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Roadmap Report on Nanoparticles

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This document is pending final approval by the EC.

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 from experts participating in a Delphi-like panel. In addition, W&W has added where relevant its views and opinions, in each case identifying clearly the status of such statement. The views expressed do not necessarily reflect those of the European Commission.

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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 industry including SMEs, research organisations, and public bodies in general and the EC in particular.

This report is one of the three final deliverables of the NRM project (together with the reports on the fields 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 if 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

A Delphi-like approach (hereafter referred to as Delphi panel) 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

One roadmap has been prepared for each of the four aforementioned topics. These roadmaps are/ have been presented in 8 National Conferences and one International Conference during the 4th quarter of 2005.

1.4 Structure of this report

This roadmap begins with the definition of *nanoparticles* (section 2.1) and the identification and description of their most remarkable properties (2.2). Wherever possible, concrete applications have been linked to potential offered by new or improved nanoparticle properties – with respect to other (nano)material categories.

Section 2.3 focuses on the nanoparticles / nanocomposites pipeline, including nanoparticles production (2.3.1), nanoparticles functionalisation (2.3.2), potential later incorporation into nanocomposites (2.3.3) and application (2.3.4) steps. For each of these steps, we have detailed most relevant technologies and main barriers pointed out by the experts. Whenever possible, we have also identified ways to overcome these (breakthroughs). In the applications section, we have provided a list of the most common nanoparticles applications being researched worldwide. Detailed graphics (based on the input from the experts) provide an overview of the (estimated) state of development of these applications in 2005, 2010 and 2015. Additionally, we have included a graph representing the risk involved against the expected market growth of each application during the next decade.

The next section (2.4) provides an estimated evolution of price and worldwide volume production of certain types of nanoparticles. Section 2.5 briefly reviews non-technological aspects of nanoparticles. We have not focused too much on this chapter since other initiatives / projects already cover them.

The last section (2.6) is devoted to conclusions and recommendations. It includes different subsections covering aspects such as most relevant applications (2.6.1), expert's opinion on top applications (2.6.2), EU positioning in the field (2.6.3) and final conclusions and recommendations (2.6.4). Annexes at the end of the document include the list of participants in the Delphi panel and a few statistics worth mentioning, as well as a glossary of terms and an overview of applications.

In this document, certain pieces of text have been highlighted to capture the reader's attention. Text highlighted reflects that, according to W&W's opinion, there is a topic there suitable for future FP7 research.

2 ‘Nanoparticles / nanocomposites’ Roadmap

2.1 Definition of nanoparticles

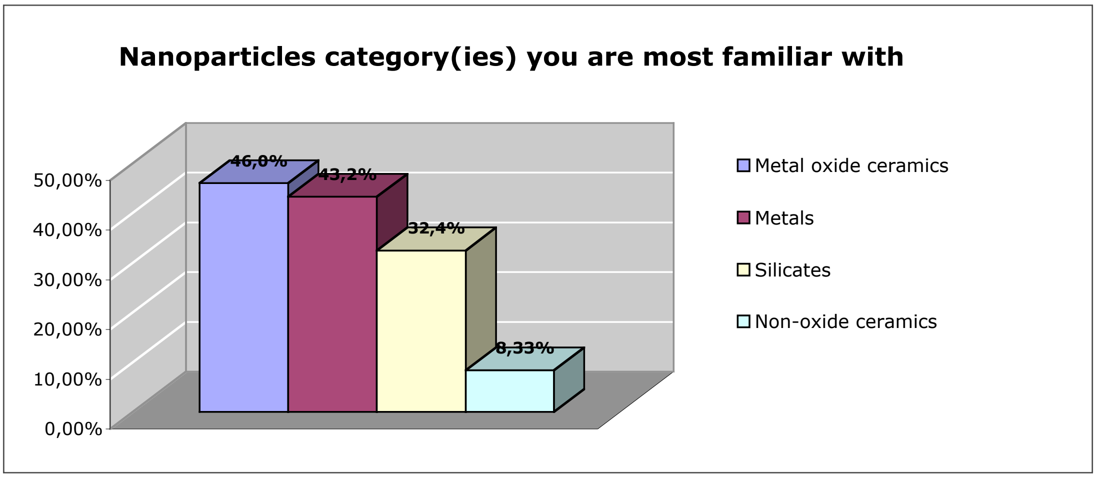
Water-repellent effect nanoparticle coating Courtesy of BASF

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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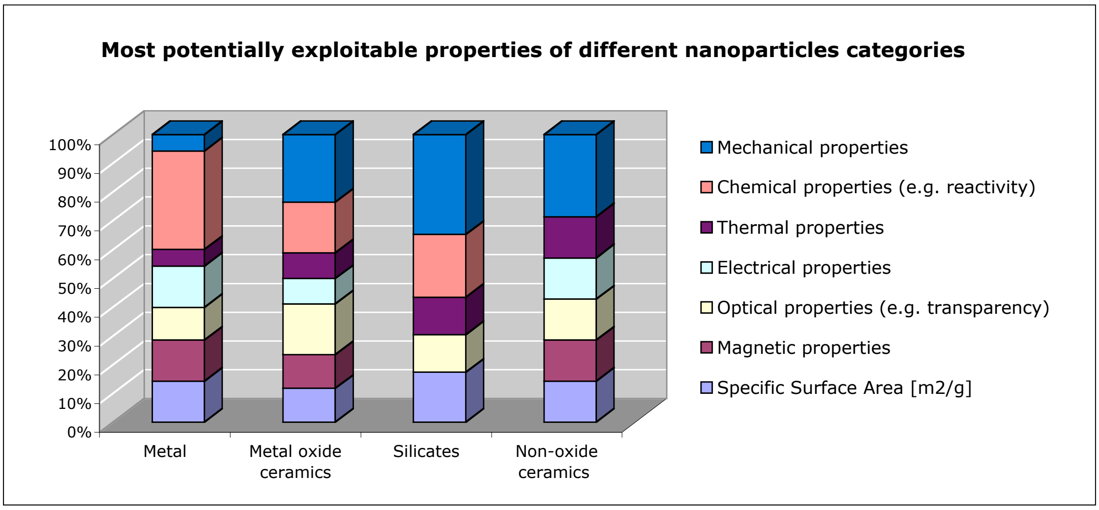
[1] It should be noted here that there are two significant areas of application where the critical dimension is substantially above the 100 nm range: biological and light-related applications. Substantial work using nanoparticles for drug delivery uses particles up to 400 nm or more, which is still small 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 producing nanoparticulate fillers can offset this.

For silicate nanoparticles, their 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 molecular weight substances by vastly increasing the average path the molecule has to travel 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 semiconductor 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.

Chemical properties (e.g. reactivity)

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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.

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. This can lead to a reduction in the required amounts of the commonly-used platinum group precious metals (widely used in fuel cells and in catalytic converters) and the opening up of new possibilities for less-commonly used metals such as gold, which only becomes an effective catalyst in many cases when it is in nanoparticulate form.

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 and incorporated in wound dressings. 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

In composites, depending on the chemistry of the nanoparticle, its aspect ratio, dissemination and interfacial interactions with the polymer matrix (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.

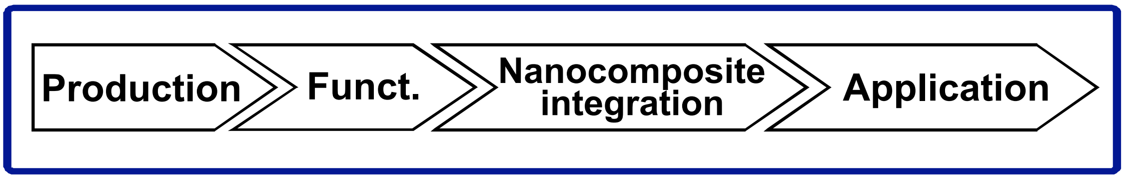
In spite of this, and according to the opinion of some experts, certain nanoparticle-based composites will have a brief heyday and then be overtaken by nanotubes composites. There is no doubt that in terms of mechanical properties, nanotubes are poised to make a very important contribution to this field,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



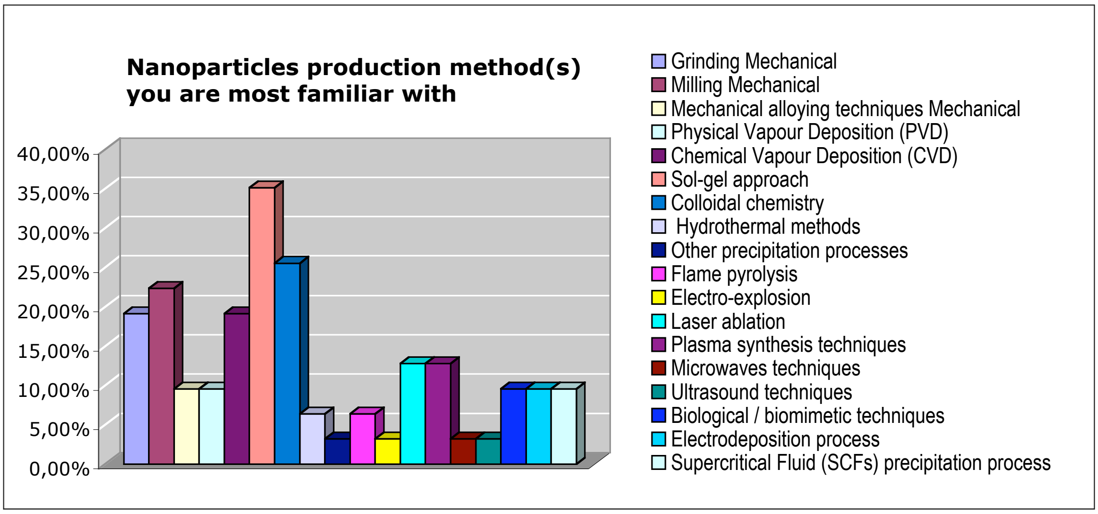
It should be remarked that this is not always a linear approach with sequential independent steps. In many cases each and every different application has one or a few specific production, purification and functionalization processes to obtain the desired properties for the lowest amount of time and money.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

2.3.1 Nanoparticle 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.

There is extensive literature describing different production technologies for the manufacture of nanoparticles. The following paragraphs give an overview of the <u>main barriers</u> 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:



<u>Solid state methods</u>

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

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 <u>cost</u> as well as <u>heterogeneous size distribution</u> 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. Closed-loop processes might help to solve this problem.

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 (e.g. those that are ductile enough to form a wire) 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 nanoparticle 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’)

A common perception among experts is that for silicate nanoparticles, the 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 justified 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, for example, 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. More significantly, the existing commercialisation of nanoclay barrier composites in packaging, beer bottles being a notable example, clearly demonstrates that certain applications can support existing added costs (this will especially be the case where there is no existing material that can fulfil the same function).

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.

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 at least 5 years to fully understand all solutions.

Others methods

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.

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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.

2.3.4 Nanoparticles applications

Existing and potential 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 as diesel additive to improve combustion efficiency)
- Automotive catalytic converters
- Miniaturised varistors (e.g. doped ZnO)
- Fuel cell catalysts (e.g. platinum in PEM cells)
- Conducting polymers for bipolar plates in fuel cells
- Improved electrodes in batteries and supercapacitors (increased capacity, more rapid charging)
- Increased efficiency of hydrogen generation from water (e.g. from solar)
- Catalysts for gas to liquid technologies, coal gasification technologies, biodiesel and other synthetic fuels, etc,

Healthcare/medical

- Targeted drug delivery
- Alternative drug and vaccine delivery mechanisms (e.g. inhalation, oral in place of injection).
- Bone growth promoters
- Cancer treatments
- Biocompatible coatings for implants
- Sunscreens (e.g. using ZnO and TiO_2) / cosmetics
- Biolabeling and detection (e.g. using Au)
- Carriers for drugs with low water solubility
- Fungicides (e.g. using ZnO)
- MRI contrast agents (e.g. using superparamagnetic iron oxide)
- New dental composites
- Biological binding agents (e.g. for high phosphate levels)
- Antiviral, antibacterial (e.g. Ag), anti-spore non-chemical creams and powders (using surface tension energy on the nanoscale to destroy biological particles)

Engineering

- Cutting tool bits (e.g. WC, TaC, TIC, Co)
- Spark plugs (e.g. using nanoscale metal and ceramic powders)
- Chemical sensors
- Molecular sieves
- Wear-resistant / abrasion-resistant coatings (e.g. using alumina, $Y\text{-}Zr_2O_3$)

- Nanoclay-reinforced polymer composites
- Lubricants and sealants / 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
- Enhanced thermal spray coating techniques (e.g. based on TiO_2, TiC-Co)
- Inks: conducting, magnetic, etc. (using metal powders)
- Flame retardant polymer formulations
- Rubber composites such as car tyres (e.g. carbon black)
- Anti-scattering layers in photographic film

Consumer goods

- Anti-counterfeit devices
- Barrier packaging using silicates
- Ski wax
- White goods (e.g. anti-scratch, easy-cleaning coatings, etc.)
- 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 (e.g. anti-bleaching effect, scratch resistance, etc.)
- Tiles coated (e.g. anti-scratch using alumina)

Environmental

- Water treatment (photo-catalyst treatments, e.g. using TiO_2)
- Self-cleaning glass (e.g. using TiO_2 based nanostructured coatings)
- Anti-reflection coatings
- Sanitary ware
- Soil remediation (e.g. using Fe)
- Controlled delivery of herbicides and pesticides
- Anti-fouling coatings (reduce chemical use)

Electronics

- Nanoscale magnetic particles for high-density data storage
- EMI shielding using conducting and magnetic materials
- Electronic circuits (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 visualisation of innovation funnels in 2010 and especially 2015 might give the erroneous impression that in the future, basic R&D (and in some cases even applied R&D) becomes obsolete. This is of course not the reality. It is important to note that the application status visualized in the funnels represents the advancement of the first pioneer applications; the forerunners of a large field of applications.

In reality, each of the application areas visualized in the funnels is the tip of an iceberg of related applications, and each of them will continue to inspire basic research as well as new possible investigation routes. However, in the Nanoroadmap Delphi exercise, the experts were not asked to identify such new basic and applied R&D areas; they were asked to position the spearhead applications in a relative sense, comparing which ones were expected to reach the market first.

The following three paragraphs each cover one *snapshot* of the overall nanoparticles roadmap. One for the current state of the art (2005), 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. 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.

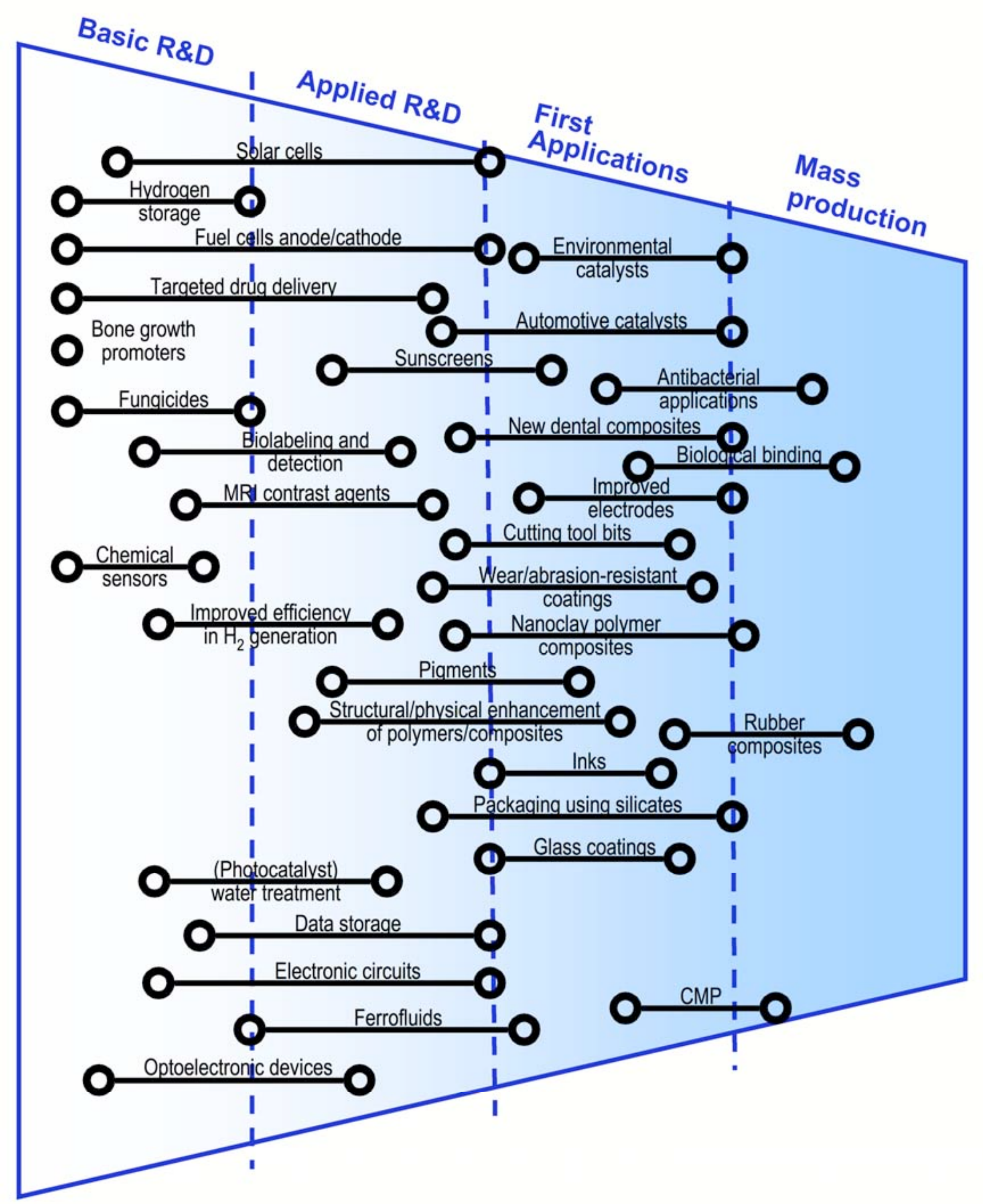
Mass production and incremental research (Mass production)

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.

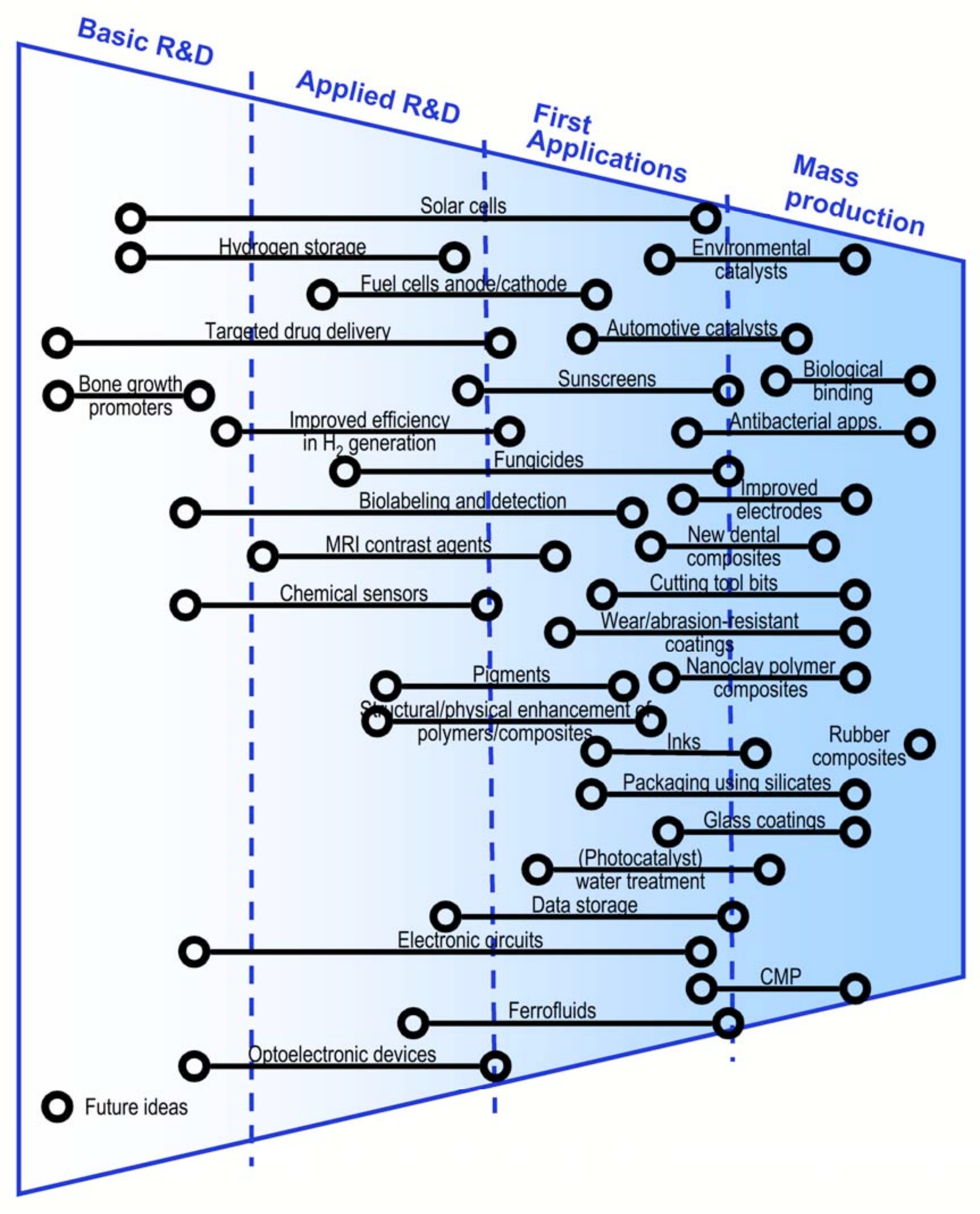
For further information about the added value of nanoparticles for each of these applications together with indications about suitable types of nanoparticles to be used in the respective applications, please refer to Annex III. Overview of applications.



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.

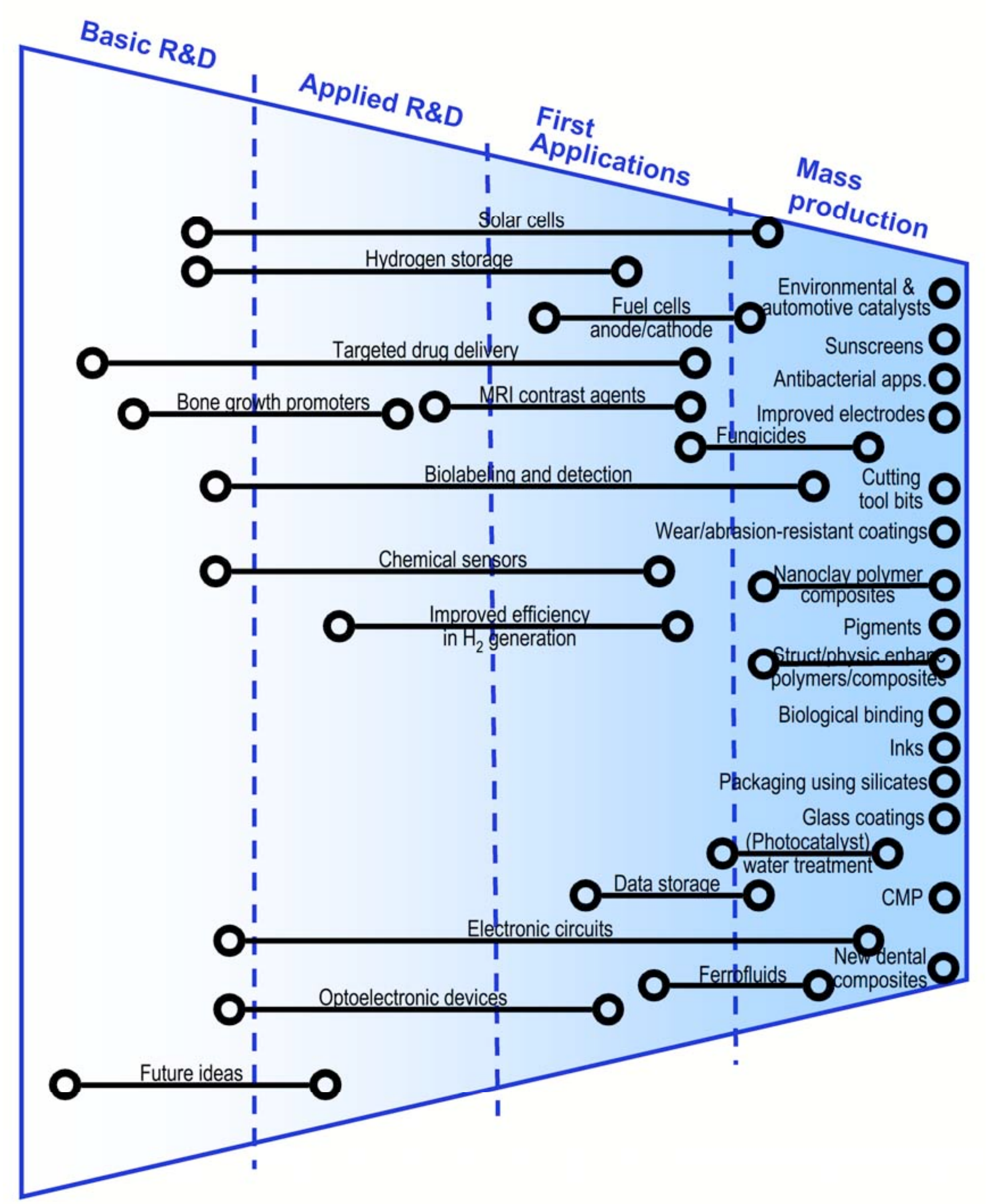
After five years many more applications will have come into fruition. A good number of the potential applications currently considered will be most probably entering into first commercial applications, with some of them already approaching the mass production phase.



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.



Below are some ideas of futuristic applications that could enter the basic / applied R&D phases by 2010 - 2015:

- Manufacture of small nanoparticles with extremely (even atomically) precise size and crystal orientation. This is especially important for catalysis but also for creation of composite structures with fine-tuned properties (especially optical and electrical). These capabilities are only just being touched on and will probably only get to applied R&D by 2015, with plenty of basic research still going on.

- Self assembly of complex hybrid inorganic nanoparticles / organic materials with novel properties (especially electrical and with potential in smart biomaterials and devices). Basic R&D phase in 2010, moving into applied R&D by 2015.

- Design of novel bulk materials through computer modelling of nanocomposite elements. This will still be in basic R&D in 2015, maybe applied for some simple cases.

- Direct biological control / treatment through intracellular delivery of interference RNA. This is just getting into applied R&D but the bulk of it will still be in basic by 2015.

- Catalysts for creation of advanced liquid fuels from solar energy. Probably basic research starting around now and maybe getting into applied by 2015.

- Superconductors - some basic research now. Likely still basic in 2015, maybe applied.

- Physical nanosensors (e.g. magnetic, electrical, mechanical) – requires precise control of size. Basic R&D phase in 2010, applied by 2015, maybe even first applications.

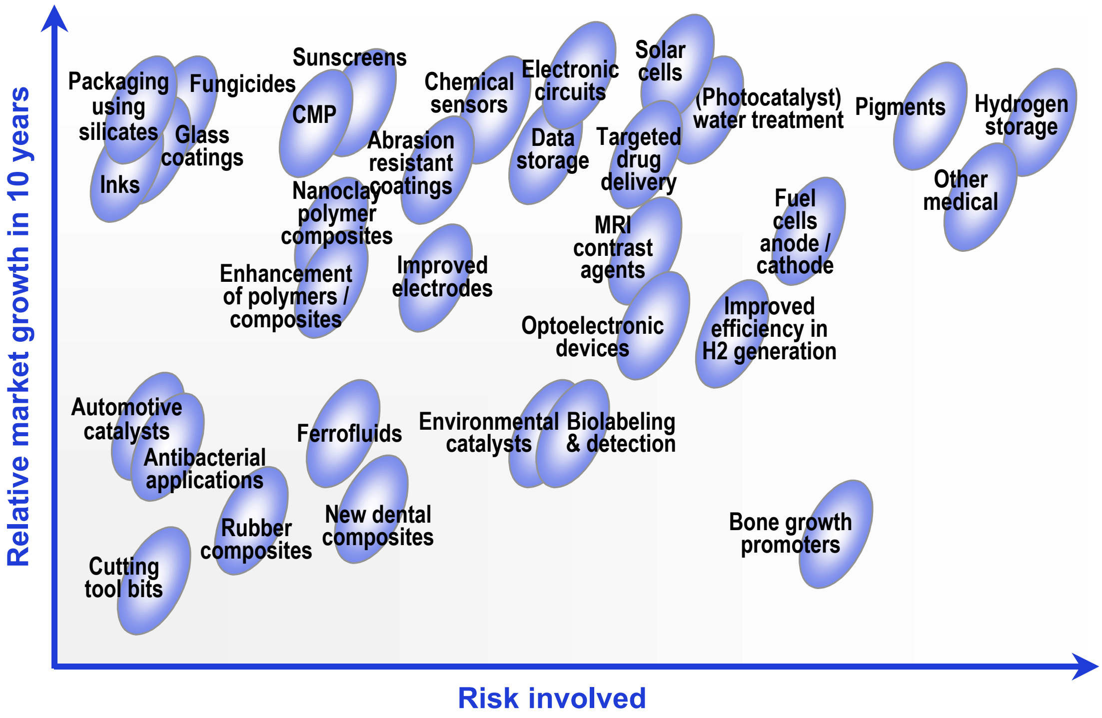
- Multilayered *designer* nanoparticles. These are only just in the basic research phase.

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 gathered 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.

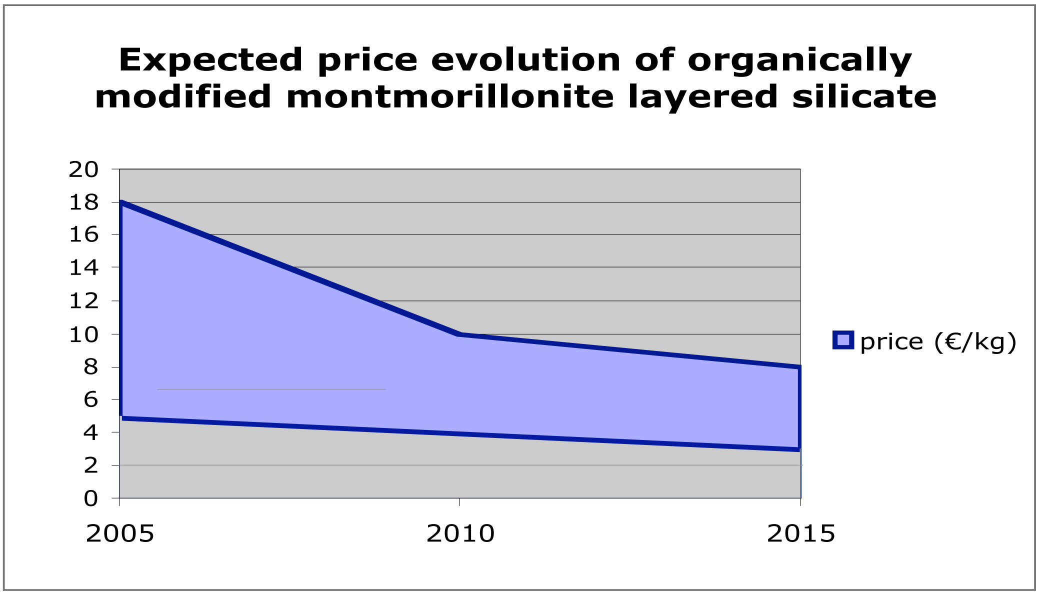
2.4 Estimated evolution of price & worldwide volume production

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.

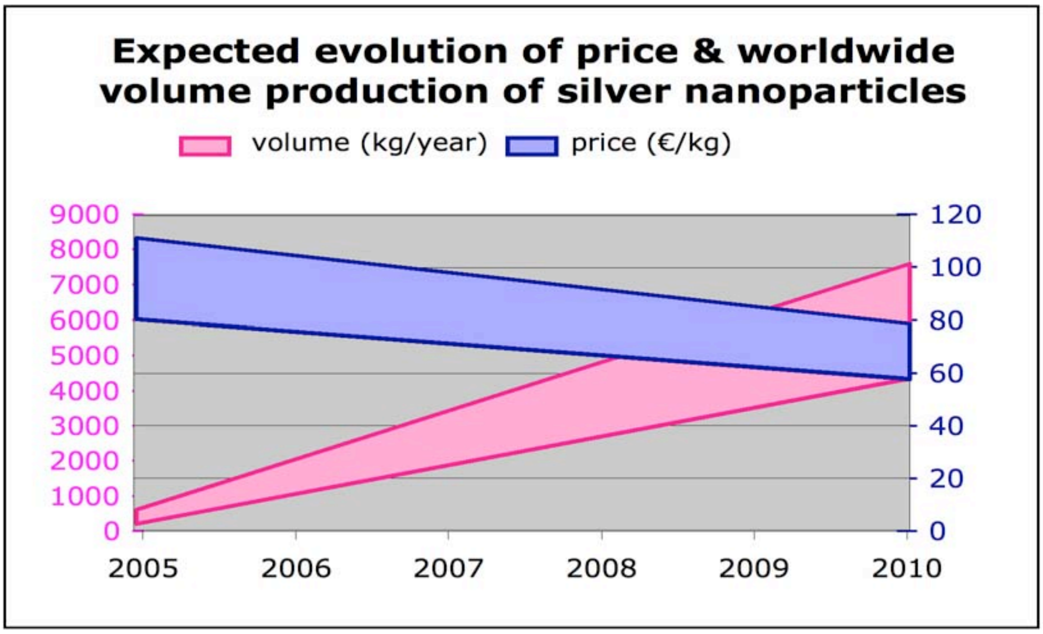
While academic researchers typically do not handle this type of information (estimations), companies are not always eager to show everything they can do (or cannot do), mainly for competitiveness reasons. Furthermore, technological advancements may result in small jumps in the production capability that 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.

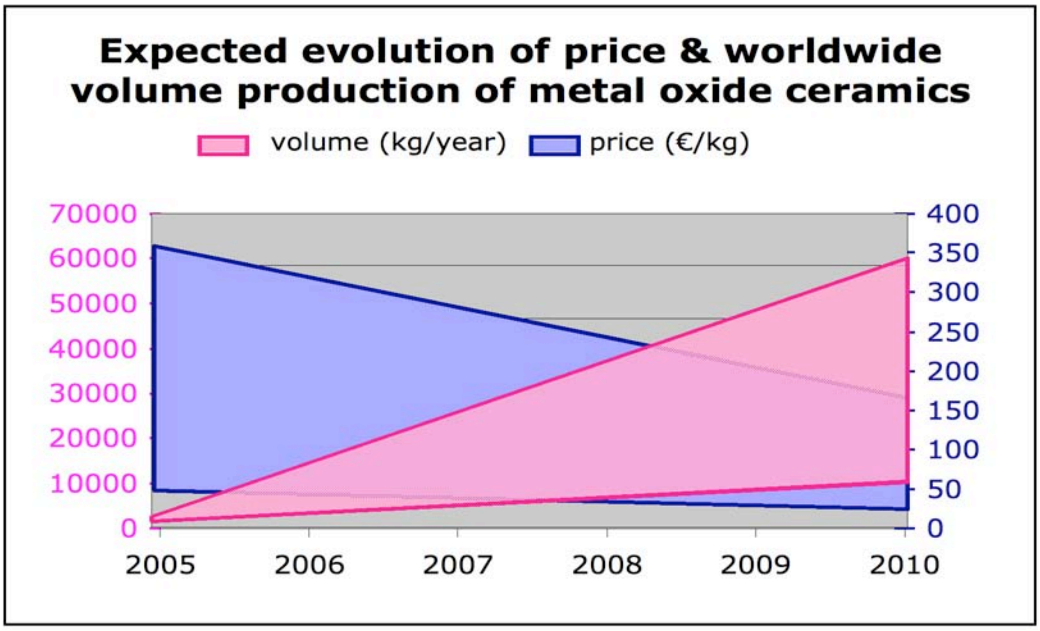
Organically modified ***montmorillonite* layered silicates** are used to reinforce polymer composites. Improvement in e.g. mechanical and/or barrier properties can be achieved by having the clay exfoliated to nano-scale sheets in a thermoplastic compound. Some functional properties (e.g. transparency, 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 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

Of all areas of nanotechnology beyond the futuristic, nanoparticles have generated by far the greatest concerns. The 2004 Royal Society report on ethical, health, safety and social issues (www.nanotec.org.uk) recommended that nanoparticulate forms of well-known materials be treated as a new chemical because of the novel ways they can interact with biological systems (for instance their ability to enter cells) and uncertainty about persistence in the environment. Much research remains to be done in understanding these interactions but some of the results so far do not offer great reassurance.

Clearly the way in which nanoparticles are used affects their likely interaction with biological systems. When incorporated in a composite material exposure at any time is going to be low and here the risks are unlikely to be high, although they remain unknown until biological interactions are better understood. However, some applications involve direct exposure to nanoparticles, such as drug delivery systems and sunscreens and cosmetics. In the former any risk is likely to be outweighed by benefit (though, again, this cannot be stated with confidence at this stage) and the population exposed will generally be small. For sunscreens and cosmetics, however, large populations are exposed to significant amounts of nanoparticles for moderate or zero benefit and it is here that the risk of adverse consequences is greatest. It is conceivable that discovery, to late in the day, of a major health issue could lead to a public backlash against all nanoparticle applications or even nanotechnology as a whole. Since European public opinion is far more reactionary than in other parts of the world such an outcome could present serious obstacles to research, development and sales within Europe.

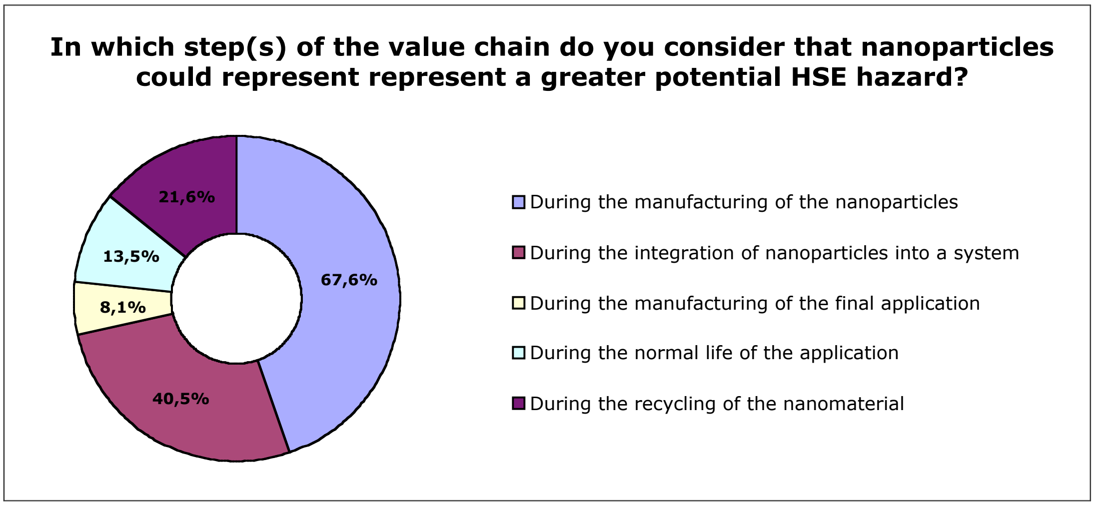
Nanoparticle applications that likely present little risk, such as uses in composites, nevertheless will often involve production stages during which workers can be exposed. A white paper recently published by Cientifica, called *Nanotechnologies: Risks & Rewards* declared *“Many academic establishments 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.

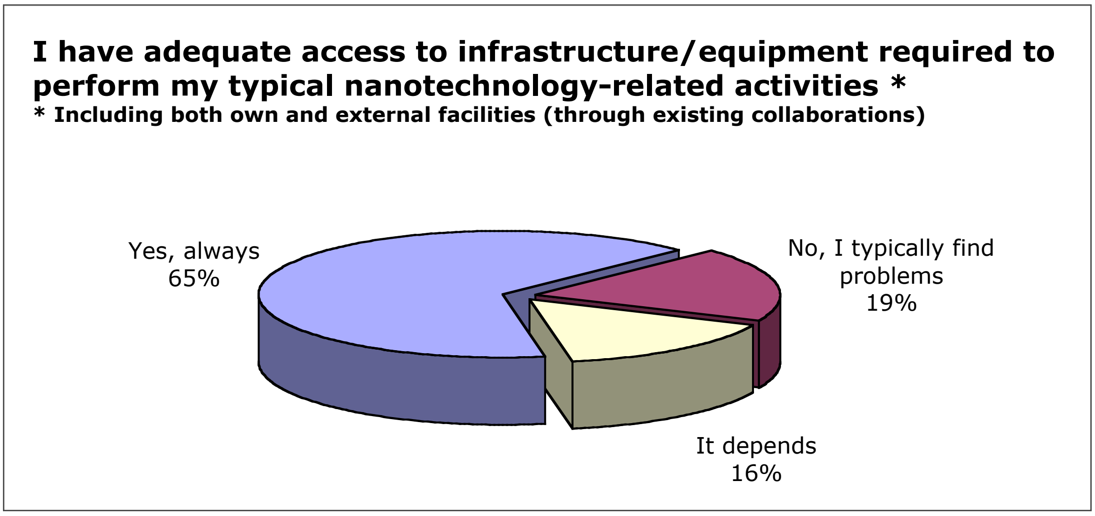
The following figure highlights the steps in the value chain of nanoparticles where the participants in the Delphi panel think that a greater potential HSE hazard may occur.

The manufacturing stage has the 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. The low assessment of risk during use reflects the fact that only a subset of applications probably present any risk here. 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.



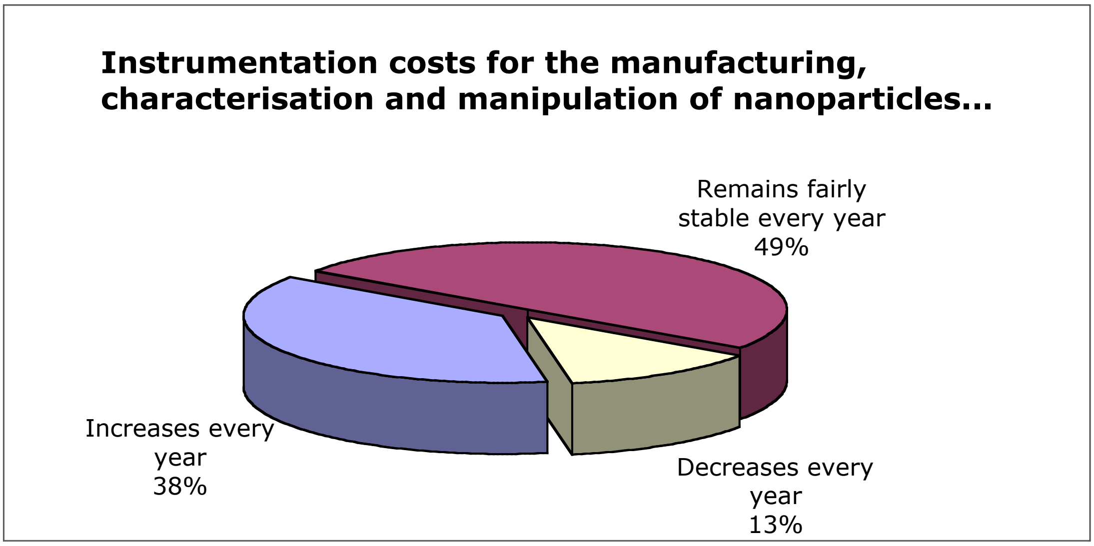
Infrastructure requirements

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.



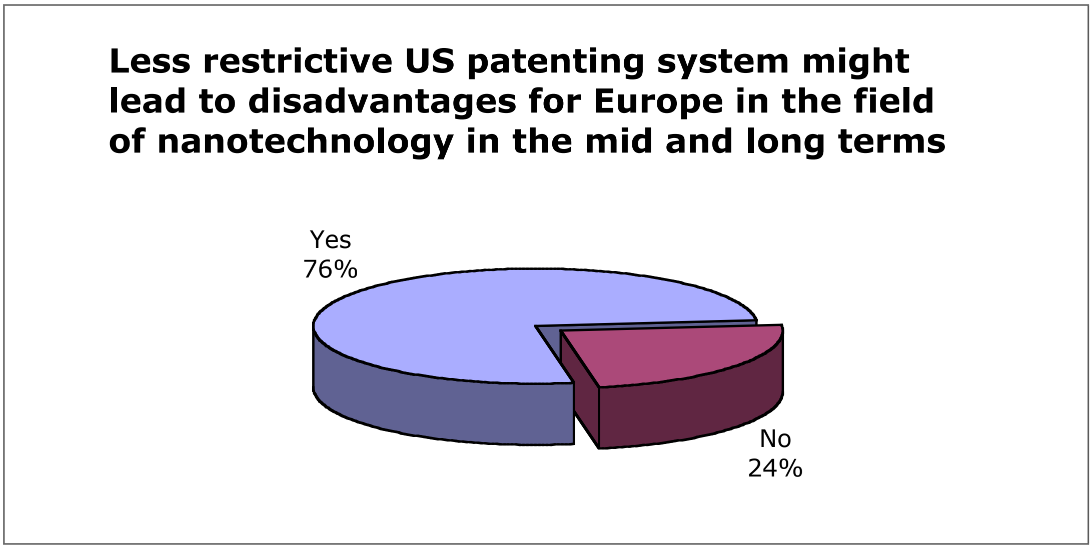
Instrumentation costs

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 Dissecting the application landscape

Given the enormous variety of nanoparticles and uses to which they can be put, any attempt to prioritise investment or research focus needs to start by identifying components of the nanoparticle application space that have clearly different dynamics, needs, barriers and potentials and then to identify the most significant of these and describe their characteristics.

Nanoparticle mass production

The first obvious component is bulk production of nanoparticles. The number of applications requiring large quantities of product is limited, but the markets for the applications are very large, most notably composite materials. These in turn can be divided according to the properties in which the nanocomposite offers an advantage over alternatives.

Bulk structural materials are by far the largest potential market. Improved strength can be of value in everything from machine parts to aircraft frames to buildings and bridges, and from furniture to toys and kitchen utensils. Nanoclay polymer composites represent the most advanced application in this space but they suffer from pricing problems, which the experts polled for these reports suggest might never be overcome for most applications. Thus, despite the reasonably advanced state of development of such composites, commercialisation has so far only be seen in limited places, such as high-wear components in cars. An additional concern for the future of such applications is the potential for composites based on carbon nanotubes to vastly outperform those based on nanoclay. Thus cost here is the major challenge and a difficult one. However, other properties of nanocomposites can provide significant added value, as will be seen later, but the markets are inevitably more limited in terms of nanoparticle production volumes.

Metallic and ceramic composites for bulk materials are at a less developed stage and thus warrant significant applied research and exploration of alternative production methods. There is a grey area here between nanoparticle composites and nanocrystalline materials but at least one promising new steel has involved manufacture in a rolling process using nanoparticles. However, in terms of large volume requirements for materials, most markets, such as automotive or civil engineering and construction, are again very price sensitive.

Moderate production of nanoparticles for composites is more likely to be driven by composites with special properties. The gas barrier properties of nanoclay composites are already used widely in beer bottles, where, until their creation, plastic containers were not an option - an example of a novel property rather than an incremental improvement. Food packaging offering longer shelf life also promises to justify the higher production costs for nanoclay composites, as do applications requiring flame retardant properties. These are sizeable markets but the volumes of nanoparticles are relatively modest. The real value is in the material into which they are incorporated.

Additional areas where reasonable nanoparticle production volumes might be seen are in cosmetics, agricultural delivery systems (e.g. pesticides), environmental remediation, various catalyst applications, lubricants, abrasives (CMP), sealants, adhesives, and coatings. Each of these tends to have specific and different requirements for the nature of the nanoparticle, providing little opportunity for more than moderate economies of scale.

Thus the conclusion has to be that, at this stage, it is difficult to see great potential for the extensive mass production of any form of nanoparticle on a scale comparable to, say, carbon black for use in car tyres, though widespread structural nanoclay use cannot be ruled out if sufficient price reductions can be achieved (the main barrier). A wide variety of niche applications could generate significant demand but the greatest value will be in the stage of incorporation of the nanoparticles into final materials. Many of these final materials will make quite specific demands on the nature of the nanoparticle, which suggests that the most profitable scenarios for nanoparticle-based products involve relatively low-volume, specialist materials. It follows that refinement of production processes with an eye to increased control over size, structure etc. represent a promising avenue to pursue, probably more promising than simple scalability of production, i.e. mastery rather than economy. This fact makes the landscape open for smaller operators such as start-ups and SMEs and identifies the chief technical barrier in nanoparticle production as control of size and morphology.

Functionalisation

Though this isn't an application in itself, it warrants separate consideration. As stated above, most bulk material applications of nanoparticles derive their greatest value from the nature of the derived product rather than the raw nanoparticles. Key to achieving this in most cases is functionalisation, whether to aid incorporation in a matrix or to allow effective delivery. The variety of ways of functionalising nanoparticles is almost endless and thus this represents an enormous space to explore. Though in many cases a company will be looking to functionalisation to satisfy a specific need (effective nanoclay dispersion in polymer, for instance, took many years of experimentation with functionalisation), and this raises important issues of intellectual property and secrecy, it could be argued that developing general capabilities in this space could lead to significant results. The growth of a service industry based around such expertise is conceivable. Again this is an area that is open to small independent companies. Actual production of composite masterbatches is likely to be dominated by established large players but they could source functionalisation capabilities from smaller companies.

No particular barriers in this area have been identified - it is more a case that functionalisation of nanoparticles is a fairly young field with much learning still to be done.

Bulk nanocomposites

The features of these applications were largely covered under the discussion of bulk nanoparticle production. To summarise, they tend to be relatively or very sensitive to the cost (the chief barrier) of raw materials and functionalisation steps but are relatively tolerant of variation in nanoparticle size and morphology. The potential market is of course enormous, representing the bulk of everything man-made around us.

Not mentioned so far is a class of materials that may not be classed as composites but can often be considered bulk materials based on nanoparticles, and these are aerogels. Here the primary desired property is usually thermal insulation and they represent a nice example of a barrier recently overcome - the materials were previously quite fragile. New nanoparticle-based aerogels are orders of magnitude stronger than previous ones, opening a range of new markets, for example in clothing. The novelty of the new applications can likely support the material cost while the drastically improved strength justifies it in many other applications (strength improvements for nanoclay composites, by contrast, are only around 10-15%).

More novel bulk nanocomposites (which can support greater production costs) should not, of course, be ruled out.

Coatings

This is again a wide variety of applications but certain characteristics are common among them. Nanoparticle quantities used are not great but their characteristics and uniformity (monodispersity) are often important. Many technologies for applying coatings are well established and easily adapted to use of nanoparticles (the controlled use of molecular-scale interactions, however, for example in various approaches to self-assembly, is a young discipline). Equally, the function of many nanoparticle coatings is not new but simply an improvement, often a dramatic one, over previous technologies (e.g. non-stick, abrasion resistance). However, a number of novel properties emerge from the use of nanoparticles.

The market represented is very large and diverse, and there are many cases of commercialisation already, such as anti-scratch coating on spectacles or cars, anti-fouling coatings on ships, anti-wear coatings in machine parts, self-cleaning materials, and more.

Two key attributes of this application space are fine control over final morphology at the nanoscale and diverse requirements in terms of material to be applied and substrates to be applied to. These in turn place constraints on control of nanoparticle size (and sometimes morphology) and demands diverse functionalisation capabilities. The area also presents great opportunities for self-assembly since this effectively only needs to operate in two dimensions rather than three (multiple self-assembled monolayers offer potentially great flexibility in terms of matching substrates to desired surface behaviour). The use of multiple self-assembled layers opens up a range of unexplored potential properties and behaviours.

Price sensitivity (for raw materials) is relatively low, with processes often representing the greatest cost. A key technical barrier in many applications, especially ones relying on self-assembly to create well-defined nanostructures using nanoparticle, is control of size and morphology.

In vivo / medical applications

The characteristics of this collection of applications are dictated by their interaction with biological systems. Whether the objective is imaging, alternative drug delivery mechanisms (inhalation, cutaneous, oral with protection from digestive enzymes), targeted delivery of drugs or nanoparticles to destroy tumour cells (through heating, magnetically-induced rupture or radiation), the nanoparticles are constrained to be within a certain size range, often need a specific finer nanostructure and frequently need to be functionalised. Raw materials production costs are generally of little relevance since the quantity of materials are generally very small.

Biolabeling / diagnostic / biosorting / analysis applications have similar characteristics.

The critical value in these applications is the *capability* that is achieved, which is often novel. Nanoparticles are thus simply a component in a system that is dependent on many factors for success - barriers, beyond those of obtaining fine control of size and structure, are often not connected with the nanoparticles themselves.

Catalysts

Many nanoparticulate formulations of catalysts derive their value simply from increased surface area. This application has been made more interesting, though, by the discovery that some materials only exhibit catalytic activity when in nanoparticulate form, opening up a new range of applications or alternative pathways. Specific control of size and morphology of catalytic nanoparticles is not, in theory, essential, but offers a gradual improvement as the material improves in this respect (in general, the smaller the better - platinum catalyst particles in proton exchange membrane fuel cells are around 2 nm). However, one structural aspect can be particularly important, which is the ability to create nanoparticles that present a specific crystal face to the reaction medium. This is because different faces can selectively catalyse different reactions and result in significant changes in yield balances between competing end products.

The other main factor to consider with catalysts is even distribution on a support (if a support is used, as it is in fuel cells, for example). Again, this represents a requirement that produces gradual improvements in efficiency.

Thus, though precise control of nanoparticle size and layout is not essential for catalysis, it is important and can be commercially critical, for instance in the production of synthetic fuels from biological materials, coal or waste. Production costs of nanoparticles are not very relevant - raw material costs are often more so since many important catalysts are precious metals.

Other applications

The above application categories cover many of the previously mentioned applications, but not all. However, other applications, some with substantial potential, generally show similar characteristics to the above categories. Some examples are:

- solar cells - similar requirements to both coating and catalyst applications
- improved electrodes - similar to catalytic applications
- antibacterials, antivirals, antifungals - similar to catalytic applications
- sensors - similar to medical applications (strict size and morphology constraints but the value lies in the system/device as a whole)
- pigments / inks - similar to coatings
- propellants / explosives - similar to catalysts
- data storage media - similar to coatings

Clearly this is all a simplification and generalisation of a diverse landscape but it allows the identification of the most important and common key requirements for many applications, and thus a focus for research and investment. These requirements will be summed up later.

2.6.2 The experts' opinions on top applications

At the moment, the main field in terms of highest revenues, according to the experts, 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. It should be stressed that such qualitative judgements are notoriously difficult especially over a field as broad as this. Do you judge on the value of the market for the product, which indeed makes the nanosized grains in disk drives a formidable size, or, say, the value of nanoparticles used in an application? In the latter case nanoclay in composites may be reaching impressive levels whereas the amount of nanomaterial used in hard drives is small.

However, 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 much in line 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. As previously stated, though, where the function of the composite is not reinforcement but something such as reduced gas permeability (which requires relatively little material in comparison with bulk structures), the cost can much more easily be justified, as witnessed by the widespread use in this area already. 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. This has probably just about happened in packaging but not in structural reinforcement, where not a great deal seems to have happened since the their commercial use in cars made headlines in 2001.

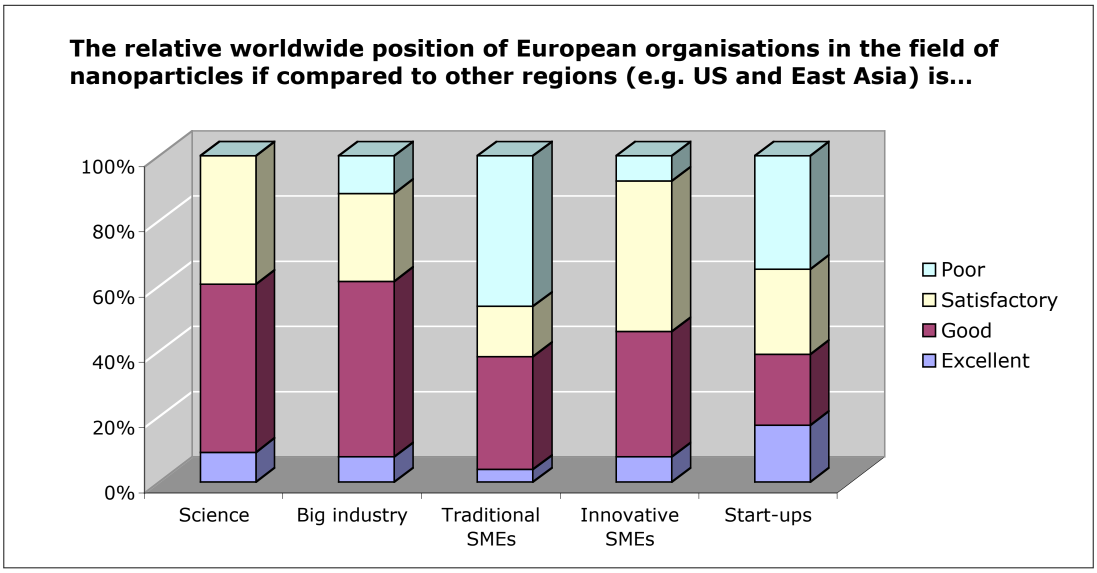
Certain health-related applications are also expected to provide remarkable benefits, if finally developed successfully. Examples of existing/potential applications have been mentioned in this report before. However, there is an application that because of its huge potential impact is worth considering separately. This is the field of **drug delivery**. Nanoparticles can be used as vehicles to deliver drugs or vaccines orally or through inhalation, avoiding the need for injections (very important in the third world) and through the use of associated antibodies the drugs can be taken to only the areas they are needed, thus minimising) the side effects in the body as a whole (this has the potential to breathe new life into drugs that were effective but failed trials because of toxicity). A market entry barrier for this application stems from arduous approval process by regulatory bodies (e.g. Food and Drug Administration - FDA). However, in the long term *dendrimers* are likely to be in a better position than nanoparticles (as classified in this report) for targeted 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 deserve mention as a class of significant current and near-future applications. 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.

2.6.3 EU positioning in the field

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.

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.

2.6.4 Final conclusions and recommendations

Main barriers

A principal technical barrier in many applications is accurate control of size and morphology of particles. In some cases adequate functionalisation will also represent a barrier. In both cases scaling these capabilities, once achieved, to reliably, quality-controlled, industrial production, represents a challenge, and one that Europe has traditionally often had difficulty meeting. Along with this concern about 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 free state that can interfere with human and animal life. This aspect is not addressed sufficiently, as many others have pointed out before.

Expanding this concern to include the increasing application of nanoparticles directly to the skin, we can recognise a barrier that may arise in future - public hostility based on the discovery, too late, of ill effects on health. This argues for early HSE research and openness.

In terms of costs, the barrier cannot be generalized. As mentioned above, most applications outside of bulk structural composites are relatively price insensitive. 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 in terms of commercialisation within Europe unless there is a shift of 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.

Additionally, support structures need to be in place for solving key technical problems, especially relating to functionalisation. These structures, be they technology transfer services or commercial entities themselves, need to be able to operate on a level (i.e. at a pace and with a level of reliability and control) commensurate with commercial development.

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.

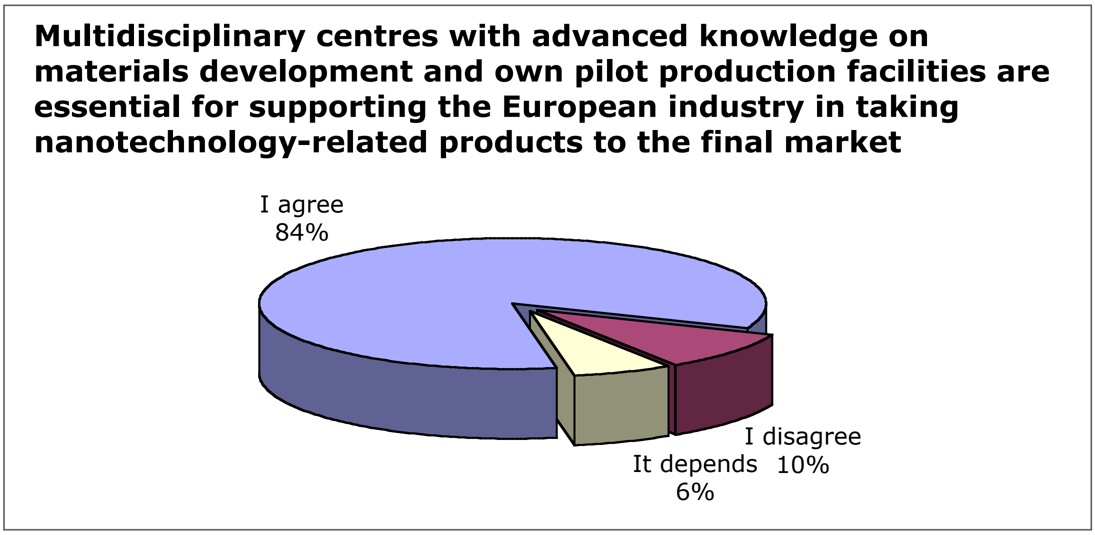
Final recommendations

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, more importantly, an increased reproducibility between batches, which will help to meet strict standards of most demanding application fields. 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 and capabilities 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 either the resources or 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.

This is not to say, however, that there aren't a number of opportunities for start-ups. The creation of nanoparticles with very specialised properties offers opportunities, especially where the end application does not have a requirement for high volumes, such a medical applications. The area of sensors also allows for the creation of devices with novel application spaces. The normal arguments for supporting any technology start-up apply here.

As far as technical focus of basic research goes, the key capabilities that offer the most potential for improvement and resulting application are fine control of nanoscale structure (i.e. size and morphology) and functionalisation. In the former a key capability is the discipline of self-assembly, which will ultimately be the path to the most dramatic new materials. Hierarchical self-assembly represents a powerful new paradigm in which capabilities could be rapidly increased with sufficient backing. Continued improvements in characterisation, imaging etc. are to be welcomed but there does not appear to be a gap in this area. The other vital area in which to strongly support research is that of computer modelling and simulation. The ability to predict properties of complex materials through computer simulations is still in its infancy but will become an enormously powerful tool in future, allowing the bypassing of much laborious experimentation.

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)

We would like to express our special gratitude for the collaboration of **Mr. Paul Holister** in the review of this document.

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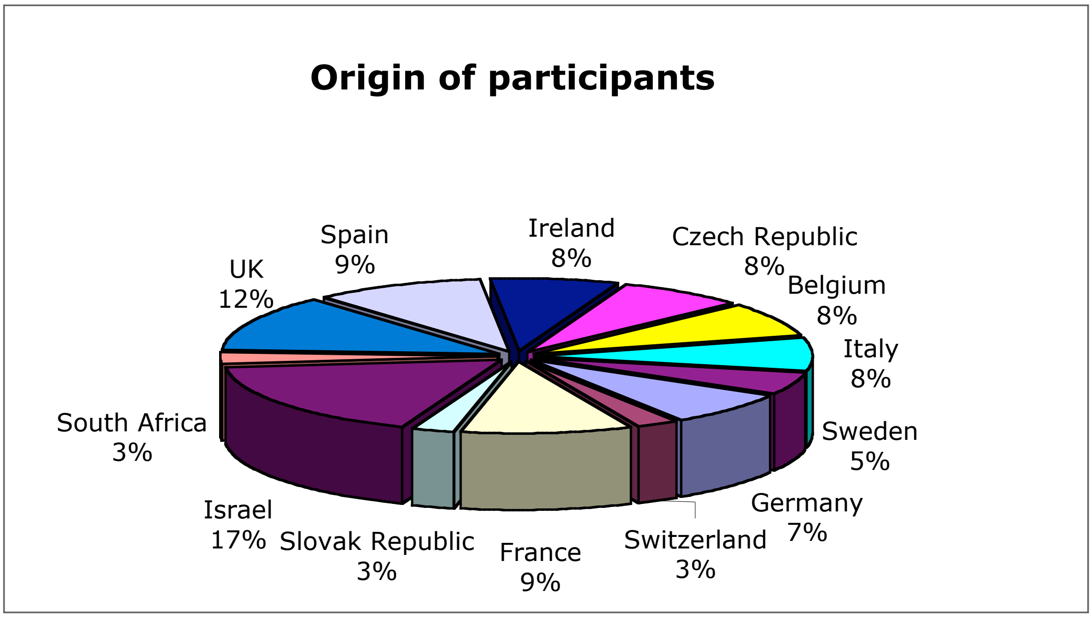
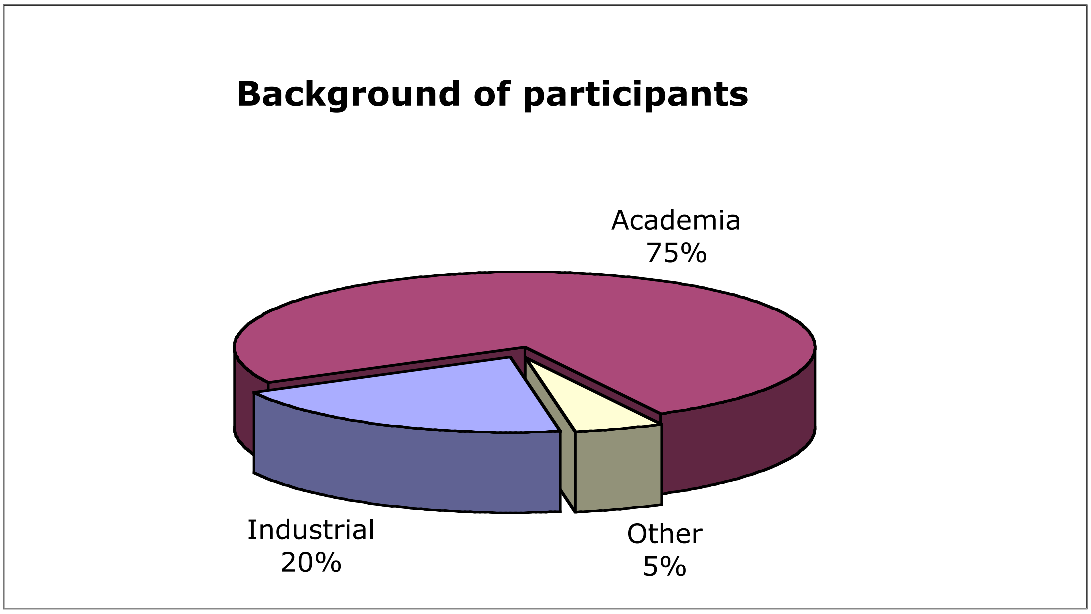

Origin of participants
Spain 9%
Ireland 8%
Czech Republic 8%
UK 12%
Belgium 8%
Italy 8%
South Africa 3%
Sweden 5%
Germany 7%
Israel 17%
Slovak Republic 3%
France 9%
Switzerland 3%


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 latter 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).

Wear-resistant / 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

Barrier 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 allows 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 treatments (e.g. photo-catalyst treatment)

- **Added value of nanoparticles**:

  Higher activity and performance.

- **Most suitable types of nanoparticles**:

  Metal oxide ceramics, TiO_2.

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 particle 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).