotechnology bring to reduce/eliminate the need for in-situ observation?
- Which research path could be explored?

2.3.3 Patterning methods

Patterning methods have been widely used in the semiconductor industry and some other applications could benefit from these technologies. Main bottlenecks lie on the size of the area to be patterned, the size of these patterns (depending on the wavelength or the size of the tip/stamp) and the chemical specificity required.



2.3.3.1 UV-Lithography

This process uses ultra-violet light to transfer a pattern onto a surface. The surface is coated with a polymer thin film (e.g. normally over a semiconductor substrate) that acts as a resist. The UV light passes through a mask containing the desired patterning and the pattern is transferred to the surface. In the post-treatment step intended to remove part of the semiconductor material, the polymer thin film protects parts of the semiconductor substrate to remain intact. The resolution of the patterning process depends on the wavelength (energy) of the radiation and the numerical aperture of the lens (masks).

<u>Main barriers to success, ideas to solve problems, comments</u>:
According to the experts this is a well-understood technology limited by the size of patterns that can be achieved. Recent research is exploring the use of extreme UV to downsize the patterns. Main technical barriers are related to the resist (polymer thin film). The adhesion to the substrate has been largely solved, according to the experts.

With regard to cost factors, this process requires very expensive equipment for features below 100nm. The fact that it’s a low throughput process has also a negative impact on cost-effectiveness.

Feedback solicited:

- What could nanotechnology bring to increase process throughput?
- Which research path could be explored?

2.3.3.2 Nanoimprint lithography (NIL)

NIL is similar to photolithography or electron beam lithography, except that a stamp is used to create the pattern in the resist. The resist is a thermoplastic film (e.g. PMMA). Once the substrate and resists are prepared, the stamp is heated and pressed into the thin film / substrate to transfer the desired pattern. Then the stamp is cooled down and removed. Then the patterned thin film is ready to undergo the following post-treatment steps. In principle NIL could get resolutions below 10 nm.

Main barriers to success, ideas to solve problems, comments:
According to the experts, at the lab scale the equipment is easily made; however, proper alignment and the need to avoid stamps distortions are issues to be addressed to make this a robust approach ready for industrial up scaling. Other process limitations are the difficulty to align multiple layers and the process applicability limited to very specific substrates.

Feedback solicited:

- What could nanotechnology bring to address presently identified bottlenecks?
- Which research path could be explored?

2.3.3.3 Electron beam nanolithography

Electrons have higher energy (shorter wavelength) compared to UV light and this is used to produce patterns with features with magnitudes below that of those achieved by UV light (reaching 0.5 nm). Electrons are emitted from the electron gun of a scanning electron microscope and directed to the sample using electron optics. The electron beam is computer-driven and the process is run in a vacuum chamber. This process requires specific resists sensible to the electron wavelength. Actually, the resist impedes reaching the maximum resolution.

Main barriers to success, ideas to solve problems, comments:
According to the experts, the resist is one of the main bottlenecks for this process development. Besides that, the fact that the electron beam can't pattern the surface all at once (as the UV process does) makes the process very expensive for large area surfaces.

Due to the high energy of the electrons, the region of the resist affected by their impact is much bigger than the area where electrons impact (it's the so-called proximity effect) and has a negative impact on the quality of the patterns.

2.3.3.4 Ion beam lithography

Ion beam lithography is a maskless process using an ion beam for depositing (or removing) many types of materials (incl. conductors and insulators). As compared to e-beam lithography, the main limitation is the limited penetration depth of ions into the resist layer but it addresses e-beam limitations such as the proximity effect or resist's sensitivity. According to the experts, price is the main limitation for this process development.

Feedback solicited:

- What could nanotechnology bring to control the penetration effect?
- What could be done to reduce production costs?
- Which research path could be explored?

2.3.3.5 DipPen nanolithography

This is a direct-write technique that uses an Atomic Force Microscope (AFM) to deliver molecules (e.g. chemical inks) to the surface. Its main advantage is that the same device (AFM) can be used for surface's imaging and writing. DPN could also be used to create nanoresist able to withhold the etching process. The control variables for DPN are: relative humidity; tip-surface contact force; scan speed; temperature; use of surfactants.

Main barriers to success, ideas to solve problems, comments:
According to the experts, this process is too slow and only applicable to small and specific substrates. The key issue when formulating the "inks" is that of getting a good flow of ink through the AFM head.

2.3.3.6 Inkjet

Inkjet processes (also known as drop-on-demand) consist on print-heads that are used to create a pattern formed by ink drops onto the substrate's surface. Each of the print-heads can consist of several nozzles and this process could be used in large areas (e.g. over 24 inches) by enlarging the print-heads. After the pattern is applied, a curing step is normally applied to stabilize it. Main applications for this process are MEMS and large-area displays.

Main barriers to success, ideas to solve problems, comments:
According to the experts, the control of droplets' position is a critical limitation for higher resolution. This is considered a multi-dimensional problem involving research on the print-heads, the substrate, the ink and the interactions thereof. According to the experts, there's a lot of work on this area (especially by print heads manufacturers). Experts also pointed out the need for fluids' formulations that both suitable for the print-head and for providing the desired pattern.

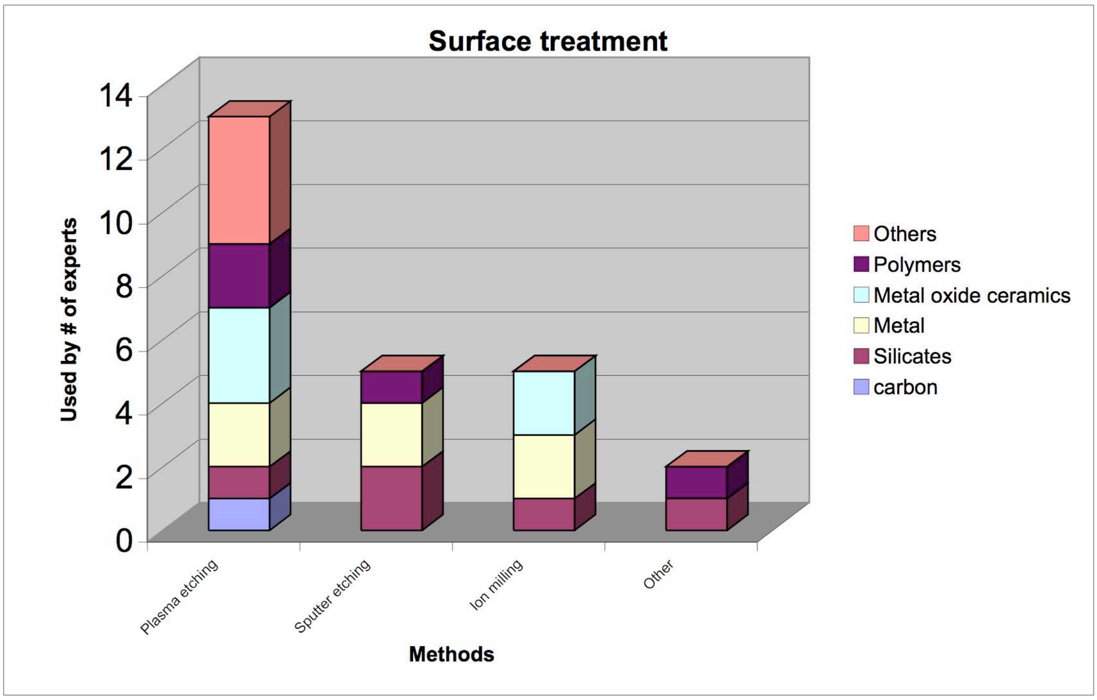
2.3.3.7 Other patterning methods

The new set of tools offered by nanotechnology is fostering the development of new techniques. As a main characteristic, these new techniques use tools that are inexistent in present production lines and very scarce in R&D laboratories. The common objective is to push down feature resolution limits. Normally this leads to a higher complexity, low throughput and applicability limited to (very) small area. These processes include Soft lithography (only applicable to specific substrates), X-Ray Lithography (very complex), Scanning probe lithography or Heated AFM (the last two lacking chemical specificity)

Feedback solicited:

- Do you as expert agree with this statement?

2.3.4 Surface treatment



2.3.4.1 Plasma etching

(Dry) chemical plasma etching replaces the wet processing method that uses solvents for producing the pattern and uses power (in opposition to spontaneous) to drive the reactions. Plasma etching process consists on the following steps: reactive species generation, diffusion to the solid, adsorption at the surface, reaction at the surface, reactive cluster desorption and diffusion away from the substrate.

Main features are its good selectivity, its fast etching rate and that results in highly isotropic characteristics. Ion energy is lower than in the ion milling process.

<u>Main barriers to success, ideas to solve problems, comments</u>:
According to the experts there are still some technical barriers blocking this process further application: the adhesion mechanism of organic systems to given surfaces, the need for improved selectivity, homogeneity and for getting perpendicular etched walls.

Besides these technical barriers, this technology is considered to be very specific to each application and there’s a lot of work to be done to communicate its potential to industrial end-users.

<u>Feedback solicited</u>:

- What could nanotechnology bring to address presently identified barriers?
- Which research path could be explored?

2.3.4.2 Ion milling

This is a physical method where ion particles are accelerated by an ion beam and directed to the surface of a substrate. The ions remove any material not protected by a resist material by relieving the bonding energy between the individual atoms in the structure and ejecting the host atoms. The substrate is normally mounted in a rotating table inside a vacuum chamber. Several alternatives of this process combine physical and chemical routes (Reactive Ion Etching) where ions also react at the surface materials (e.g. forming another gaseous material).

Main barriers to success, ideas to solve problems, comments:
It is a highly anisotropic and, according to the experts, a slow and non-selective etching process. The last is especially important in multi-layer thin films.

Feedback solicited:

- What could nanotechnology bring to address presently identified barriers?
- Which research path could be explored?

2.3.4.3 Sputter etching

This is a physical method based on the same mechanism than sputter deposition. Sputter deposition works as follows: ions are generated and directed at a target material to sputter atoms from the target; then, the sputtered atoms get transported to the substrate through a region of reduced pressure and condense on the substrate, forming a thin film. The big difference in sputter etching is that substrate is now subjected to the ion bombardment instead of the material target used in sputter deposition. As compared to ion milling, ions/atoms do have a higher energy.

Main barriers to success, ideas to solve problems, comments:
According to the experts this is not a well-controlled and highly anisotropic process.

Feedback solicited:

- What could nanotechnology bring to address presently identified barriers?
- Which research path could be explored?

2.3.5 Thin films' applications

2.3.5.1 Introduction to main applications and identified bottlenecks

The possibility of transferring specific or expensive properties to a nanometer-sized coating makes the list of potential applications almost endless and could have an impact in almost every industrial sector.

There are applications already in the market (e.g. thermal insulating or self-cleaning windows) or on their way out of industries' R&D labs (e.g. chips or M-RAM). However, for many other applications, several years will be required to get to a similar stage of development (and investment). For all of them there's plenty of room for improvement.

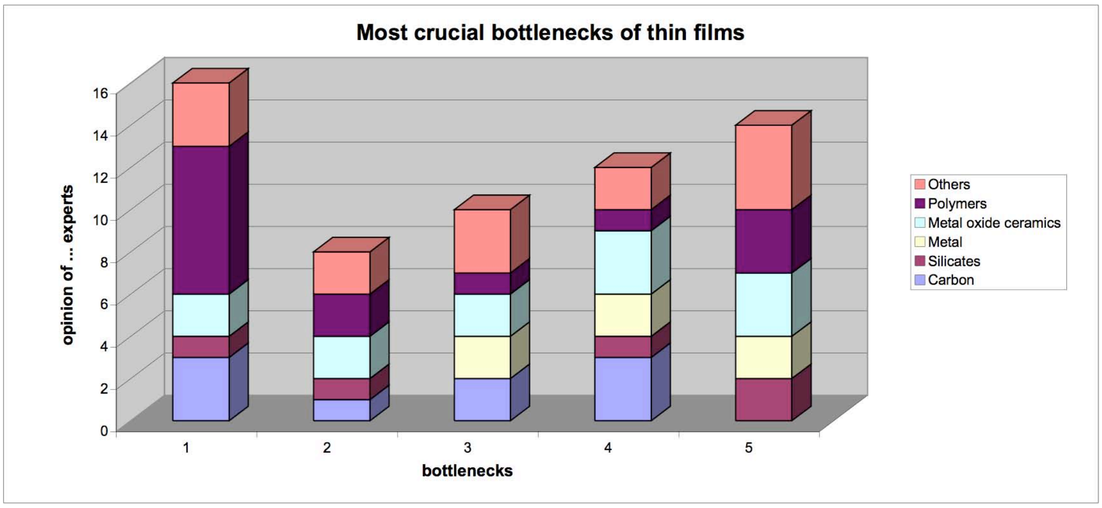
<u>According to the experts, main generic bottlenecks in thin films research are</u>:

1. Lack of understanding of adhesion mechanisms between thin-film/substrates and between different layers.

2. Lack of software for modelling and simulation of thin films formulation and performance resulting on long development time and expensive trial-error approaches.

3. Lack of equipment for meaningful and quick characterisation

4. Lack of understanding of industrial environments that require integration into existing production process, reliability and high value/cost ratio.



5. Other scientific or technical barriers pointed out by experts are:

- Lack of understanding of interfaces and nucleation properties (for metal and metal oxides),

- Difficulties for homogeneously coating complex 3D

- Lack of understanding of decomposition process during spraying – plasma chemistry (for silicates)

- Difficulties for achieving compounds stoichiometrically stable (metal oxides).

Experts were asked to identify crucial bottlenecks considering different types of materials. Answers show that (except for metal thin films), the lack of understanding of adhesion mechanisms between thin film and substrate and how properties are transferred and influence thin film properties are a common bottleneck that must be addressed.

The fact that many technologies are application-driven makes the understanding of industrial requirements a repeatedly highlighted bottleneck both for experts from academia and industry. That’s especially relevant in the semiconductors’ industry, where technologies should be integrated into existing industrial production processes if they’re to be applied within the next 10 years.

Software availability is also a broad bottleneck. However, overcoming this barrier requires first to overcome the afore-mentioned ones.

Similarly, the lack of appropriate equipment is also considered a bottleneck in all material-related research except for silicates (probably due to the broad and long used made of thin film technologies by the semiconductors industry).

2.3.5.2 Overview of applications considered

The following is a list of most relevant applications of thin films and coatings.

- Thin Film Transistors (TFTs)
- Large-area electronic devices (e.g. displays)
- Solar cells (e.g over glass or polymer substrates)
- Planar waveguides (for optical components' integration)
- Non-volatile memory (M-RAM)
- Micro electro-mechanical systems (MEMS)
- Friction reducing surfaces
- Thermally insulated windows
- Self-cleaning surfaces

Other thin film applications include a.o. electrochromic glasses (e.g. Tungsten Oxide layer), coatings for anti-glare, anti-misting mirrors (e.g. using TiO_2 over glass), anode and cathode materials (batteries, capacitators and/or supercapacitators) or superconductivity-related applications (e.g. microwaves' filters or Fault Current Limiters).

<u>Remarks:</u>

- Due to the broad range of thin films' applications included in the first questionnaire it has not been possible to gather enough answers for meaningful comparisons.
- W&W has summarised the initial long list of applications into a shorter list, focusing on those considered more important.
- Would you feel that there's an important application missing or not properly summarized, we kindly ask you to indicate it and to provide information on its foreseen development as well as on the benefits brought in by thin films.
- W&W has not focused on sector specific applications; however, would you feel that there's any sector specific application warranting special attention, we kindly ask you to inform us.

2.3.5.3 Timeline for applications' development

The following paragraphs give an integrated overview of the different stage of development of the applications listed above. The following three paragraphs each cover one "snapshot" of the overall thin films roadmap. One for the current state of the art, one for the state of the art as predicted in five years from now (2010) and one in ten years from now (2015). The following distinctions have been made in the following figures:

Basic Research & Development Phase (Basic R&D)

Applications in this phase have received the interest of at least one or more researchers in the world. Some applications might still be in early development, while others are tough to develop and need a lot of basic research to be fully understood.

The object of basic R&D is to validate the original hypothesis. Various applications are currently in this phase.

Applied Research & Development Phase (Applied R&D)

After the hypothesis is validated, research typically (but not necessarily) moves from pure research labs to more commercial labs and companies.

Applied R&D will eventually result in a proof of concept, a successful demonstration model. While the production issues might not have been solved yet, a successful prototype / model has been validated.

Production Research & Development Phase (First applications)

After first demonstrator models and prototypes, initial, usually prohibitively expensive, small amounts of products may be produced. At the same time, if these prove successful, companies will seek to upscale production processes.

Generally at some point, demand increasing sufficiently to offset the investment needed to start bulk production. This phase ends at that point when is clear and possible to start this bulk production.

Mass production and incremental research (Mass production)

The final development phase, in this phase production has reached bulk amounts and research focuses on incrementally improving the products.

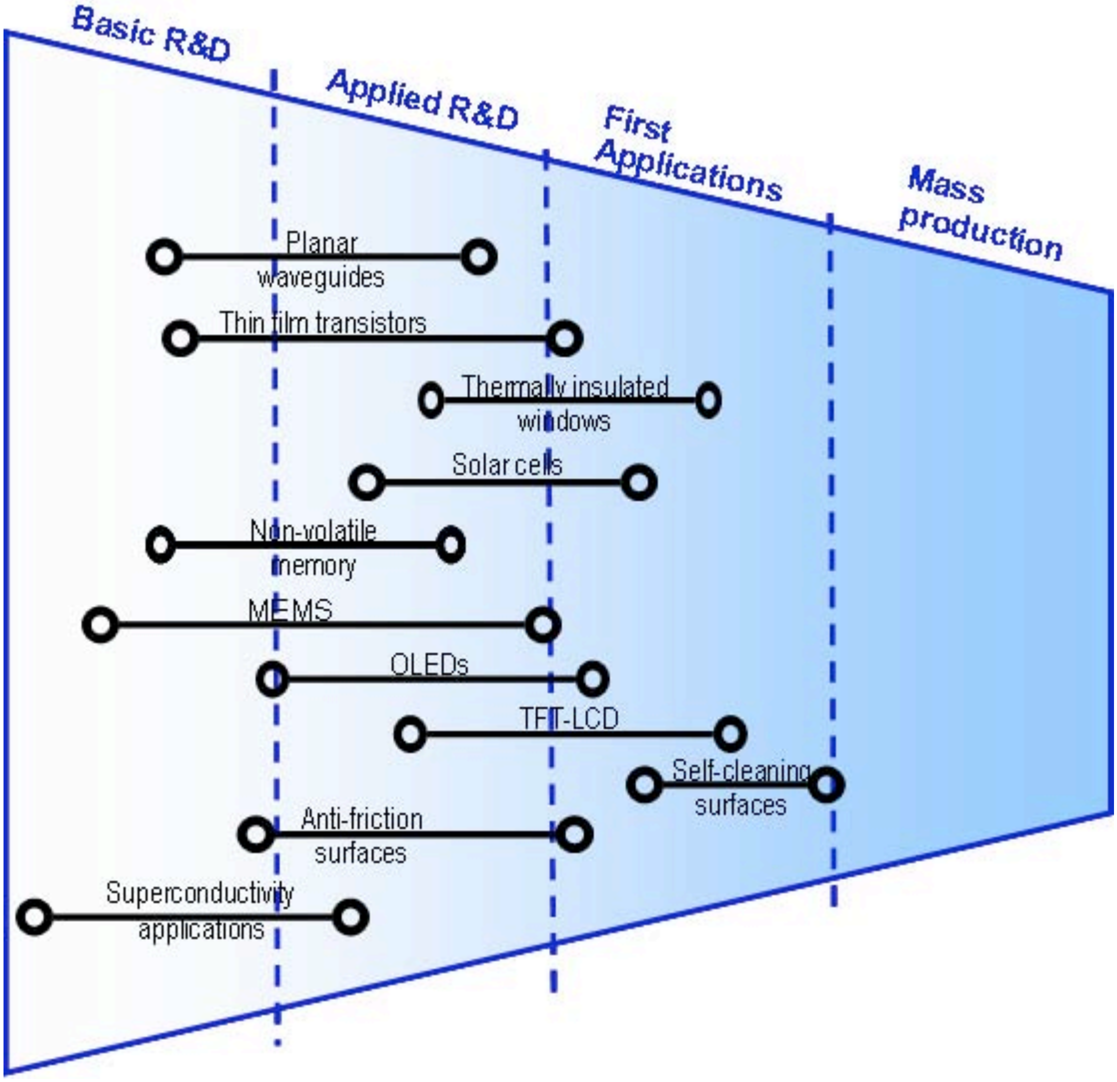
After this phase even more phases can be discerned (market maturity, end of life cycle, etc.) but these have not been taken into account when creating the following figures.

Feedback solicited:

Do you as expert agree with the position assigned to different applications in the following figures?

Overview of current applications (2005)

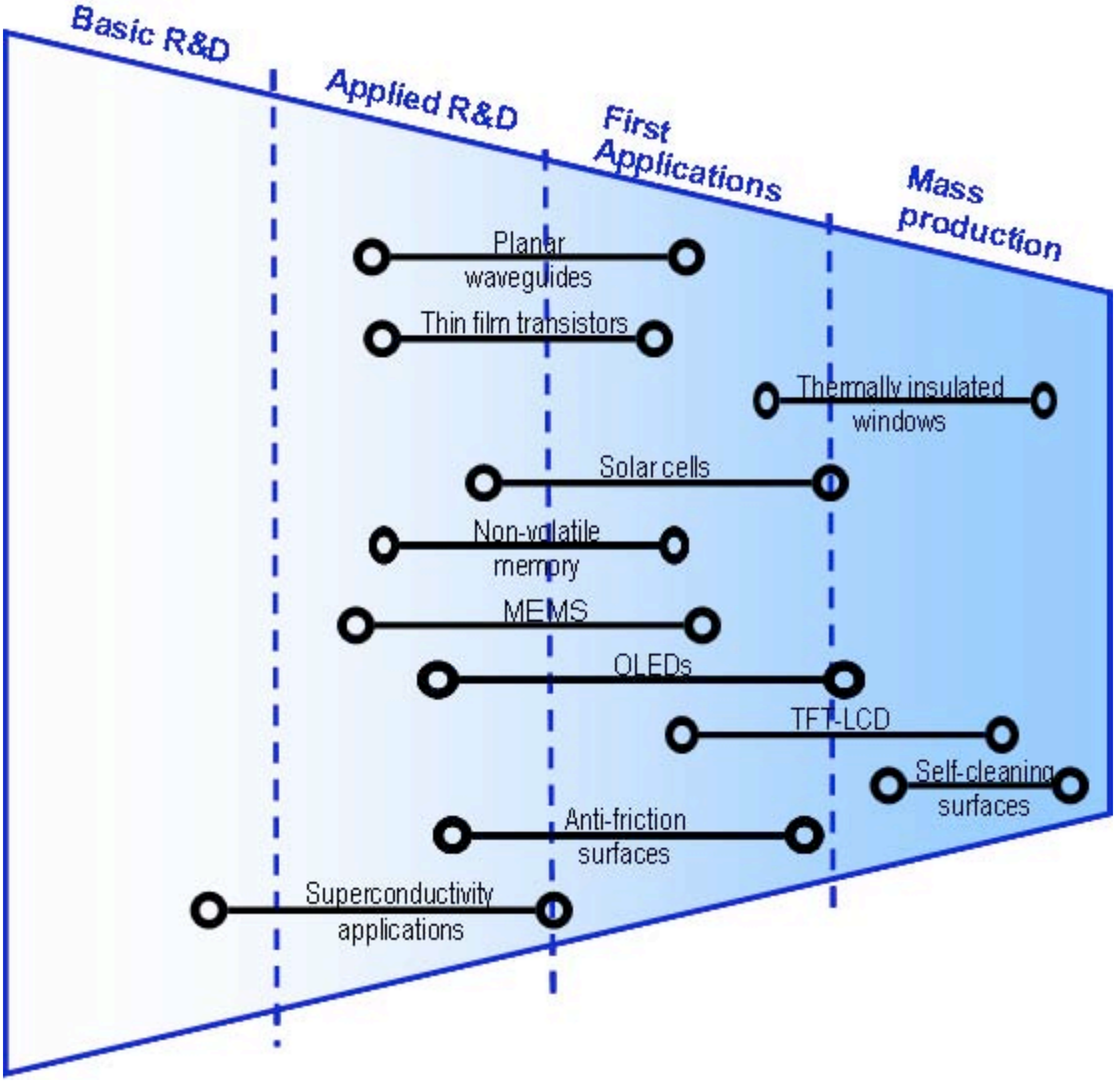
The figure presents an overview of the current state of development of different applications of thin films. The input data for the preparation of the figures in this section has been gathered from the experts participating in the Delphi panel.



Overview of applications in 2010

The following figure is an overview of the expected state of development of different applications of thin films in year 2010. Data for the preparation of the figures in this section has been gathered from the experts participating in the Delphi panel.

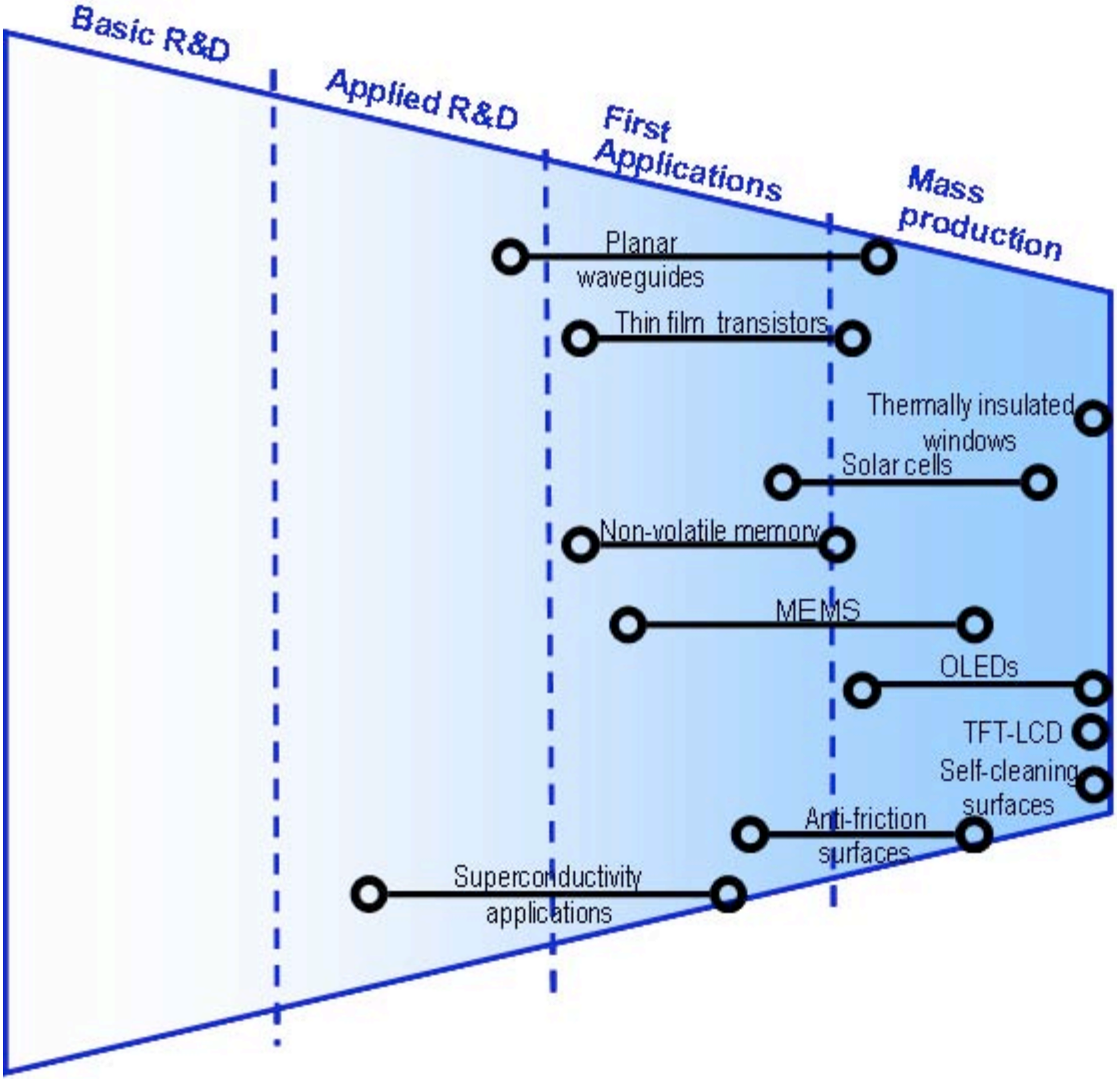
After five years many more applications will have come into fruition. A good number of the potential applications currently considered will be most probably entering into first commercial applications, with some of them already approaching the mass production phase.



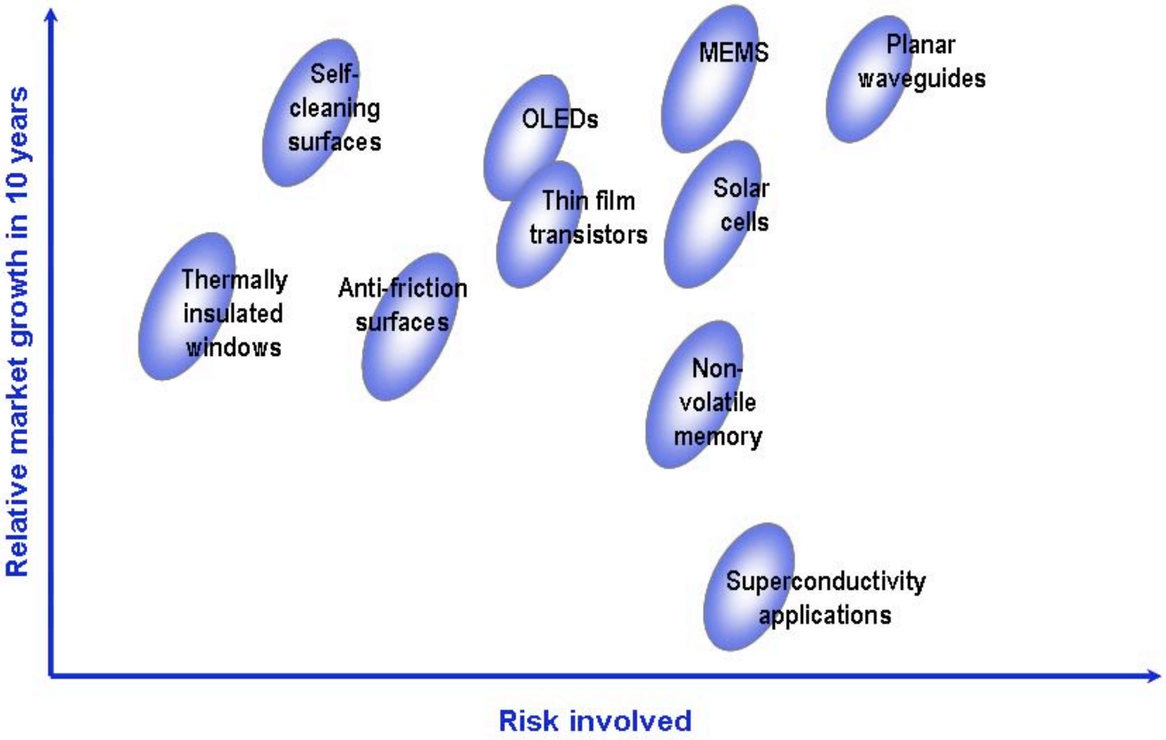
Overview of applications in 2015

The following figure is an overview of the expected state of development of different applications of thin films in year 2015. Data for the preparation of the figures in this section has been gathered from the experts participating in the Delphi panel.

By 2015 many applications currently in development will be actual markets and currently still wild ideas may be ready to move to the market.



2.3.5.4 Risk involved vs. expected market growth in the next decade



2.3.5.5 Description of main applications

Thin Films Transistors (TFT)

Thin films are used as a layer of electrically insulating material (usually SiO_2) called gate channel. Above the channel there’s the Gate that provides the electric field to switch on/off the transistor. The trend has been to make transistors faster by making them smaller (e.g. shortening the gate length thus shortening the path to be followed by charged particles) and reducing the thickness of the gate channel (to strengthen the gate field and maintains the maximum current even with less thickness). The problem to solve is that making the gate channel thinner allows current to leak, thus wasting power, heating the transistor and reducing its performance.

Over the last years, research focused on deformation of Si crystals (strained Si) for improved performance. With regard to thin films, the strain is produced depositing layers of strained material (e.g. silicon-germanium) over the wafer surface.

There’s the possibility to exploit thin-film technology in large surface area. Thin-film technology is CMOS compatible and therefore enables integration with Si integrated circuits. Some applications have already been developed: thermal actuators, resonators and air gap Thin Film Transistors (TFTs; based on Polymorpohous Si or nanocrystalline ZnO). As described below, other TFT applications are under development.

Large area displays

Thin film silicon is well established for many **large-area electronic devices** such as **LCD or OLED displays**. Besides the improvements described below, the possibility to apply Si thin films over a polymer flexible substrate (instead of glass) could ultimately lead to flexible devices broadening the range of potential (high added-value) applications.

Liquid Crystal Displays (LCD): They consist of a liquid crystal solution between two sheets of polarizing material. Each crystal either blocks or let light pass through depending on its alignment. These displays do require a backlight to work. A thin film transistor is used to stimulate a single crystal cell (pixel). LCDs already have significant market shares (many well-established applications such as calculators, lap-tops, mobile phones, etc.). Light Emitting diodes are considered as an alternative light source for LCD.

Organic Light-Emitting Diode (OLED): An OLED is made of semiconducting organic polymers. Varying amounts of OLEDs can be deposited in arrays on a screen using printing methods (section 2.3.3) to create a graphical colour display or lighting devices. OLEDs are available as distributed sources while the inorganic LEDs are point sources of light. Main advantage of OLED displays is that OLED displays don't require a backlight to function: they consume far less power and could be used in portable devices. The possibility to produce displays (or solar cells) as a continuous sheet rather than one panel at a time could also have a very positive impact on production costs.

Besides the use of OLEDs as displays, there's significant research looking at their exploitation as solid-state light sources. There are several running projects building first prototypes.

Solar cells

Current thin-film solar cell technologies are limited by either the ultimate efficiency that can be achieved with the device material and structure or the requirement for high-temperature deposition processes that are incompatible with all presently known flexible polymer substrate materials. Nanotechnology could address both limitations by:

- The development of deposition processes exploiting advantages of (expensive) mono or polycrystalline silicon (e.g. higher electron mobility). For instance, the combination of thin films of a-Si and c-Si.is close to commercialisation.
- TiO_2 thin films could improve photovoltaic cells efficiency over glass substrates.
- The development of low temperature processes for the deposition of thin film semiconductor materials (e.g. ZnO, CdS, $CuInSe_2$) for photovoltaic cells on lightweight flexible plastic substrates.

Magnetic RAM (Non-Volatile Memory)

Thin films have attracted great attention in recent years for their potential use in Dynamic RAMs and Multi Chip Modules (MCM) due to their high dielectric constant and relatively low leakage current. In D-RAM, each storage cell consists of a transistor and a capacitator, the last discharging quickly and having the need to be re-charged. M-RAM is built up of units called magnetic tunnel junctions that consist of 2 thin-film metal layers separated by an insulator. A tunnel junction stores a single bit of data and to write data you would only need to change its spin by applying a magnetic field. Main advantage is that there isn't the need to constantly supply electric power to maintain the data (thousands of time per second in nowadays RAM) avoiding data loss and drastically reducing power consumption.

Planar waveguides and other optical components

The optics' industry has been using thin film coatings in components like lenses, prisms, filters, reflectors or mirrors. Developments have mostly been pushed by the high demand to increase bandwidth in optical fibre networks by breaking the laser light that carries data through the network into different colours, or wavelengths. Each resulting wavelength is capable of carrying a discrete data channel.

Planar waveguides is an alternative approach for assembling and designing optical components. It consists on assembling glass fibres into single chip substrate by creating pathways in a silicon wafer. The material consists of a thin film of a material with high refractive index deposited onto a transparent substrate (e.g. polymer, glass) with lower refractive index. As compared to thin film technology presently used for optical components manufacturing (high labour involved), technology for planar waveguide manufacturing are borrowed from the semiconductor industry (much more automated and allowing for batches' production). However, there's the need for cost-effective and reliable (low-loss and ease of patterning) planar waveguide materials.

Other benefits stemming from nanotechnology developments are the possibility to better understand and exploit the surface plasmon effects to make devices such as optical modulators (using electro-optically active thin films).

Micro-Electro-Mechanical-Systems (MEMS)

MEMS consist of the integration of mechanical elements, sensors, actuators, and electronics on a common silicon substrate through microfabrication technology. The components are fabricated using compatible "micromachining" processes that selectively etch away parts of the silicon wafer or add new structural layers to form the mechanical and electromechanical devices. In MEMS, technology has been transferred from the semiconductors' industry and therefore could benefit from its developments. MEMS have been widely used in the automotive industry a.o. in air-bags accelerometers, pressure sensors, etc. Future applications include biochips, high-throughput screening devices, switches, etc.

Friction reducing coatings

Aims at protection of severe surface damage of mechanical elements by minimizing the transfer of friction energy or adhesion generated at the contacting interface. The reduction of friction in turn reduces wear damage and thereby extends the life and reliability of products. Carbon or diamond-like thin films could be applied in any applications where the material is working under friction conditions or subject to wear: machining processes such as grinding, milling and drilling or such as mechanical and transport engineering. For instance, application of a carbon thin film over steel substrate could reduce the friction coefficient by a factor of 5 or 6. Thin film technology could optimise thin film composition and thickness to specific requirements. Other materials being applied are alumina, Y-Zr2O3, etc. Although there are friction-reducing coatings on the market, substantial improvement (perhaps zero friction coatings) could be within reach.

***Feedback solicited**:*

Do you as expert agree that there's still basic research to be done to understand the principles behind the tribology phenomena?

Thermal insulation in windows

Glass is a cheap material to produce in large quantities and it's easy to process. Moreover, it's very transparent, very resistant to scratch and to environmental effects and it's shape stable. However, the thermal portion of the electromagnetic spectrum is almost 100% led through and, therefore, leads to bad insulation properties. Nanotechnology could address this limitation at a competitive cost by applying (e.g. Silver) thin films on both sides of the window. The use of spectrally sensitive thin films could simultaneously provide protection from sunlight whilst maintaining adequate lighting.

Self-cleaning surfaces

This application is already in the commercialisation phase. It consists on TiO_2 thin film and is due to photocatalytic activity and hydrophilic properties. Several big players in the flat glass industry (e.g. Pilkinton, St Gobain, and PPG) have introduced commercial products in the marketplace. Although experts criticize the real cleaning functionality of these first applications, the effect is quite noticeable. Main RTD topics are now to increase the cleaning effect (to have the same cleaning in less time, to require less light for the cleaning to function properly, to be able to clean bigger and more persistent stains). Nanotech has mainly brought the transparency of the TiO_2 containing layer, and might bring paths to improve the abovementioned performance indicators.

Other applications

Other applications of thin films include:

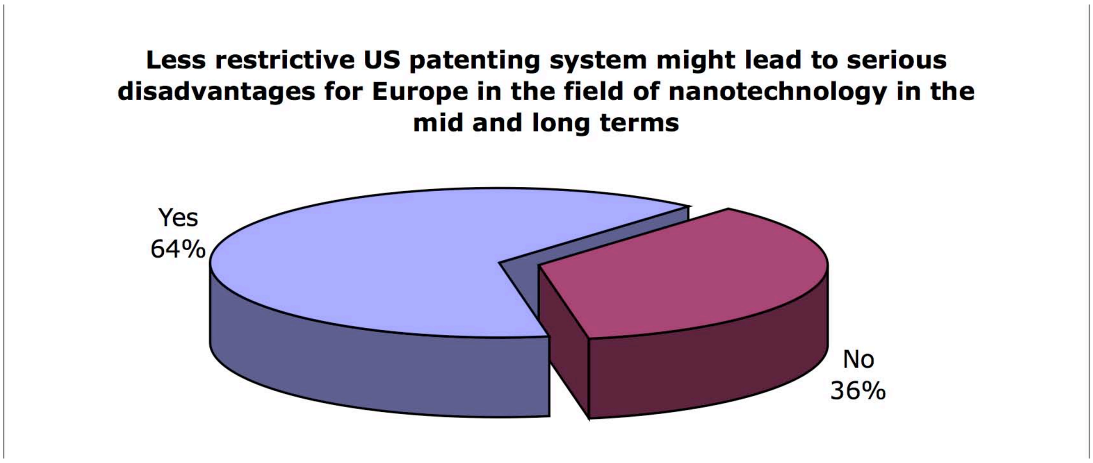
- Electrodes for a.o. fuel cells, batteries, super-capacitators or solar cells. Thin films could be used both in anode/cathode and electrolytes, significantly increasing the capacity and improving the electrochemical property. Indium-Tin-Oxide or other metal-oxides are used in (nanoporous) thin films.
- Superconductivity applications: The low microwave losses of High Temperature Semiconductor (HTS) thin films enables the coupling of a large number of resonators to microwave filter devices with much sharper frequency characteristics than conventional compact filters. They are already in use in commercial and military microwave filter systems. Another application presently under development is as Fault Current Limiter (FCL) in power applications (YBCO thin films). FCL prevents overloads from the grid components thus enabling longer lifetimes and avoiding investment cost due to the over-dimensioning.
- Applications benefiting from electrochromic properties, where colour changes when changes in the applied voltage are applied. The material generally used in electrochromic glasses is a Tungsten oxide layer.
- Thermo-electric applications (e.g. power generation, sensors and valves): engineering of nanostructured TE materials gives hope to achieve a selective diffraction of phonons due to the high density of grain boundaries and leads to a decrease of thermal conductivity but maintaining high electrical conductivity.

Other markets such as automotive, aeronautics or machinery presently benefiting from coatings' utilisation may also benefit from thin films provided that acceptable production costs and volumes can be reached. For instance, polycarbonate headlamps and the entire car glazing would benefit greatly from nano-sized anti-scratch thin films.

2.4 Non technological aspects

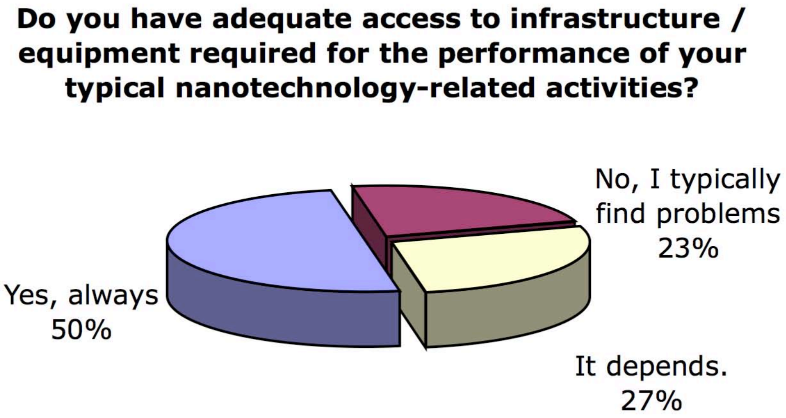
2.4.1 *Legal aspects (incl. patenting systems)*

The protection of intellectual property stemming from nanotechnology-related research is one of the key issues for sustainable European competitiveness. According to 64% of the experts, the fact that the US is less restrictive when granting patents may suppose a disadvantage for Europe. The same percentage is obtained within experts working for industry.



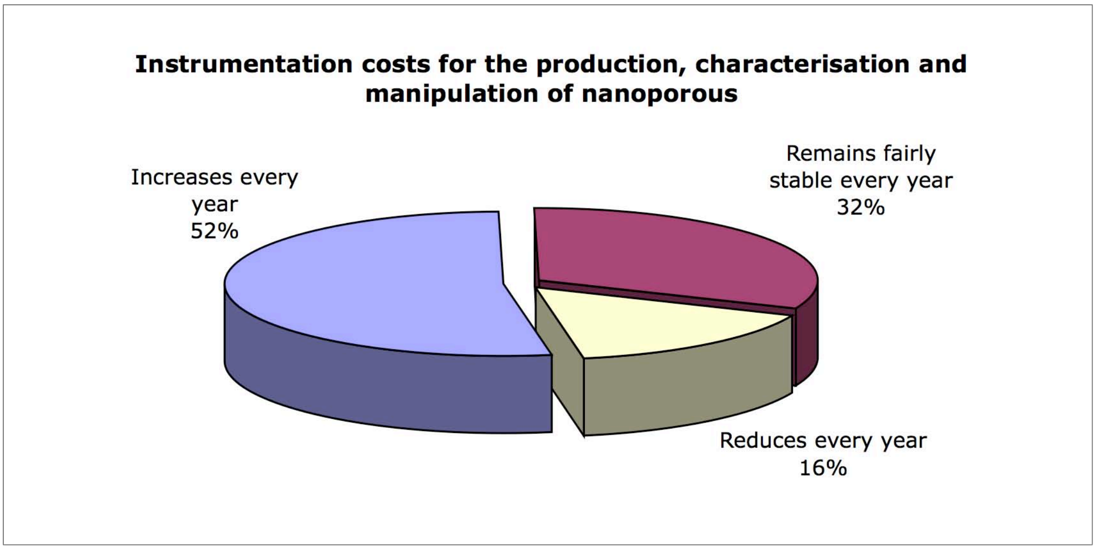
2.4.2 *Infrastructure requirements and instrumentation cost*

Most of the experts do not have problems in acceding to the required infrastructure; although close to 25% do find problems. In general, “standard” nanotech-related equipment is sufficiently available whereas specialised equipment is rather scarce and, in some countries, requires establishing international collaborations to get access to it.



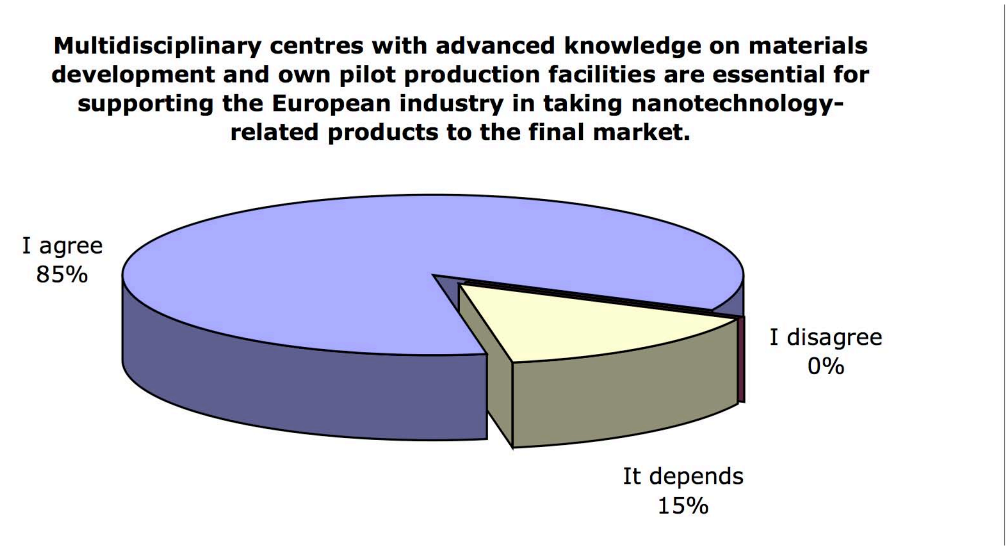
Specific issues highlighted by the experts are the lack of available equipment for preparing test samples with specific properties and/or structure as well as to perform final tests for research validation. In some cases, available facilities are the boundary conditions that define what type of research is undertaken and not the other way around.

Linked to the accessibility to the required equipment/instrumentation, most of the experts agree that cost increases every year or remains fairly stable. This percentage is even higher according to industrial experts.



According to some experts, the fact that equipment complexity rises and requirements tighten leads to sustained increase in R&D costs. In most cases, there is not the need to completely change the equipment used but to upgrade it with new modules. On the contrary, some experts think that the number of equipment suppliers (also from other sectors such as inkjet or CVD technology) is increasing and maintain the cost fairly stable.

When asked about the convenience of having pilot production plants close to the research labs to facilitate technology transfer to industries, most of the experts agree that that would be beneficial. The fact that this type of centre could be used for providing skills to co-workers is very much appreciated.



2.4.3 Health, safety and environmental aspects

According to the experts there are environmental issues related to the utilisation of different solvents. That’s the case of two well-established processes such as the sol-gel or the electrodeposition process. The large volumes used increase the impact.

2.5 Conclusions

2.5.1 Most relevant applications

Bottlenecks identified by the experts are not limited to scientific or technical barriers (e.g. better adhesion) but also include aspects like processes price or throughput as well as the understanding of industrial requirements. This could be seen as an indication that thin film applications are closer to the market than those of for example nanotubes or dendrimers.

By 2015, most of the applications described in this report would have already reached at least initial commercialisation stage. However, thin films' (potential) applications have presently reached very different development stages. While there are some applications already in the market (thermal isolating or self-cleaning windows), there are some others on its infancy (e.g. planar waveguides for optical components' integration). Moreover, exploitation of thin film properties is in most cases partial and has a lot of potential for improvement.

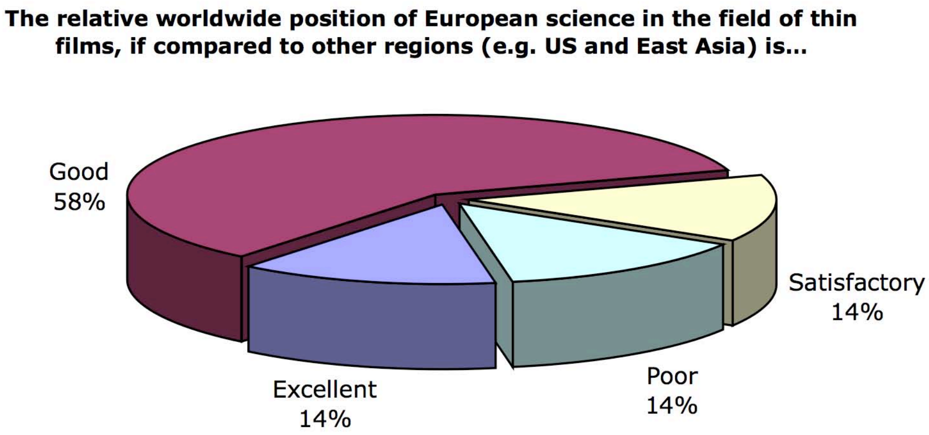
In general, most of thin film applications deal with developments in the semiconductors' industry: transistors, displays, solar cells, MEMS or planar waveguides. Therefore, developments in one of these applications could have a beneficial impact on the others. These are foreseen to be the most relevant applications for the future.

The fact that most of these applications are related to capital-intensive sectors (with long pay-off returns) could slowdown the adoption of new technologies. Actually, the deployment of new technologies has been already outlined in several sector specific roadmaps like the Nanoelectronics roadmap or the International Technology Roadmap for the Semiconductors' industry.

Besides the semiconductor-related applications, low-friction coatings show a great promise and have almost endless applications. However, their attractiveness highly depends on the final performance / cost ratio. Nowadays, there's still substantial research to be done as researchers are still struggling to understand the basic principle behind tribology phenomena.

In some cases, thin films could also contain embedded nanoparticles to reach the desired properties. Therefore, applications' development would also depend on these nanoparticles availability (in time, quality, volume and price).

2.5.2 EU positioning in the field



2.5.3 Final conclusions and recommendations

<u>Main barriers</u>
Thin films and coatings have been applied in many industries over the last decades; however, nanotechnology is now providing the tools for much precise characterisation and production.

The overwhelming challenge is to better understand the adhesion mechanisms between the substrate and the coating as well as between multi-layers. This has a crucial impact on all thin films' properties and is especially relevant for new materials being explored. The possibility to coat complex 3D geometries would also broaden the range of thin films applications.

However, the broad possibilities for thin films applications could also have a contra-productive effect. Experts in specific processes are not experts in all the markets this process could be applied to. The lack of understanding of industrial requirements is considered a bottleneck for all materials being researched. This is especially relevant because thin films are part of material systems and should be integrated into other (most of the times existent) production processes. For capital-intensive industries, this may block new technologies implementation within the next 5 to 10 years. Actually, sector-specific roadmaps (e.g. electronics) already foresee that many of presently researched processes and materials will never get out of the R&D lab.

Price and barriers related to production volumes have been highlighted by many experts for many production processes and are a crucial issue to be addressed.

Amongst non-technical barriers, experts highlighted the lack of young researchers, the limited interest from industry (especially in the case of silicates) or dissemination of state-of-the-art functional nanocoatings to end-users (e.g. for polymers). Also, some environmental issues (as found in other nanomaterial areas) have yet to be overcome in order to allow industrial scale application in a sustainable way.

As in other nanotechnology areas, the bi-directional communication between industrial and research communities is far less than optimal. Several factors are to be considered:

- Available literature is either too commercial (focused on markets' potential with few references to technological barriers/challenges) or too scientific (illegible for no R&D-intensive industries).

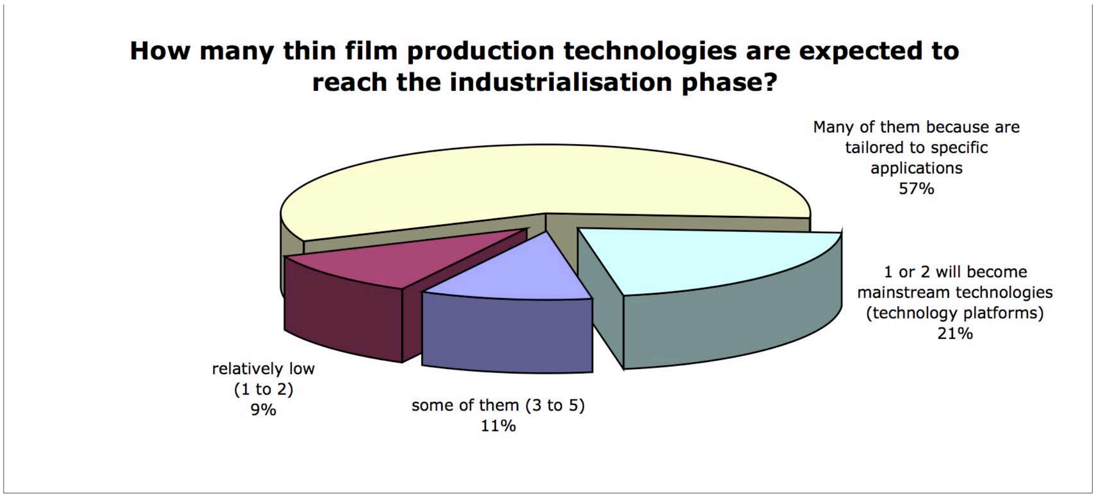
- There's a huge amount of terms for referring to very similar processes and/or materials. As in other nanotechnology fields, the lack of an agreed on terminology is hindering a transparent discussion between industry and research.

- Above all, a comparison between different processes is almost inexistent.

Scenarios for further development of thin films

In general, thin films' process development does not differ very much from developments in other areas of nanomaterials research. As it happens with the production of nanoporous materials or nanoparticles, the use of sophisticated processes (e.g. CVD or PVD) implies a low throughput and expensive equipment.

In many cases new technologies development is driven to fulfil specific applications' requirements. Although these developments might be helpful for competitiveness in a certain area, there are very limited opportunities for technology transfer to other sectors. Therefore, the risk of not succeeding is substantially higher. The fact that the number of technologies being investigated is steadily increasing raised the following question: how many thin film technologies would reach the industrialisation phase?



According to the most of the experts many technologies will reach the industrialisation phase. However, a significant number of experts (30%) consider that only 1 or 2 will reach this phase and probably become technology platforms around which new developments could be pursued.

As in other technology areas, the technology development path is very much linked to the investments made and to the intermediate results obtained. The term "hype" is, in many cases, associated to nanotechnology as it was to previous "technology revolutions" (e.g. Internet). Actually, many start-ups having received substantial investments do not exist anymore.

In W&W's opinion, thin films development very much depends on whether or not these processes can find (perhaps simple) market applications that generate the cash flow for financing long-term research.

As outlined before, thin films applications could perhaps be clustered in 2 main groups: high-tech (almost all related to semiconductors) and medium-tech. There are two main differences in production processes that could explain each technology application to certain industries:

- Process temperature has a high impact both on the process energy consumption and the equipment required (processes like PVD or CVD work at temperature around 400 and 1000 ºC whereas the sol-gel process works at room temperature) as well as on the degradation of the raw material.

- Use of vacuum chambers (normally for better process control and impurities avoidance) may require a huge adaptation of industry production lines. Use of vacuum chambers has a large influence on the size of the area to be coated. This seems not affordable in many medium-tech traditional sectors.

These processes (and related applications) development will probably follow completely different paths.

With regard to bottom-up approaches like self-assembly or positional assembly, self-assembly seems closer to its industrial applications but still far away (probably some 20 years or more). Again, although these approaches have almost endless possibilities, the need for intermediate applicable results is of the outmost importance. Industry and society might be unwilling to pay increasing costs for long-term high-risk/high-reward processes unless clear milestones are defined and reached.

Preliminary / Final recommendations

Thin films are probably one of the less exotic fields of nanotechnology (e.g. as compared to nanotubes) and are already being applied. In general, there’s a fierce worldwide competition in applications related with semiconductors. Countries like Taiwan or South Korea are heavily investing in this area (and not in others!) together with, of course, the US and Japan. Therefore, Europe may need to choose some limited research fields to reach the critical mass required for global competition.

In semiconductor-related applications, SMEs and especially spin out companies could play a role on bringing new top down approaches up to the level where they could be undertaken by larger industries (as some successful SME do in the pharmaceutical sector).

Regarding low-tech applications, there’s perhaps less need for making tough choices. In non high-tech sectors (e.g. self-cleaning surfaces or thermal insulating applications), SMEs could play a stronger role in technology development as market applications either exist or could be expected very soon. In general, this fits better with SMEs boundary conditions: scarce financial resources and R&D capabilities.

Considering that price and production volume/throughput is considered to be one of the main bottlenecks, in W&W’s opinion R&D efforts should shift more towards production up scaling. Even if in pilot plants, the increased volume would increase material availability for research purposes and most like increase the number of researchers and technicians working in this field. Moreover, most of the experts agree that creating production plants close to research centres would very much facilitate technology transfer to EU industries (please refer to page 38 for further comments on this).

Finally, there's the need for a better alignment of research and industrial (or societal) interest. Research into solutions for environmental impact of some thin film related technologies (most notably sol-gel technologies) must be done, if these technologies are to find large-scale applications in a sustainable way.

Regarding medium-tech industry sectors, there's the need to communicate thin film potential as compared to existing possibilities and indicating development timelines. Communication should be targeted at both R&D and managing people.

W&W feels that the combination of transparency with chemical, mechanical or thermal functionality offers huge potential for exploitation. In this area, the self-cleaning and / or thermally insulating windows are first applications that could be followed by many more. It seems an area where the EU has key strengths, where it also has a strong industry, but where really ambitious research is not (yet) seen. Looking at the potential in construction, in optical industry (spectacles, etc), in automotive, in packaging, in clothing, it seems a platform technology that could be addressed bringing together agile SME's, powerful industries and smart universities.

Feedback solicited:

- *Do you as expert agree on the above-mentioned conclusions?*
- *Would you add any other conclusion to the above-mentioned ones?*

Annex I. List of participants

Remark: This list will not be included in the draft roadmap report sent to experts for validation; Experts will be asked for permission to include their names in the final report

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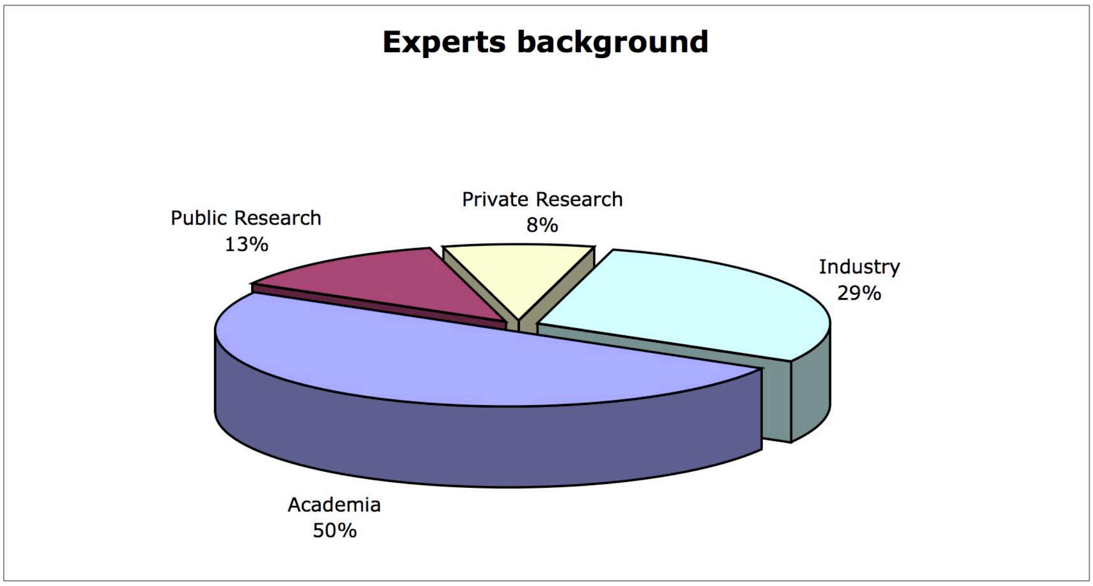
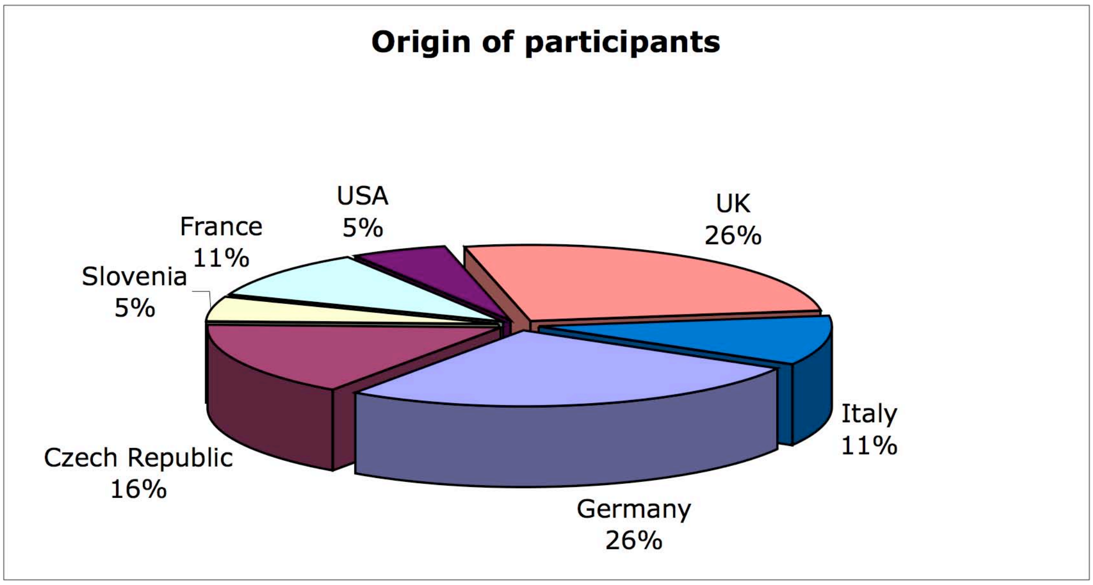

Experts background
Private Research
8%
Public Research
13%
Industry
29%
Academia
50%


Origin of participants
USA
5%
UK
26%
France
11%
Slovenia
5%
Italy
11%
Czech Republic
16%
Germany
26%