Nanomaterials
Guide for the SUDOE space industry

2014

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More information on the CarbonInspired 2.0 is available on the Internet (http://www.carboninspired2.com).

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1. Introduction

1.1 *CarbonInspired 2.0 presentation*

CarbonInspired 2.0 is a transfer network for the integration and dissemination of knowledge about high value added products based on nanoparticles for the SUDOE space industry, stimulating the innovation using nanotechnology and promoting the competitive edge in the region. CarbonInspired 2.0 is co-financed by the O.P. INTERREG IVB SUDOE through ERDF funds and it is mainly aimed at industrial enterprises located within the Southwest European Space.

This space is composed by 30 regions and autonomous cities, extended over an area of 770.120 Km2, which represents the 18.2% of the European Union (EU-27) surface. Its population is 61.3 million inhabitants, which represents the 12.4% of the European Union (EU-27) total population.

The main goals of this Project are:

- Expand and increase the added value demonstration prototypes made on CarbonInspired for automobile and building sectors, amplifying the platform scope to the whole industrial sector on SUDOE space, covering new key technologies based on a larger range of nanoparticles;
- Capitalize the acquired knowledge, focusing the innovation strategy towards the generation of specific and adapted training activities;
- Promote a sustainable and long-lasting transfer network with a structural character that provides support to the enterprises on the creation of new projects and products;
- Improve the financial and competitive situation of the industry in the SUDOE space, as due to the approach of new technologies of high value added for the generation of new products and high value training.

The partnership of the project that has created CarbonInspired 2.0 belongs to five different regions of the SUDOE Space, strategically located to assure the proximity to enterprises and a wide coverage of the network's activities.

Galician Automotive Technology Centre

The Galician Automotive Technological Centre (CTAG) is a technological center created in 2002 by initiative of the Cluster of Galician Automotive enterprises (CEAGA) as a private nonprofit foundation, that aims to improve competitiveness of the companies within the Galician and Spanish country, with the use of new technologies and promoting the development, research and technological innovation. One of the CTAG's most relevant research lines and the one with more international success is the research in new materials, focused on three scientific fields of knowledge: biomaterials, nanomaterials and composites.

With a team of more than 300 engineers and technicians, CTAG is an ideal partner for developing new innovative products using CAD (Computer-Aided Design) product design and CAE (Computer-Aided

Engineering) simulations tools. On validation's side, CTAG is equipped with climatic, vibration & acoustics, fatigue, materials, engine, electronics and ergonomics laboratories fitted with the ultimate testing facilities such as triaxial shakers integrated in acoustic and climatic chambers, a dnamic drive simulator, etc.

Technological Plastic Institute (AIMPLAS)

AIMPLAS is a center for innovation and technology located in Valencia. Since its foundation in 1990 as a non-profit research association, AIMPLAS has been striving to promote direct contact with companies in all sectors linked with the plastic industry in order to detect their needs and determine the required actions to meet them. AIMPLAS provides a personalised and integral solution for companies belonging to the sector through the coordination of technological services (testing and laboratory services) and R&D projects. AIMPLAS also promotes and coordinates the purchase of new technologies, both at equipment and knowledge level, to meet the current and future needs of the sector.

One of its R&D strategies is focused in nanocomposites and materials for the building sector, and this reflects in the fact that 20% of AIMPLAS clients come from this sector. AIMPLAS is a member of the Application of Nanotechnologies in Materials and Products for Construction and Living (RENAC).

AIMPLAS Laboratories have the largest number of ENAC (ISO 17025) testing accreditations for the Plastic Sector in Spain. Since 2000, AIMPLAS has been involved in more than 50 EU projects, 16 of them as coordinators.

University of Aveiro

The University of Aveiro (UA) is a public institution with the mission of formation intervention and development, the research and the cooperation with society. Created in 1973, it soon became one of the most dynamic and innovative universities of the country. The UA is a privileged partner of enterprises and other national and international entities, cooperating with them in different projects and programmes and providing them with important services. Therefore, the UA is a research space where innovative products and solutions are developed to contribute to the advance of science and technology. The Centre for Mechanical Technology and Automation is a research unit of the Mechanical Engineering Department and a member of the Scientific Platform of Applied Nanotechnology of the University of Aveiro (NuaPLACIRIN). Research in TEMA is highly industry focused, and covers different areas such as Fracture Mechanics, Applied Energy Biomechanics, Transportation Technology, Simulation Software Development and Nanotechnology.

Researchers in TEMA have a wide experience in carbon-based nanomaterials, such as carbon nanotubes functionalization and processing, graphene synthesis and functionalization and deposition of nanodiamond films for electronics and tribological applications.

IK4-TEKNIKER

IK4 -TEKNIKER is a technological center located in Eibar, legally constituted as a private not-for-profit foundation. Its mission is to help the industrial sector to increase its innovative capacity by means of generating and applying technology and knowledge in order to be more competitive.

IK4-TEKNIKER is the center for Mecatronics, Manufacturing Technologies and Micro/Nanotechnologies, focusing on the following major areas: Design of Industrial and consumer products; friction, wearing and lubrication-related problem-solving; ICT incorporation, development of new organic, inorganic or hybrid materials and high precision, miniaturization and micro/nanotechnologies. The industrial sectors with which IK4-TEKNIKER works most closely generally come under the wide concepts of manufacturing production, along with other areas that are mainly certain sectors emerging around revolutionary new technologies: machine tools and their accessories, auxiliary automotive industry, energy, aerospace, mechanical capital goods, biomedicine, electronics and ICTs and chemistry.

The researchers of the Surface Chemistry Unit of IK4-TEKNIKER, which belongs to the Nanocit Group, have a wide experience in surface treatments of carbonaceous nanoparticles and its corporation into polymeric matrices for the obtaining of nanocomposites for thermal energy storage, construction and automotive sectors.

Association for the Development of Education and Research (ADERA)

ADERA is a non-profit private organization focusing on teaching and research between universities, research centers and companies in the Aquitaine region. ADERA develops and multiplies links between research and industry and coordinates over thirty technology transfer units providing technological services in various fields of activity. They provide services such as characterizations, trials, tests, control, formulation, consulting, expertise, training, prototyping, pilot lots, industrialization and research & development actions.

Member of the Association of Structures of Research Contracts ASRC (*Association des Structures de Recherche Contractuelle*), ADERA acts on behalf of Research partnership Facilities to public entities and is contracted with the establishment of higher education of Aquitaine. It is the operator of management of the University of Pau and Pays de l'Adour (UPPA, *Université de pau et ds Pays de l'Adour*) and also of the Research and Higher Education Center of Bordeaux (PRES, *Pôle de recherché et d'enseignement supérieur*) within the frame of the new legistative dispositions (law of 18th of April 2006) and regulations (bill of 29th of June 2007).

ADERA develops innovative technologies s for example stimulating the introduction of nanoparticles in different materials or to functionalize plastic matrixes.

1.2 *General Contextualization*

Nanotechnology is the application of scientific knowledge to manipulate and control matter at the nanoscale in order to make use of size- and structure-dependent properties and phenomena, as distinct from those associated with individual atoms or molecules or with bulk materials [1]. This field presents new opportunities for the development of everyday products with enhanced performance, reduced production cost and using less raw material. Fitting neatly with the European Union agenda for smart, sustainable and responsible growth, nanotechnology will potentially help address key societal challenges facing the region, such as the medical needs of an ageing population, more efficient use of resources, developing renewable energy to meet the enhanced commitments on energy efficiency, carbon emissions reduction and climate change [2].

Following the European Commission guidelines, nanotechnology has a key role transversal to several sectors [2]. The semiconductor sector, for example, supports over 100 000 direct jobs in the region (and thousands more, indirectly). Europe must secure its role in other emerging nano-markets as well, taking the opportunity to develop profitable companies in new materials, processing equipment and device technologies. Europe's pharmaceutical industry, for example, stands to benefit from the growth in the nanomedicine sector, particularly in cardiovascular treatments, anti-inflammatories, anti-infective, anti-cancer agents and central nervous system therapeutics. But while the region is at the forefront of research, it risks being usurped by the US, which is taking a lead in the number of patents, with a rapid progress in commercialization.

Nanotechnology also presents an opportunity to rejuvenate traditional industries, like chemicals and catalysts, papermaking and agriculture, bringing innovations in sustainability, processing, energy efficiency, recycling, emissions control and waste treatment. These sectors stand to be transformed, giving Europe a clear margin of difference and added value over the global competition.

Solutions to the most major challenges facing Europe such as a secure affordable energy supply and reduced greenhouse gas emissions could also be provided by nanotechnologies and innovations in existing technologies. According to the International Energy Agency, big investment is needed to overhaul the world's current energy system by 2050 and limit climate change to 2˚C. While this represents an enormous challenge, it also presents a technological opportunity: more efficient solar photovoltaics, wind turbines, energy conversion technologies, energy efficient insulating materials and carbon capture membranes, to name but a few will be required. In the next five to ten years alone, the low-carbon energy market including energy efficient technologies and alternative fuel vehicles, could be worth more than 1 billion euros. As well as the economic opportunity and the environmental imperative, the European Union (EU) also has a legal obligation, having pledged to a 20% reduction in emissions, increase in renewables and improvement in energy efficiency by 2020.

However, there are still question marks about the application of nanoparticles and nanomaterials, mainly because of the lack of information about their properties, applicability, but also due to concerns over possible adverse impacts of nanotechnology on the environment and health.

1.3 *Motivation*

This guide was prepared by the CarbonInspired 2.0 network and intends to make a summary review of nanoparticles and nanomaterials used in several industrial sectors, also showing the prototypes developed by CarbonInspired 2.0 consortium, providing example of practical applications, security issues and market.

The guide begins with the description of main concepts associated Nanotechnology, describing the different definitions of the nano-terminologies. Posteriorly, the guide will show the nanomaterials categorization for industrial applications, presenting the different categories of nanomaterials with industrial applications. Then, chapter 4 will describe the different methods of production and manipulation of nanomaterials, specially the carbon-nanomaterials (carbon nanotubes, graphene). Chapter 5 will show an overview of the current nanotechnology application in the SUDOE space, based on the questionnaires' results, describing the current nanotechnology impact in the SUDOE space industry. Chapter 6 will present a review about the industrial applications of nanotechnology in industry. Chapter 7 will describe the prototypes that are being developed for each partner of the CarbonInspired 2.0 consortium. Lastly, the guide will present the environmental impact and health issues concerning nanotechnology, describing the current major concerns regarding nanotechnology.

2. Nanotechnology concepts

Nanotechnology describes the characterization, fabrication and manipulation of structures, devices or materials that have one or more dimensions that are smaller than 100 nanometers. This area has established itself as a key enabling technology for a wide range of applications, thus becoming a top priority for science and technology policy development, being already used in hundreds of products among the industrial sector, namely, electronic, healthcare, chemical, cosmetics, composites and energy. Therefore, it is essential to provide industry and researchers with suitable tools to assist with the development, application and communication of nanotechnologies [1]. To understand the technological importance of nanotechnology in the industry, it is important in a first phase, to establish the global terminology and definitions related nanotechnology, in order to promote common understanding and consistent usage across the industrial sectors where nanotechnologies are being developed and used [1].

Nowadays, there are still several entities and researchers that don't correctly define the difference between nanoparticle and nanomaterial.

The term nanoparticle doesn't have a unique definition. Using a standard from 2007, nanoparticle is defined as a particle with a nominal diameter (such as geometric, aerodynamic, mobility, projected-area or otherwise) smaller than about one hundred nanometers [3]. On a standard from 2008, nanoparticle is defined as a particle that has all its three dimensions on the order of 100 nm or less, and may be referred as nano-object [4]. Nanoparticles with sizes below 20 nm are those for which the physical properties may vary more drastically in comparison with the conventional size materials. Another common notion is nanostructured nanoparticles, consisting of particles with structural features smaller than 100 nm, which may influence their physical, chemical and/or biological properties [4].

Nanomaterial is a material with any external dimension in the nanoscale or having internal structure or surface structure at the nanoscale [1], which could exhibit novel characteristics compared to the same material without nanoscale features. It may refer to a material with just one dimension at a nanometer scale (as in the case of nanolayers, thin films or surface coatings), two dimensions at the nanoscale (such as nanofibers, nanowires, carbonnanotubes, inorganic nanotubes or biopolymers) and three dimensions at the nanoscale (such as nanoparticles, fullerenes, dendrimers or quantum dots). The hierarchical relationship between many of the above mentioned terms is presented in the following figure 1.

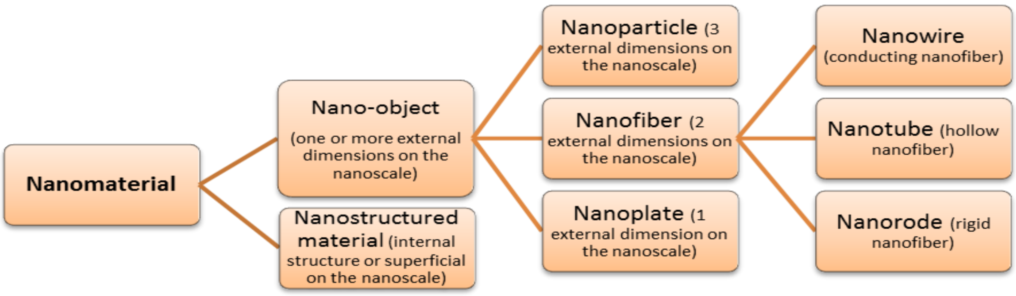


Figure 1 - Hierarchical relationship between terms

There are other core terms and definitions to particles in the field of nanotechnologies, so the guide in table 1 shows a summary of the general terms used in the nanotechnology.

Table 1 - General terms [1, 3, 4]

Term	Definition
Nanoscale	size range from approximately 1 nm to 100 nm. Note 1: Properties that are not extrapolations from a larger size will typically, but not exclusively, be exhibited in this size range. For such properties the size limits are considered approximate. Note 2: Properties that are not extrapolations from a larger size will typically, but not exclusively, be exhibited in this size range. For such properties the size limits are considered approximate.
Nanoscience	study, discovery and understanding of matter in the nanoscale, where size- and structure-dependent properties and phenomena, as distinct from those associated with individual atoms or molecules or with bulk materials, can emerge.
Nano-object	material with one, two or three external dimensions in the nanoscale. Note 1: Generic term for all discrete nanoscale objects.
Nanostructure	composition of inter-related constituent parts, in which one or more of those parts is a nanoscale region. Note 1: A region is defined by a boundary representing a discontinuity in properties.
Nanostructured material	material having internal nanosctructure or surface nanostructure. Note 1: This definition does not exclude the possibility for a nano-object to have internal structure or surface structure. If external dimension(s) are in the nanoscale, the term nano-object is recommended.
Nanoaerosol	aerosol comprised of, or consisting of, nanoparticles and nanostructured particles.
Engineered nanoparticle	nanoparticle intentionally engineered and produced with specific properties.
Engineered nanomaterial	nanomaterial designed for a specific purpose or function.
Manufactured nanomaterial	nanomaterial intentionally produced for commercial purposes to have specific properties or specific composition.
Nanofluid	dilute liquid suspension of nanoparticle with at least one of their main dimensions smaller than 100 nm.

3. Nanomaterials categorization for industrial applications

Nanomaterials cover a heterogeneous range of materials, with a classification by types not completely clear of controversy. So, this guide shows an overview of high potential nanomaterials for industrial applications [5], divided into seven categories, namely:

3.1. Carbon based nanomaterials

3.2. Nanocomposites

3.3. Metals and Alloys

3.4. Biological nanomaterials

3.5. Nanopolymers

3.6. Nanoglasses

3.7. Nanoceramics

3.1. Carbon based nanomaterials

Carbon is known to be the most versatile element that exists on Earth. It is an element that adopts chemical bonds of distinct character and with different hybridizations (sp, sp^2, sp^3), forming until 4 covalent bonds and showing different structures of carbon (allotropes). The best known examples are diamond, graphite and fullerene, showing distinct properties and structures. Carbon nanotubes (CNT, SWCNT, MWCNT), carbon nanofibers (CNF), carbon black, graphene flaks and fullerenes are nanomaterials that have been used in several industrial applications.

Carbon nanotubes (CNTs) were discovered in 1991 by Iijima [6], being a cylindrical carbin molecules with a few nm in diameter and with a length that can reach several microns. Single-walled carbon nanotubes (SWCNTs) can be thought of as layer or carbon atoms wrapped around itself, while multi-walled carbon nanotubes (MWCNT) are as a series of concentric SWCNTs with different diameters, Figure 2.

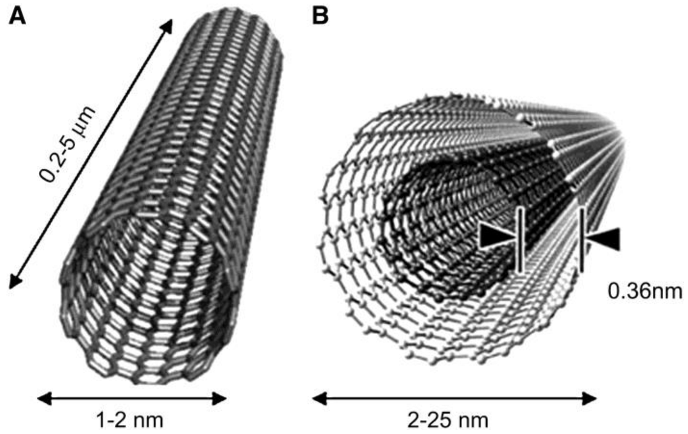


Figure 2 -Conceptual diagram of: (A) single-walled carbon nanotube (SWCNT); (B) multiwalled carbon nanotube (MWCNT)

Fullerenes are composed of an even number of sp^2 hybridized carbon atoms that form 12 pentagonal rings and m hexagonal rings, where m =(n-20)/2 and n is the number of carbon atoms in the molecule. C_{60} is the smallest fullerene that full fills the isolated pentagon rule, which states that the pentagons should be separated from each other by hexagons to avoid the inherent instability associated to fused pentagons. The carbon atoms of C60 form a truncated icosahedron where each atom is placed at a vertex. This geometric arrangement, formed by 12 pentagons and 20 hexagons, makes all carbon atoms equivalent, Figure 3.

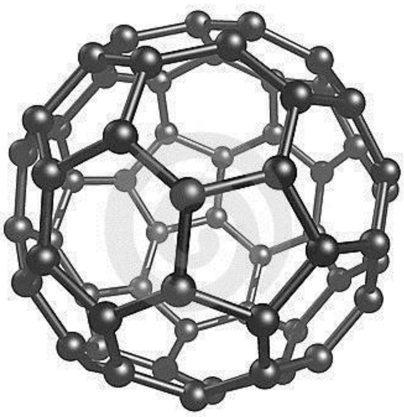


Figure 3 - Molecular structure of the C_{60} buckyball.

Graphene, one of the allotropes (carbon nanotube, fullerene, diamond) of elemental carbon, is a planar monolayer of carbon atoms arranged into a two-dimensional (2D) honeycomb lattice with a carbon–carbon bond length of 0.142 nm [7], as illustrated in Figure 4. Graphene is the material with the highest electrical conductivity known so far. The thermal conductivity of graphene is higher than that of both carbon nanotubes and diamond. Graphene is also, as of 2012, the strongest material known to man. It has a breaking strength about 200 times greater than that of steel.

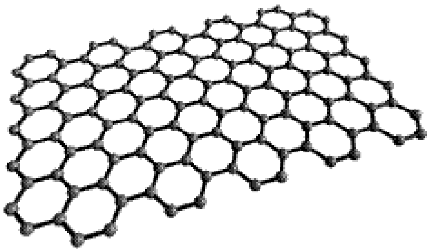


Figure 4 - Schematic of a graphene layer.

Carbon based nanomaterials are most widely mentioned in the field of energy applications and have potential applications in the fields of hydrogen storage and electrical energy storage.

Batteries and capacitors are the most prominent applications in the field of energy storage.

Solar cells and fuel cells are further potential areas of application of carbon based nanomaterial in the field of energy related applications.

Biosensors are the next most common application mentioned in literature having more publications than the wider topic of medical & health. In the category medical & health two applications are specified. It was also recognized that for carbon based nanomaterials the investigation of transplants and tissue engineering is of more interest than drug delivery systems. A further interesting application is its use for filters. Of relatively low interest is the use of carbon based nanomaterials for conductive fillers for compound material.

Table 2 - Physical and applicable properties of different carbon-based materials [8]

	Graphite	Diamond	Fullerene	Carbon nanotubes	Carbon Fiber
Specific gravity (g/cm^3)	2.9-2.3	3.5	1.7	8.0-1.8	1.8-2.1
Electrical conductivity (S/cm)	4000^p 3.3^c	$10^{-2} – 10^{-15}$	10^{-5}	10^2 - 10^6	$10^2 – 10^4$
Electron mobility ($cm^2/V.s$)	$\sim10^4$	1800	0.5-6	10^4-10^6	$10^2 – 10^4$
Thermal conductivity (W/m.K)	298^p 2.2^c	900-2320	0.4	2000-6000	21-180
Coefficient of thermal expansion (K^{-1})	$-1x10^{-6p}$ $2.9x10^{-5c}$	$(1-3)x10^{-6}$	$6.2x10^{-5}$	Negligible	$\sim1x10^{-6}$
Thermal stability in air (˚C)	450-650	<600	<600	>700	500-600
Tensile Modulus (GPa)	1000^p 36.5^c	500-1000	14	1000	100-500
Tensile strength (GPa)	$\sim10^p$ 0.01^c	1.2	N/A	>10	1.0-5.6
Cost/Price (US$/g)	>10	>5	>1	<0.5	>10

3.1.1. Trends and relevant nanomaterials for future industrial applications

The major emphasis in research activity of carbon based nanomaterials in recent years has been in their production and characterization, which is observed in national and EU funded projects and in scientific review articles. In a special edition of Materials Research Society Newsletter (MRS) on April 2004, Prof. M.S. Dresselhaus observed that main emphasis in carbon nanotube research has been in the synthesis towards the well-defined production of nanotubes of precisely determinable structure and, hence, precisely determinable properties. Research has now achieved a good understanding of the structure and many basic properties of Single Wall Nanotubes (SWNT), and their interrelation.

Basic understanding of nanotube growth mechanism however is still lacking. This information is important because of the close dependence of nanotube properties and their geometric structure. This approach is a particular prerequisite for the application of nanotubes in electronic devices.

Major breakthroughs in the production of nanotubes are emerging. For example, Thomas Swann & Co Ltd. has recently begun the commercial production of high purity single and multiwalled nanotubes (MWNT). This breakthrough was achieved as a result of ongoing collaboration with Cambridge University (UK), which solved technical issues in scaling up laboratory procedures for the production of nanotubes. The produced nanotubes have an average diameter of 2 nm and a length of several microns, a purity of 70-90% and costs of about 250 euros/g.

Field emission is seen as one of the most promising applications for carbon based films. The most attractive forms of carbon for this application are carbon nanotubes which are capable of emitting high currents. Controlled deposition of nanotubes on a substrate has recently become possible, but there is a concern for the long term stability of the films. Investigations have shown that the film can degrade due to resistive heating, bombardment from gas molecules by the emitted electrons or arcing. Electrostatic deflection or mechanical stress can also cause a change in the local shape of the emitter and a decrease in its effectiveness.

Applications in nanotube flat panel displays have been anticipated and a demonstration model has indeed been produced by Samsung. Field emitting diode (FED) displays will overcome the drawbacks of liquid crystal flat screens, such as low image quality and a restricted field of view. The viability of nanotubes for such applications are in question, and problems in the correct deposition of the tubes, phosphor lifetime and charging of the spacers also need to be overcome.

There are applications in lighting elements as well as in microwave amplification and early examples are commercially available. Materials for energy storage are a major area of research for carbon nanomaterials. Nanoporous carbon and carbon nanotubes can be considered as the important materials in this field.

The literature search showed most activity for carbon nanotubes concerning the last three years, while interest in nanoparticles and fullerenes are shown to be decreasing. The model category for application of carbon nanomaterials in the literature is energy storage. The low level of activity in fullerene research is reflected in the list of current and recent research projects, where they are not a major subject of investigation.

Other important materials concerning publications are carbon nanofilms and carbon based nanocomposites, with diamond like carbon layers being an important material.

Nanocomposites and nanofilms are very important areas in research and it seems that currently there is a growing interest in developing new materials in this category.

The patent activity shows the most success in research for carbon nanofilms. The ability to produce pure carbon nanomaterials and a growing understanding of the growth processes is leading to an upsurge in the investigation of composite materials as well as an investigation of the effects of incorporating carbon nanomaterials in other materials.

3.2. Nanocomposites

A composite is a material with more than a component. The nanocomposites are a subset of composites which use the unique properties of materials at the nanoscale. The promise of nanocomposites lies in their multifunctionality, the possibility of making unique combinations of properties unachievable with traditional materials. They include control over the distribution in size and dispersion of the nanosize constituents, tailoring and understanding the role of interfaces between structurally or chemically dissimilar phases on bulk properties.

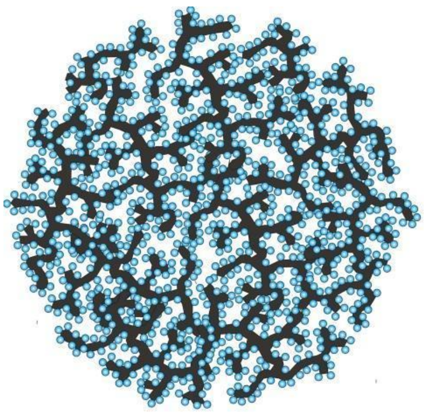


Figure 5 - Scheme of a silicon-carbon nanocomposite granule formed through a hierarchical bottom-up assembly process [9].

For example, polymer/ceramic nanocomposites (polymer matrices filled with ceramic nano-powders) are a promising material for embedded capacitors that combine the high dielectric constant of ceramic powders and the process ability and flexibility of polymers.

Nanocomposite materials can also be obtained from the mixing of carbon nanoparticles and a polymer matrix. Among carbon nanomaterials, the most common are carbon nanotubes. The graphitic properties of CNTs and their large aspect ratio make them a common filler material with enhanced physical properties.

In the following, an overview about the topics of the trends and future applications in this category is given:

The General trends influencing the uptake of nanomaterials in products are:

•Risks of nanoparticles and materials for health and environment and new or adapted norms and regulations;

•Need for surveillance of environmental and security risks;

•Ambient intelligence;

•Ethics of science and technology;

•Investment in technology development.

A more detailed insight into each of these topics is described in the following sections.

3.2.1. Trends in energy applications

Nanotechnology has the potential of significantly reduce the impact of energy production, storage and use. Even if we are still far away from a truly sustainable energy system, the scientific community is looking at a further development of energy nanotechnologies. With the advent of nanomaterials, materials research is expected to play an increasing role in sustainable technologies for energy conversion, storage and savings.

Polymer matrix composites may be applied in energy storage for mobile as well as electrical transport technologies. Bottlenecks (in 2000) were durability, reliability, the absence of recycling facilities.

In energy saving, nanocomposites can be used to improve the features of electrical cables.

There are several energy applications that include electrically conducting composites in fuel cells, batteries and hybrid systems. The polymer itself can be made electrically conductive, or conducting ions can be added to the polymer.

3.2.2 Trends in medical & healthcare applications

Nanocomposites would be a solution to overcome the problems associated to ageing and cost effective healthcare. Therefore, it is important to perform an investment and a study about the general materials used in healthcare, according to legislation.

For example, nano-clay-based composites may be applied in medical applications such as protein delivery, as well the core-shell materials. The hydroxyapatite, calcium carbonate and ceramics are materials applied as nanocomposites for tissue engineering, active and passive implants.

In sum, nanocomposites are already applied in several medical applications such as imaging, diseases diagnostics, biomimetic and biological materials, dental applications and under skin nanosensors.

3.2.3 Trends in materials for automotive and aerospace applications

The use of nanocomposites in vehicle parts and systems is expected to improve manufacturing speed, enhance environmental and thermal stability, promote recycling, and reduce weight.

Nanocomposites are already applied in several applications as an improvement of light and material characteristics in vehicles, transparency windshield, improvement in security, lacquers among others.

For example, General Motors R&D and Montell USA have developed thermoplastic olefin (TPO) clay nanocomposites with reduced weight and good dimensional stability for exterior automotive applications. The Audi replaced the ventilator of interior heating of A3, made from conventional painted thermoplastic (Acrylonitrile butadiene styrene, ABS) by nanocomposites, obtaining anti-scratch components with a more luxurious look. Renault is adding CNTs to their thermoplastics (polypropylene, PP) to produce the fenders of Mégane and Clio Sport, which can be electrostatically painted, improving the protection against scratches. Nanoclay-filled composites have been introduced by General Motors as body parts of the GMC Hummer H2 and Chevrolet Astro van. Honda Acura TL's back seats are also made of Nanoclay-filled composite.

Picture 6 shows the timeline for the commercialization of products based in nanocomposites by automotive players.

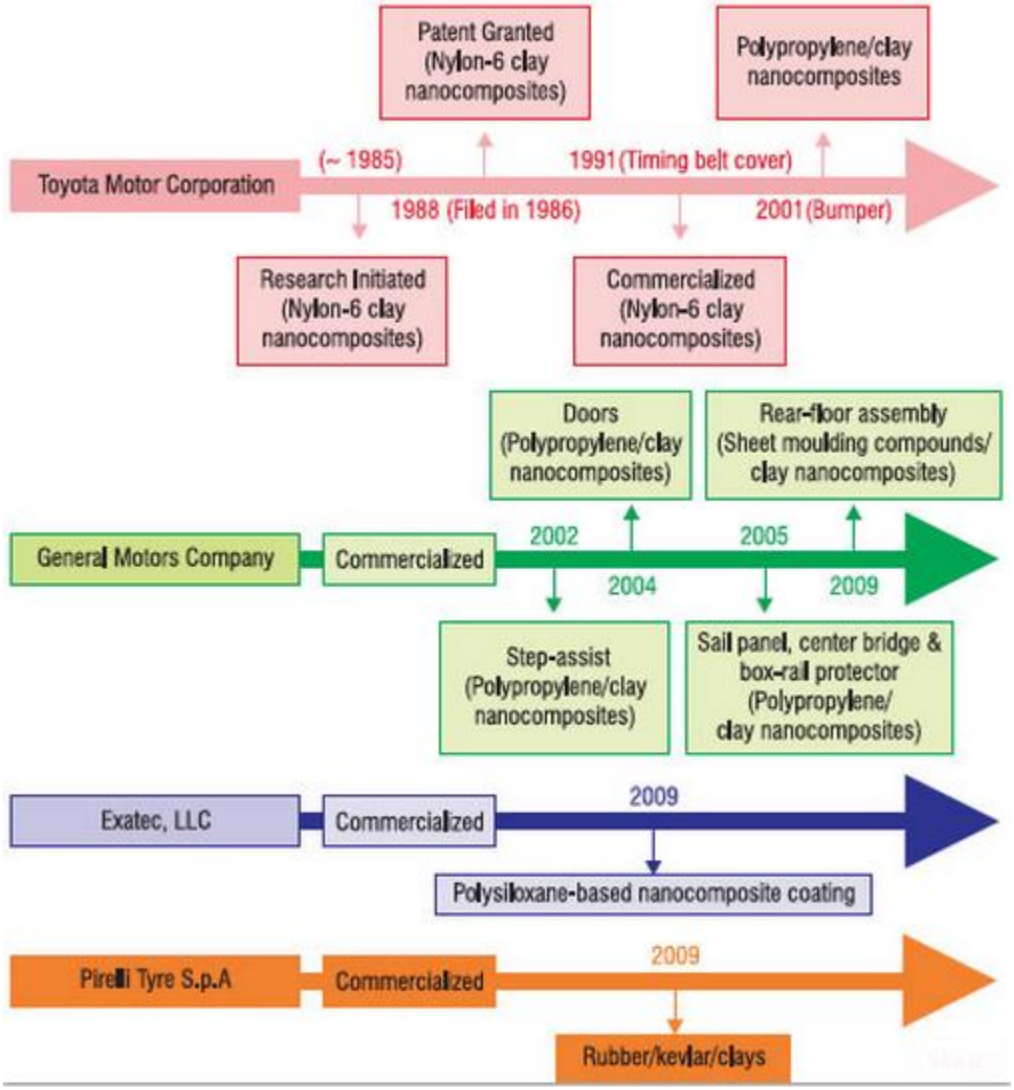


Figure 6 - Timeline for the commercialization of products by automotive players [10].

3.2.4 General trends in materials

The experimental work in nanocomposites area has shown that almost all types and classes of nanocomposites have new and improved properties, when compared with equivalent composite materials, that can decrease the costs of production.

The nanocomposites of polymer/ceramic material (polymeric matrixes filled with ceramic nanoparticles) are a promising material to produce incorporated capacitors in plastic materials, because these materials combine the high dielectric constant of ceramic material with the flexibility of processing of polymers. The nanocomposites of polymer/metallic material (polymeric matrixes with dispersed metallic nanoparticles) combine performance and flexibility of processing.

It is also possible to obtain nanocomposite materials through of the mix of carbon nanoparticles with a polymeric matrix. The carbon nanotubes are more common, due to their graphitic properties and their high aspect ratio, being very used as filling material.

3.2.5 List of relevant nanomaterials for future industrial applications

The materials which are most promising for relevant applications are:

Matrix materials filled with nanoparticles or fibres:

1) Polymer matrix nanocomposites

- Polymer matrix filled with nanoclays:

  o *POSS in polymers*

  o *Rubber with clay*

  o *Polyolefin with layered clays*

  o *Hydrophobic fumed silica*

- Polymer nanocomposite matrix filled with normal fibres

- Polymer / resin / textile matrix filled with carbon nanotubes (coating and bulk Polymer matrix filled with metal and ceramic nanoparticles:

  o *Hydrated Alumina in Polymer*

2) Ceramic matrix nanocomposites

- Ceramic matrix filled with nanocarbon / aquasomes

- Ceramic matrix nanocomposites for bone

- Zr or Al based ceramic nanocomposites

- Ceramic matrix filled with nanopolymer

3) Metal matrix filled with nanopolymer composites

- Nano-nanocomposites:

o *Quantum dots*

o *Core shell nanoparticles (including gold shell nanoparticles)*

o *Carbon - nanoceramic coating*

- *Carbon nanotube – polymer nano-nanocomposites*
- *Textile – nanoceramic or ceramic – polymer nano-nanocomposites*
- *Metal – ceramic nano-nanocomposites*
- *DNA-linked nanoparticles / polymer-DNA complexes*
- *Dendrimer nanocomposites*
- *Cerium-oxide nanocomposites*
- *Polymer-carbon nanotubes-nanoclay particles nano-nanocomposites*

3.3. Metals and Alloys

Metals and Alloys are a class of nanomaterials that incorporate gold (Au), silver (Ag), platinum (Pt) and palladium (Pd) alloy, copper (Cu) nanopowders, iron (Fe) nanoparticles, nickel (Ni), cobalt (Co), aluminium (Al), zinc (Zn), manganese (Mn), molybdenum (Mo), tungsten (W), lanthanum (La), lithium (Li), rhodium (Rh), among others.

Statistical analysis of collected data indicates the following main trends in research and future applications:

•Application of metal nanoparticles, in particular silver (antibacterial) and other noble metals especially in health protection, but also some special applications;

•Magnetic iron based alloys: reduced losses in energy transmission due to the small size of the grains compared to the magnetic domain size and also by interface effects on magnetic properties;

•Structural applications, with lighter metals and superior mechanical properties: Al and Mg alloys, Ti and Ti alloys – radical improvement of various kinds of mechanical properties caused by a change of deformation mechanism compared to conventional materials;

•Coatings: radically improved tribological properties; higher wear resistance, less friction, better corrosion resistance, sustainable production process, etc. The improved properties are connected with uniformity of the structure when it is regarded in the micro-scale;

•Mg and its alloys as a material for hydrogen storage: the promising properties are connected with high diffusion rates for hydrogen and increased solubility limits in the nanoscale material.

The nanostructured and nanocrystalline metal materials offer radical improvements of properties or new functions that can play a crucial role for SMEs searching for innovative solutions and high competitiveness of the products they offer. This is in some respect reflected by the increasing number of patents in the recent years. The fast increase of patents concerns nano-powders, mainly of noble metals as well as aluminium. The powders are suspended in a fluid or another material. In this case the most important property is the high contribution of surfaces of the particle to the properties or function of the material they are embedded in. This results in a high material activity which could be used as catalyst or as source of ions for antibacterial properties, etc. The second rapidly developing field concerns light metals with improved mechanical properties. Here the specific mechanical properties of nanostructured materials are: high strength (that for some special methods of production can be combined with ductility), high fatigue limits, elevated temperature strength, corrosion or wear resistance, etc.

Interestingly however, the number of patents in this field is not as high as it would result from the number of papers. Much research is focused on magnetic materials, where for very small grain size, the material may become magnetically soft, thus a decrease of energy losses when it is applied as a transformer core or in other applications with oscillating magnetic fields is considered. This leads to energy saving during energy transmission.

The number of patent and papers concerning bulk metals and nanopowders is approximately identical but bulk metals are divided into magnetic materials and structural materials whereas the application of nanopowders is more strongly focused on the antibacterial and catalytic activity. Also the review of industrial applications shows some stronger highlights on the application of nanopowders.

On the other hand, it seems that few research projects in the searched data bases are concerned with metallic nanoparticles with applications in medicine, contrary to the number of patents.

3.3.1. Trends for industrial applications

The forecasts see wide application of metals and alloys in microsystems, including microelectromechanical systems (MEMS), bioMEMS, nanoelectromechanical systems (NEMS), optical, electronic, electrochemical microsystems, for multifunctional devices and systems for chemical and biological analysis/detection, drug delivery/discovery, tissue engineering, chemical and materials synthesis, energy conversion and storage. Here production of microparts (microgear, microsprings, complex shapes) from nano-metals will be a critical success factor.

For example, the figure 7 shows a nano-biosensor containing silicon nanowires used for diagnosis of diseases and monitoring of therapies.

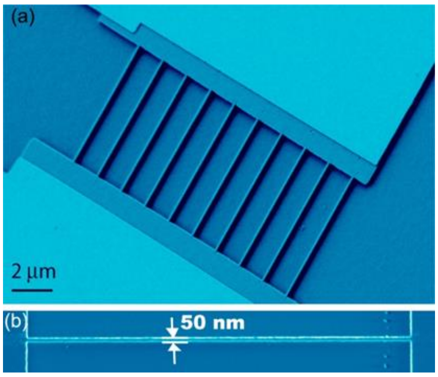


Figure 7 - Scanning electron micrograph with the functional part of a nano-biosensor containing silicon nanowires [11].

As far as surface treatment, wear and corrosion resistant coatings applied by electrodeposition for instance to repair heat-exchangers, decreased wear and friction. Besides coating, the surface treatment of metal parts to produce a nanostructured layer on their surface will play an important role. Various methods of surface treatment (which can be also implemented by SMEs) can be seen here.

In summary, according to the contribution of experts, nanometals have an enormous potential for applications in electronics, construction, power transformation, energy storage, telecommunications, information technology, medicine, catalysis and environment protection, with high possible impact in the areas of technology related to energy, health and materials.

3.3.2. Relevant nanomaterials for future industrial applications

In the category "metals" the following nanomaterials are most promising for future applications in which two subcategories are defined:

1) **Bulk nanostructured metals and powders:**

- *Titanium (Ti)*
- *Titanium Aluminium alloy (Ti-Al)*
- *Ti-transition metals alloy (Fe or Ni or Cu)*
- *Magnesium Nickel alloy (Mg-Ni)*
- *Fe-Cu-Nb-Si-B alloy*
- *Fe-transition metal alloy (Co, Ni, Cr, Cu, Zr)*
- *Al-transition metal alloy (Fe, Ni, Ti, Zr)*
- *Al, Mg, Al-Mg alloy*

2) **Nanopowders of noble metals:**

- *Silver (Ag)*
- *Gold (Au)*
- *Platinum (Pt)*
- *Palladium (Pd)*

3.4. Biological Nanomaterials

Applications of biological nanomaterials were searched for by means of a patent search on biological nanomaterials. Most of the patents can be grouped into the following groups:

•Self-assembling systems

o *Peptides*

o *DNA*

o *Proteins*

•Actuators

•Motors

•Sensors

•Drug delivery

•Specific filtration

•Memory devices

Almost half of the patents focused on different immobilization strategies rather than actual self-assembling based on the properties of the biomolecule. Three different strategies can be categorized as follows:

1. Non-organized surface + self-assembling biomolecule;

2. Organized surface + biomolecule;

3. Self-assembling biomolecule + inorganic material.

Biomolecules can be peptides, proteins, DNA, lipids or combinations between them. For example, single stranded DNA can be used as a tag to immobilize peptides and proteins in an ordered array format to a oligonucleotide coated immobilization surfaces. These surfaces can be 2D surfaces, 3D particles or beads made of various materials, e.g. glass, silica, polymers and metals. Site-directed, ordered immobilization is advantageous in biosensors, micro/nanoarrays, biochips and nano-composite materials which can be used in applications such as detection and quantification of genes, diagnostics of various compounds, assaying protein target interactions, proteomics, drug development and screening or the use of catalytic enzymes. Immobilized biomolecules can be used to modify the properties of the surface or to introduce an added functionality as binding activity.

Most of the examples in the literature deal with 2D crystallization and 3D self-assembly of proteins and peptides making lattices. Such 3D constructions can be used as structural or functional elements such as molecular sieves or to be used for drug delivery. Peptides can form different types of nanostructures such as nanopillars, -crystals, -rods, -wires, -tubes, - filaments, -fibers and -shells. The self-assembling protein or peptide can be inserted as binding activity for a semi-conducting material or an antigenic determinant for immunization purposes. Possible applications for semi-conducting materials might be optical detectors, biological sensors, well-ordered liquid crystal displays, light-emitting displays and nanometer scale computer components. Nucleic acid molecules can be used to form nanoscale devices e.g. resistors, capacitors, inducers, transistors, wires, switches, memory devices and nanoscale containers for drug or other materials. Also nanoscale filters and molecular sieves can be constructed. In addition 3D assemblies of surfactants or lipids can be used to deliver biomolecules across cell membranes.

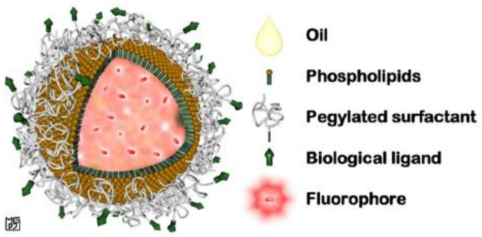
3.4.1. Trends for biological nanomaterials

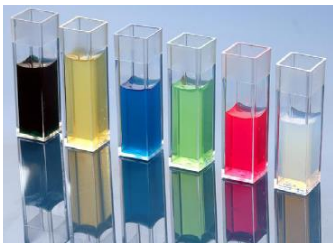
One of the main trends for biological molecules is the use of molecular self as a mean to manufacture nanostructures for various nanodevices. A wide magnitude of different materials and approaches are currently being investigated. However, it seems that bioanalytical applications are relatively developed. This is perhaps due to the large effort on biosensors that has been going on for a few decades and that is now getting a new boost from nanotechnology.

The use of biomolecules in the energy sector has so far been rather limited. Although there are in principle possibilities for applications (such as using biological light-harvesting complexes for solar energy capture), so far, the formats are not very compatible. If such applications were to be made, it is very likely that they would heavily rely on biological nanomaterials. Lately there has been some focus on fuel cells for using chemical redox reactions for production of electricity. Some success has been reported for such devices that include biomolecules. In this case, it can be seen that the performance of such devices might be boosted by nanostructured biomaterials.

Most of the applications are related to health & medical areas. Typical examples include arrays (chips) for large scale DNA or protein screening. Drug delivery is another deeply studied example. Various self-assembled peptide structures can be designed to release compounds under specific conditions. In the sector “materials”**,** the self-assembling properties of the biomolecules are mainly used.

CEA-Leti, a company that helps bridge the gap between research and production of nanotechnologies, has transferred its patented Lipidots® Nanovector technology to Capsum Cosmetics [12]. Lipidots (Figure 8a) correspond to a lipid-based nanoparticle with an oily core, a monolayer of phospholipids and a pegylated coating. One of the advantages with this new technology is the manufacturing process behind this – it’s simple, efficient, and allows for a high and clean turnover of the product without the use of any solvents, making Lipidots® a key angle for pharmaceutical and cosmetics companies to help enhance the way their products can be delivered [12]. Lipidots® will be important for drugs that are not easily soluble; to provide a delivery system for highly potent drugs ensuring that the active agent reacts with specified tissues and not surrounding healthy tissue in the body; and for drugs that will fall soon out of patent (i.e., to provide a patent extension) [12]. Cosmetic application is just one of the major investments for Lipidots®; this innovative technology transfer method is becoming a key component to boosting pre-clinical development of LipImage 851TM, a liver cancer detection system [12]. The Lipidots® technology will help transport this liver cancer agent to targeted malignant cells (focusing on the early stages of liver cancer). Additional application for Lipidots® includes in vitro diagnostics, photo therapy, fluorescence imaging, and vaccination (Figure 8b) [12].





Examples include biological arrays for formation of 2D organization of semiconductor nanoparticles. Self-assembly is seen as a route to designing materials with tailored properties, such as responsive materials. The biological recognition of various molecules (such as the antibody antigen interaction) can be used to build nanomaterials with specific permeation selectivity. Several of the biological materials that have interesting properties are nanostructured composites that involve biomineralization. Examples of materials that scientists are trying to mimic include bone, tooth or mollusk shells.

For materials where mechanical action is desired, many groups have been studying biological molecular machines. Biomolecular motors are envisioned to be able to be part of materials in such roles as: molecular assembly lines, construction of nano-networks or as a part of adaptive materials. Some of the possibilities that are being pointed out are based on proteins, such as:

- actin networks;
- kinesin motors;
- myosin motors;
- ATP synthease motors.

3.4.2. List of the relevant biological nanomaterials for industrial applications

PROTEINS-based materials

- Self-assembling materials:
- ➢ Proteins that form 2D structures:
    - o *S-layer protein*
    - o *Hydrophobins*
    - o *Chaperones*
- ➢ Self-assembly based on avidin-biotin interactions, barnase-barstar interaction etc..

- ➢ Nanocontainers

- ● Functional protein units:
- ➢ Bacteriorhodopsin

- ➢ Nanopores

- ➢ Proteins for molecular recognition

    - o *antibodies, single chain antibodies*

    - o *Specific molecular recognition*

    - o *antifreeze protein*

- ➢ Conformation switching proteins

- o *periplasmic carbohydrate binding protein, calmodulin*

- ➢ Biological nano-motors

- o *Kinesin*

- o *Actin-myosin*

- o *DNA interacting enzymes*

- o *ATP synthase*

PEPTIDES

- ● Peptide-based self-assembling materials:
- ➢ Nanostructured peptides (nanopillars, -crystals, -rods, -wires, -tubes, - filaments, -fibers and -shells)

- ➢ Nanocontainers

- ➢ metallic nanowire

- ➢ peptides templates for silicon particle formation

- ● Peptides for molecular recognition
- ➢ peptides recognizing metal surfaces, carbon nanotubes

- ● Template forming peptides
- ➢ Metal nanowires, silicon particles

CARBOHYDRATES

- ● crystalline cellulose

- Lectins for molecular recognition

VIRUS PARTICLES

- structured materials using virus as structural components

LIPIDS

- Nanocontainers and Liposomes
- lipid bilayers as support or template for self-assembly

DNA

- 2D DNA lattices
- 3D cages and networks
- Hybrid structures of DNA and protein
- DNA templates:
  - *Nanowires*
  - *Nanomechanical DNA device*

COMPOSITES

o Magnetsomes

o ferritin

o Ca-biomolecule composites

3.5. Nanopolymers

Nowadays, the polymers are applied in drugs, packaging, carriers with the goal to replace other materials used by Humankind. Nanotechnology is already making a major impact on new product introductions throughout the world, in many industry sectors. Many of these new products are based on the material property changes that may be achieved by incorporation of ingredients, at the nanoscale, into the polymeric system. When nanoparticle becomes a great topic in enhancing polymer's mechanical property, it is a natural combination into microcellular foam.

Most of nanopolymers are at an early stage of market development described applications are often still at research and development stage.

3.5.1. Trends for nanopolymers

Nanoparticles could be an ideal nucleating agent and even dispersion can generate interfacial volume as nucleus for microcellular morphology. This nano-microcellular polymer could be a great product with an impressive performance/weight ratio; excellent physical, mechanical and thermal properties. The nanopolymers are one of the most important nanomaterial for the future. Nanopolymers have applications in medicine, energy and materials science.

The nanofibres, hollow nanofibres, core–shell nanofibres, and nanorods or nanotubes produced have a great potential for a broad range of applications including homogeneous and heterogeneous catalysis, sensors, filter applications, and optoelectronics. The Table 3 shows an overview of polymer nanofiber applications.

Table 3 - Overview of polymer nanofiber applications [13].

Nanosensor	Military Protection clothing	Life science applications	Cosmetic skin mask	Filter media	Tissue engineering scaffolding	Other industrial applications
Thermal	Minimal impedance clothing	Drug delivery carrier	Skin cleaning	Liquid filtration	Menbranes for skin	Micro/Nano electronic devices
Piezoelectric	Trapping aerosols	Hemostatic devices	Skin healing	Gas filtration	Tubes for blood vessels	Electrostatic dissipation
Biochemical	Anti-bio-chemical gases	Wound dressing	Skin therapy	Molecule Filtration	3D scaffolds for bone and cartilage regenerations	Electromagnetic interference shielding
Florescence chemical						Photovoltaic devices (nano-solar cell) LCD devices Ultra-lightweight spacecraft materials High eficiente and functional catalysis

Polymer nanoparticles are nanoscale polymeric units, being used in drug delivery systems or as filler material in matrix composites. Core shell fibers of nano particles with fluid cores and solid shells can be used to entrap biological objects such as proteins, viruses or bacteria in conditions which do not affect their functions. Dendrimers are highly branched molecules similar to polymers whose size and shape can be precisely controlled, exhibiting excellent properties such as low polydispersity index, high molecular mass, hydrophobic core and hydrophilic periphery. Dendrimers have been explored as drug delivery vehicles by various routes of drug administration and for other biomedical applications.

3.5.2. List of relevant nanopolymers for industrial applications

Nanopolymers are a new area in the materials science, in which it is difficult to make a material classification, the next list is a primary approximation.

•SELF-ASSEMBLED STRUCTURES:

o Lamellar

o Lamellar-within-spherical

o Lamellar-within-cylinder

o Cylinder-within-lamellar

o Spherical-within-lamellar

o Construction units types for self-assembly structures

•NON SELF-ASSEMBLED STRUCTURES:

o Dendrimers

o Hyperbranched polymers

o Polymer brushes

o Nanofibers

o Polyphosphazene

o Polymeric nanotubes

o Nanocapsules

- ➢ Eudragit: poly (methylacrylic acid-co-methylmethacrylate)
- ➢ P(MAA-g-EG): poly (methacrylic-g-ethylene glycol)
- ➢ HPMC-AS: hydroxypropylmethylcellulose acetate succinate

o Porous materials

- ➢ Polystyrene-block-poly (4-vinylpyridine) (PS-block-P4VP)
- ➢ Poly(-methylstyrene)-block-poly(2-vinylpyridine) (PMS-b-P2VP)
- ➢ Poly (2-vinylpyridine) (PVP)
- ➢ PS-PVP hybrid nanolayers

o Nano-objects

•OBTAINING NANOSTRUCTURES ON POLYMERIC SURFACES: NANOLITHOGRAPHY

o Nanoimprint

o *Soft lithography*

o *Electron-beam lithography*

o *Dip-pen lithography*

3.6. Nanoglasses

Nano- and photonics technologies hold the potential for highly efficient communication and information systems of the future, both for defense and commercial applications. Nano-optics, a newly emerged combination of these technologies, opens new horizons in photonics, with a plethora of new phenomena, new materials, new designs and new attractive applications. Many materials- and performance-related problems in photonics engineering that cannot be solved today, because of the limitations due to the properties of the natural materials used, have a potential to be successfully solved tomorrow, owing to the emergence of, and recent progress in, nanoscience, nanomaterials and nanotechnologies.

Optical technology is Olympus's core technology that has been successfully incorporated in digital cameras, binoculars, endoscopes, optical disks, and a number of other products. Concurrently, Olympus has built up enormous knowledge and experience in nanoprecision processing and measuring technology for the processing of high-performance lenses. Other innovations based on MEMS (micro-electrical-mechanical systems) include devices for measuring at the molecular level and scanning mirrors with nanopositioning capability. This technology has proven successful in the use of tissue samples, DNA and genetic material in nanobiology. Bringing together leading-edge research in Japan and abroad, fusing nanooptics, nanomaterials, and nanodevices to create nanostructures with new functions and then researching how they can be applied in biosensing devices.

Current devices are the initial applications of Single Open Endeds (SOEs), but the possibilities are expanding in several directions. SOE-based building-block functionality will be introduced both as chips and as packaged devices. Demonstrated SOE functionality spans polarizers, polarization beam splitters/combiners, filters, photodetectors and photonic bandgap devices. Dynamic control for switching, attenuation and tuning is also possible.

Monolithic integration of SOEs can be achieved by stacking SOE layers to create aggregated optical effects. Nano-imprint lithography allows direct layering on of SOEs without resorting to lamination techniques. Combining SOEs with optically active layers allows optical control circuits to be built, resulting in complex optical components "on-a-chip." Multilayer SOE integration has already been demonstrated by combining filters with photodetector arrays to create dynamic optical feedback loops.

Because SOEs are self-compatible and manufactured via wafer-scale manufacturing with relatively minor differences from device to device, the means exist to implement them.

Near-field optical microscopy shows great promise for achieving subwavelength optical resolution. Theoretical models of NSOM images are essential to utilize NSOM for nanoscale metrology. Computational tools to model and interpret NSOM images, including finite difference and element approaches, mode expansion techniques and scattering techniques, will be integrated into a general computational package to best exploit each technique.

Specific applications will include tip design and optimization, scanning of evanescent fields by small metal tips, diagnostic imaging for optical waveguides, and local nanoscale engineering of optical waveguides.

Nano-optics modelling of optical nanostructures will continue to identify and engineer optimal structures for use in quantum computing and local, intradevice optical communication. Nanotechonology materials, like glasses, crystals, and amorphous have a direct application in optics. The optical response of these materials in nanostructure format has contributed to constitute the nanooptics. Nano-optics is a branch of optics that describes the phenomena that occur when light interacts with nanostructures. That is, nanostructures are pieces of matter that are either very small in themselves or exhibit features of sub-wavelength dimensions down to a few nanometres. Small particles, sharp tips, single molecules or atoms, and semiconductor quantum dots are just a few examples that fall into this category. A major finding of nano-optics is that strongly enhanced and spatially confined optical fields can exist under certain conditions in the vicinity of nano-matter. The understanding and exploitation of such effects will have a major impact on future optical technology because it will strongly influence such important fields as high-resolution optical microscopy, optical data storage, nonlinear optics and optical communication.

The recent progress in nano-optics and nano-photonics is based strongly on the ever-improving understanding of how to tune the properties of nano-matter, i.e. its geometrical shape and material composition, and how to manipulate the incident light in the right way to achieve desired effects, such as extreme local-field enhancement or control of the flux of light at sub-wavelength dimensions. Concomitantly, modern techniques for material processing on the nanometre scale, such as high-resolution focused-on-beam milling, become more widely available, and novel, more complex (prototype) material structures can be created. A number of papers on this subjet deal with this task of getting better control over nano-optical fields.

3.6.1. Trends for nanoglasses

The current trend towards nanoscience and nanotechnology makes it necessary to address the key issues of optics on the nanometer scale. The interaction of light with matter renders unique information about the structural and dynamical properties of matter and is of great importance for the study of biological and solid-state nanostructures. Near-field optics and nano-optics in general address the key issues of optics on the nanometer scale covering technology and basic sciences. The technological side is represented by topics such as nanolithography and high-density optical data storage, whereas topics like atom-photon interactions in the optical near-field are representative of the basic sciences side. Of great importance are optical microscopy and spectroscopy which aim at selectively interacting with nanostructures and probing their physical properties on a nanometer scale.

Three branches can be considered:

•Characterization of optical devices to study the optical properties of new materials (near-field microscopes: AFM, confocal, optical near-field microscopy, tunnel microscopy);

•Production of nanostructures by optical methods (nanolithography);

•Treatment of materials by laser tools (ablation process).

Characterization of optical devices could be tunneling-electron luminescence microscopy for multifuncional and real-space characterization of semiconductor nanostructures. Time - resolved luminescence microscopy offers many advantages over conventional transmission and fluorescence microscopy. As well as the improved sensitivity inherent in luminescence microscopy, time-resolution offers the possibility of gating out short-lived fluorescence emanating from biological chromophores.

Nanolithography for production methods is the most extended technology to make nanostructured materials. Today, there are two main technologies: ion etching and electron beam, but others, like Extreme Ultraviolet Lithography (EUVL) and evanescence field based methods, are now being considered as very good alternatives in the lithography area. EUVL uses extreme ultraviolet radiation with a wavelength in the range of 10 – 14 nm, to carry out protecting imaging. Currently, and for the last several decades, optical projection lithographic techniques used in the high-volume manufacture of integrated circuits.

Evanescence waves are used in lithography to make relief in many materials, it uses the total reflation situation to write at nanometer scale.

In the material treatment the surface technology with coatings configurations has an extreme relevance. New materials are developed to ensure the aspect-ratio configuration at the nanometer scale when we would like to write on it with lithographic techniques. Laser ablation is a promising tool to create micro and nano-structures in polymers. Due to several drawbacks (i.e. high ablation thresholds, low ablation rates) it is only used in a limited number of industrial applications (i.e. drilling of nozzles for ink-jet printers and drilling of holes for multi-chip modules).

Other emergent technologies found are Dip-Pen Lithography, using a Tip to write nanostructured motives, and hidrofobic materials. Both can be used in microfluidic and interface surfaces for massive optical devices (mirrors, architecture, lighting, etc.)

3.6.2. List of relevant nanoglasses for future industrial applications

The following nano-optical materials are taken into consideration:

•Metallic glasses

•Electrochromics

•Nano-Resist for lithographic technologies

•Nanoporous glasses

o *Micropores of less than 2 nm in diameter*

o *Mesopores between 2 and 50 nm*

- *o Macropores of greater than 50 nm*

- •Nanochannel glass materials

- •Photonic glasses

3.7. Nanoceramics

Although products related to nanotechnology are already on the market (ceramics made of oxide nanomaterials, light filter substances, effect pigments, coatings, data storage layers, etc.), most areas are still in a research stage. Still the market qualification carried out by analysts and experts has been vague and full of discrepancies. However, market-relevant applications in the fields of optics, precision engineering, analytics, chemistry, automotive and mechanical engineering, materials management and medical engineering, pharmaceutics and biology are anticipated.

Analysis of the state of the art of ceramics, identification of advantages and comparison of the various production methods for nanopowders allow the conclusion to be made that for nanopowders, realistic market opportunities exist primarily in those areas where materials with novel property combinations or at least with remarkably improved tribological, mechanical or corrosion properties can be produced. Realization of the market potential will only be possible if the following basic prerequisites are met:

- Reproducible powders having constant properties and acceptable prices must be able to be produced on both small and commercial scales;

- Powder processing, structural formation and materials production must be controllable.

The analysis of worldwide research activities has shown that both public funding of basic research and specific application-related research and development for the manufacture of marketable products and venture capital funds for the establishment of startups and spinoffs are needed. It is also recognized that targeted public funding and raising of the budget for ceramic nanotechnology - especially in the USA, Europe and Japan - allow a solid foundation for future competitiveness to be laid, since competitiveness and the technological basis required for it hinge upon the availability of capital and human resources.

Significant advances in almost every area of technology can only be made if ever smaller structures and increasingly complex systems composed of the widest possible range of materials are available. Experts and analysts see particularly great potential in high performance and functional ceramics, due in part to the high annual growth rates of these materials. For expansion and opening up of new application fields in the future, these ceramics will have to exhibit novel property profiles. Through the use of nanopowders, the current disadvantages of ceramics - especially the high brittleness (low fracture toughness) - that are generally persistent at high temperatures and which result in low defect tolerance of ceramic materials and parts can be minimized.

Emphasis was placed on nanoscale nonoxide ceramics and nonoxide nanopowders, which, contrary to oxide nanopowders, are not currently available on a commercial scale. The reasons lie especially in the need of:

- Low-cost production method for preparing deagglomerated powder of constant quality and particle size distribution (a significant barrier to further development in many areas);
- Adaptation, redesign and development of innovative production technologies;
- Continuous cooperation between all links in the value-added chain, i.e., from raw material suppliers through powder, ceramic and parts manufacturers to the user, as well as the technology providers and research institutes.

Future samples key parts for the work with nonoxides are a ball bearing for silicon nitride and a drawing die for titanium carbonitride. The market analyses, research and expert interviews revealed the following trends, especially for ceramics and hard materials:

- Due to relatively high powder prices and processing difficulties, applications for nanopowders are focused primarily on films or components of composite materials, in which the nanopowders produce specific effects. Nevertheless, apart from being used in powder form as fillers, thickening agents, insulation materials and support materials in pharmaceutics and medicine, for example, ultrafine particles are increasingly being used in the form of compact ceramic materials. Applications are not oriented solely towards thin and ultrathin films - they are also aimed at sensor materials, membranes and catalysts, transparent Al_2O_3 ceramics and superplastic ceramics, to name a few. Nanopowders can furthermore play a role in transparent polymers as UV absorbers or diffusion barriers, or they can be used to attain specific magnetic or dielectric properties in polymers.

- Increasingly prominent is the use of nanopowders to reduce sintering temperatures and produce materials possessing submicrometer-sized structures. The use of these structures allows properties such as hardness and wear behavior to be improved, the sintering process and the resultant structure to be decoupled from one another and non-equilibrium composite materials to be synthesized.
- The market whose potential lies in the most distant future (and which currently has the smallest market size) is represented by the actual nanomaterials, that is, materials that possess nanoscale structures after being sintered. Such materials place extremely high demands on powder, processing and sintering technology. In the short term, considerable growth is expected to occur, especially in the area of composite materials in which one component is nanocrystalline.
- The markets mentioned can only be developed if a reproducible method for producing deagglomerated nanopowders possessing narrow grain size distributions exists. Such a method has been partially made on a commercial scale for certain oxide powders (e.g., SiO_2, TiO_2); monoxide nanopowders have yet to be produced on an adequate scale.

- In order for nanoceramics to be successfully produced from powders, the powder processing step (deagglomeration, low-defect forming) must be controllable. Over the last few years basic knowledge has been acquired and the foundations for new technologies (e.g., the so-called colloidal methods of producing ceramics) have been laid.

- A prerequisite for reduction of grain growth is an extremely narrow grain size distribution - which is currently far from being made. The extent to which improvements in sintering technology (microwave sintering, SPS, etc.) can effect a reduction in grain growth and allow these processes to be implemented commercially is presently indeterminable.

Picture 9 shows a patented nanoceramic window called Hüper Optik® nano-ceramic film. Hüper Optik® is an advanced Multi-layered ceramic-coated film that gives superb heat rejection, low reflectivity and unsurpassed durability, while most conventional films offer limited heat rejection [14]. By cutting down unbearable heat, Hüper Optik® films cool the vehicle more efficiently and reduce fuel consumption. Occupants are also protected from the harmful Ultra Violet rays to the eyes and skin. In addition to improving the overall comfort of your ride, the high performance films offer fade control and extend the life of the vehicle's interior as well [14].

Figure 9 - Hüper Optik® nano-ceramic film for front windscreen application [14].

3.7.1 Trends for nanoceramics

The individual trends listed depict the increasing importance of nanotechnology and, especially, the reproducible production of nanopowders of sufficient quality as the key to further and broader application of such technologies. Oxide nanopowders are already being produced on a commercial scale for various applications (pigments, insulation materials, etc.), and the demand for monoxide nanopowder products that make the improvements in properties shown to be possible here is increasing.

3.7.2 List of relevant nanoceramics for industrial applications

Products already in use:

- Tungsten carbide

Already mass production of powders:

- Alumina
- Zirconia
- Titania
- Silica
- Zinc oxide

Powders which are developed, basic research and early applications:

- Silicon nitride
- Magnesia
- Ferric oxide
- Ceria
- Hydroxyapatite (HAP)
- Yttria
- Silicon carbide
- Boron nitride
-

Powders which are commercially available in kilogramme scale:

- TiC
- Amorphous silicon nitride
- AlN, TiN, ZrN, TiCXN1-x, ZrCxN1-x, $MgAl_2O_4$
- Si_3N_4-TiN, Si_3N_4-AlN, Si_3N_4-ZrN, AlN-TiN, AlN-ZrN

- Si_3N_4-Y_2O_3, Si_3N_4-MgO, AlN-Y_2O_3
- ZrO_2-Y_2O_3, ZrO_2-MgO, ZrO_2-Al_2O_3, $YBa_2Cu_3O_7$-x
- $TiCXN_1$-x-Fe, Ni

4. Nanomaterials production and manipulation

Synthesis processes are as vast as the number of different existent nanomaterials. Some can even be produced using several sintering processes. Nanoparticles can be produced by milling, flame pyrolysis, laser ablation; thin films by chemical vapor deposition; carbon nanotubes by laser ablation, electrolysis; graphene by exfoliation and cleavage; fullerenes by carbon vaporization, just to cite a discrete sample of materials and processes. As with any emerging field, a vast amount of disconnected information is emerging, often spread across multiple disciplines. However, progress will depend upon cross-communication between fundamental science and the applications fields.

Self-assembly is a powerful synthetic approach for creating advanced materials out of nanoparticle building blocks. It is the process by which molecular subunits organize spatially to form well-defined supra-molecular structures, in spite of non-covalent interactions between them. However controlling the particle size and shape during synthesis is still a major challenge. Nevertheless, some physical and solid state chemical methods have been developed for making nano-sized semiconductors (quantum dots), metal nanowires, nano-belts, and nano-dots [15-17].

There are several methods of making nanoparticles. Two common ways are attrition and pyrolysis. In attrition, macro or micro scale particles are physically ground in a ball mill, a planetary ball mill, or any other size-reducing mechanism. The resulting particles are air classified to recover the nanoparticles. Air classification is a process in which the physical principles of centrifugal force, drag force and gravity are balanced to generate a high-precision method of classifying particles according to size or density. In the process of pyrolysis, an organic precursor (liquid or gas) is forced through a hole, at a high pressure, and burned. The resulting ash is air classified to recover oxide nanoparticles.

Thermal plasmas can also deliver the necessary energy to evaporate small micron-size particles. The temperature of thermal plasmas is of order of 10000°C, so that the solid powder easily evaporates. Outside the plasma region, the cooling causes the formation of nanoparticles.

Additional nanoparticles synthesis techniques include sono-chemical processing, cavitation processing and micro-emulsion processing. Sono-chemistry involves an acoustic cavitation process that generates a transient localizes hot zone with extremely high temperature and pressure gradients. These sudden changes in temperature and pressure assist the destruction of the sono-chemical precursor (e.g. organometallic solution) and the formation of nanoparticles. This technique can be used to produce a large volume of material for industrial applications [18].

4.1. Synthesis of carbon nanotubes

At the present day, there are numerous ways of making CNTs. Arc method, laser method, CVD method, ball milling, diffusion flame synthesis, electrolysis using solar energy, heat treatment of a polymer and low-temperature solid pyrolysis are some of the various processes than can be used to fabricate carbon nanotubes. Although many methods have been developed to synthesis the MWCNTs and SWCNTs, only the first three methods which are the electric arc-discharge, laser ablation and CVD are widely adopted.

The most widely used technique to produce nanotubes is the electric arc discharge, the same as used to prepare fullerene molecules [19]. Indeed carbon nanotubes were found for the first time during the examination of fullerene materials produced by the arc technique [19]. The principle of this method is based on an electric arc discharge generated between two graphite electrodes under an inert atmosphere of helium or argon [19]. The variation of process parameters such as flow rate, gas pressure, and metal concentration is needed to obtain the highest yield of CNTs which occurred in 'pillar-like tubes' either in single- walled tubes or multi- walled tubes [20]. The structures of the nanotubes produced are usually short tubes. SWCNTs with diameters ranging from 0.6 to 1.4 nm and 10 nm diameter MWCNTs, this method is relatively easy to be implemented and 30% yield will be obtained [20]. The content of impurities in CNTs produced is higher compared to other methods, and the consistency of the shape, wall, and lengths of the tubes are somewhat random [20]. Currently, there are various variations relatively to this process. For example, the Figure 9a shows a latest version of the arc-discharge method [21]. Two graphitic rods act as the electrodes: negative cathode and positive anode. The anode evaporates to form fullerenes and CNTs which are deposited in the form of soot all around the chamber walls. A small part of the evaporated material originating from the graphitic rods is also deposited in the cathode substrate which is composed of a variety of carbon products including soot, fullerenic material, and multi-walled carbon nanotubes [21]. Figure 9b shows a schematic of arc-discharge to produce CNTs [20]. Initially, the two electrodes are kept independent. The electrodes are kept in a vacuum chamber and an inert gas is supplied to the chamber [20]. The inert gas increases the speed of carbon deposition. Once the pressure is stabilized, the power supply is turned on (about 20 V). The positive electrode is then gradually brought closer to the negative one to strike the electric arc. The electrodes become red hot and a plasma forms [20]. Once the arc stabilizes, the rods are kept about a millimeter apart while the CNT deposits on the negative electrode. Once the specific length is reached, the power supply is cut off and the machine is left for cooling. Precaution needed for the important parameters are; (1) the control of arcing current and (2) the optimal selection of inert gas pressure in the chamber [20].

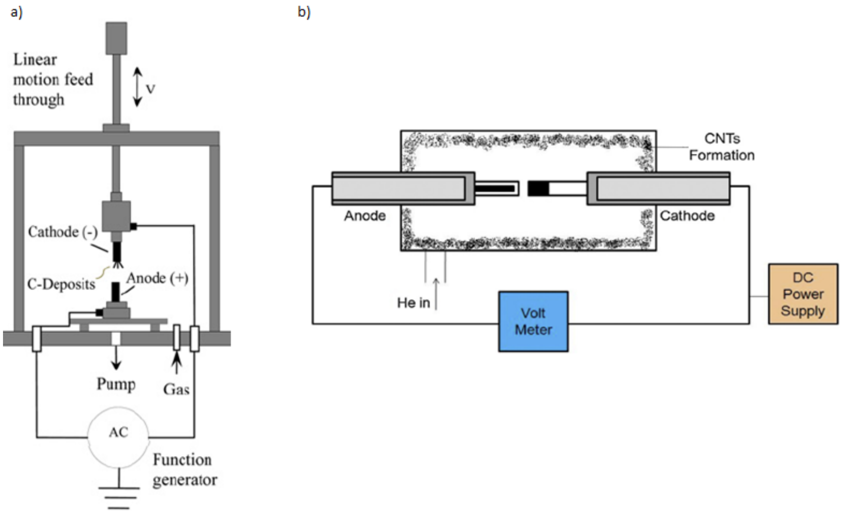


Figure 10 - Schematic: a) of the lastest version of arch-discharge to produce CNTs [21]; b) of arc-discharge to produce CNTs adopted from Ebbesen *et al.* [20]

The laser ablation method is the second technique for producing carbon nanotubes which is very useful and powerful [22]. This process is known to produce carbon nanotubes with the highest quality and high purity of single walls [22]. Laser ablation was the first technique used to generate fullerenes in clusters. In this process, a piece of graphite is vaporized by laser irradiation under an inert atmosphere [22]. This results in soot containing nanotubes which are cooled at the walls of a quartz tube. Two kinds of products are possible: multi walled carbon nanotubes or single walled carbon nanotubes. For this process, a purification step by gasification is also needed to eliminate carbonaceous material [22]. The effect of the gasification depends on the type of reactant used. The first growth of high quality single wall nanotubes was achieved by Smalley and coworkers [22]. In the same way, the laser ablation method underwent several changes over time. Figure 11a shows a graphite target placed in the middle of a long quartz tube mounted in a temperature controlled furnace [19]. After the sealed tube has been evacuated, the furnace temperature is increased to 1200°C [19]. The tube is then filled with a flowing inert gas and a scanning laser beam is focused onto the graphite target by way of a circular lens [19]. The laser beam scans across the target surface to maintain a smooth, uniform face for vaporization. The laser vaporization produces carbon species, which are swept by the flowing gas from the high-temperature zone and deposited on a conical water-cooled copper collector [19]. Figure 11b shows the setup of the laser furnace, which consists of a furnace, a quartz tube with a window, a target carbon composite doped with catalytic metals, a water-cooled trap, and flow systems for the buffer gas to maintain constant pressures and flow rates [20]. A laser beam (typically a YAG or CO_2 laser) is introduced through the window and focused on to the target located in the center of the furnace. The target is vaporized in high-temperature Ar buffer gas and forms SWCNTs [20]. The SWCNTs produced are conveyed by the buffer gas to the trap, where they are collected. The vaporization surface is kept as fresh as possible by changing the focus point or moving the target [20].

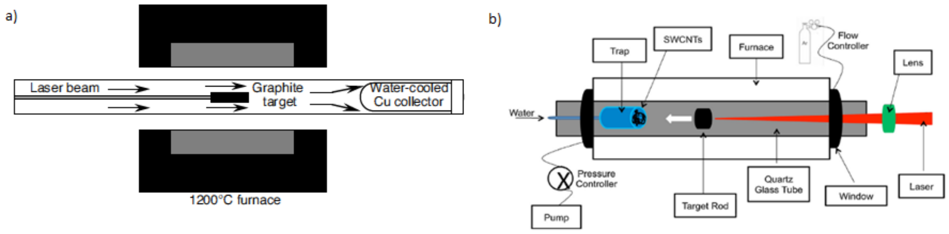


Figure 11 - a) Schematic representation of the oven laser-vaporization apparatus [19]; b) Diagram of laser furnace apparatus to produce CNTs adopted from Ando *et al.* [20].

Both arc discharge and laser ablation produce some of the most high quality nanotubes but suffer from the following disadvantages which limit their use as large scale industrial processes [20].

1. They are both energy extensive methods where a large amount of energy is required to produce arc or laser used for the ablation processes. Such a huge amount of energy is not only impossible but also uneconomical for large scale production;
2. Both methods require solid carbon/graphite as target which has to be evaporated to produce nanotubes. It is difficult to get such large graphite to be used as target in industrial process which limits its exploitation as large scale process;
3. Both processes grow nanotubes in highly tangled form, mixed with unwanted form of carbon or catalysts. Thus, the CNTs produced by these processes require purification to obtain purified and assembled forms. The designing of such refining processes is difficult and expensive;
4. The growth temperature of both methods is higher than other CNT production. As a result, the crystalline and perfection of arc-produced CNTs are generally high, and the yield per unit time is also higher than other methods;
5. The by-products in the case of the arc-discharge and laser-ablation techniques are fullerenes, graphitic polyhedrons with enclosed metal particles, and amorphous carbon.

Chemical vapor deposition (CVD) synthesis is based on cracking a gaseous carbon molecules (methane, Carbon monoxide or acetylene) to reactive atomic carbon, which diffuses towards a heated substrate, coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it binds and carbon nanotubes will be formed [23]. Excellent alignment, as well as positional control on nanometer scale, diameter and growth rate can be achieved [23]. Choosing the appropriate metal catalyst can control the production of either single or multiwall nanotubes [23]. CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube [23]. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation [23]. Thermal annealing results in cluster formation on the substrate, from which the nanotubes grow [23]. Ammonia may be used as the etching agent. The process is usually occurring in the temperatures ranges within the 650-900°C [23]. Typical yields for CVD are approximately 30%. This method is very easy to scale up, and favors commercial production. In recent years, different techniques of CVD have been developed, such as plasma enhanced CVD, thermal chemical CVD, alcohol catalytic CVD, vapor phase growth, aero gel-supported CVD and laser assisted CVD

[23]. Various CVD configurations have been developed and tested for the synthesis of CNTs, including horizontal furnace, fluidized bed reactor, vertical furnace, and basic plasma enhanced CVD [21]. Figure 12a is a schematic of CVD with a horizontal configuration, which is the most popular of the

configurations [21]. The horizontal configuration is advantageous because there is no temperature gradient within the heated zone. A variety of hydrocarbons in the form of liquid, gas, and solid states can be employed as the source of carbon feedstock. In the case of liquid or solid hydrocarbons, the vaporization process can first be achieved through the use of an external evaporator [21]. Figure 12b is another example to produce CNTs using the CVD. it comprises a quartz tube of 50 mm OD, 40 mm ID and 1500 mm length extended through two furnaces [20]. The catalyst ferrocene was placed in a ceramic boat located inside the ceramic tube at the center of the first furnace. The growth of CNTs took place at the second furnace and collected in ceramic boats which were placed at the center of the second furnace [20]. The system was initially flushed with Ar in order to ensure an oxygen free environment. In the meantime, the second furnace was heated to the desired reaction temperature [20]. Heating was continued until a steady state condition is achieved. The flow of Ar was then stopped and the first furnace was switched on till the temperature reached 150°C [20]. The gas flow for C_2H_2 along with H_2 was immediately released. The reaction was carried out for the desired reaction time when the reaction is completed. The CNT produced in the ceramic boats as well as on the inner walls of the second furnace was collected and weighed separately [20].

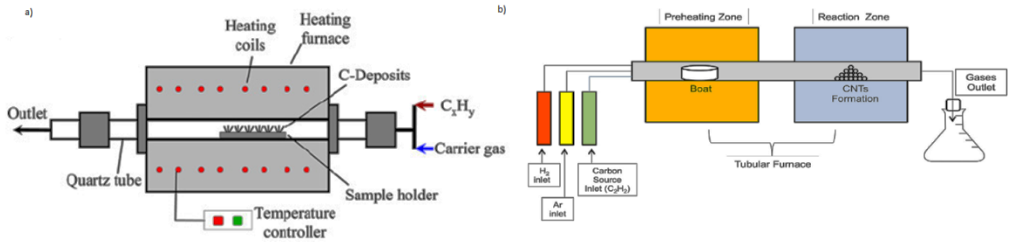


Figure 12 – a) Schematic of CVD with a horizontal configuration to produce CNTs [21]; b) Diagram of CVD to produce CNTs adopted from Mubarak *et al.* [20].

The CVD has several important advantages, which make it the preferred process in many cases. These can be summarized as follows [20].

1. The CVD is a relatively uncomplicated and flexible technology, which can accommodate many variations, and the reaction process and reactor design is simple as the reaction is easy to control and manipulate.
2. Easily available raw material abundant in the form of gases.
3. With the CVD, it is possible to coat almost any shape of almost any size.
4. Unlike other thin film, techniques such as sputtering CVD can also be used to produce vertically aligned nanotubes, fibers, monoliths, foams and powders.
5. CVD is economically competitive.

The following table shows a comparison of arc-discharge, laser ablation and CVD.

Table 4 - Comparison of arc-discharge, laser ablation and CVD [20].

Process	Arc-discharge	Laser ablation	CVD
Reaction Temperature (°C)	3000-4000	3000	500-1100
Per unit design cost	High	High	Low
Nanotube selectivity	Low	Low	High
Source of carbon	Difficult	Difficult	Easy available
Purification of CNT	High	High	Low
CNTS yield	<30%	≈70%	95-99%
Process Nature	Batch	Batch	Continuous
Process parameter control	Difficult	Difficult	Easy to control
Energy requirement	High	High	Low
Reactor design	Difficult	Difficult	Easy to design nature
Nanotube graphitization	High	High	Middle

4.2. Synthesis of graphene

Another interesting carbon based nanomaterial is graphene. Several approaches have been developed to provide a steady supply of graphene in large areas and quantities, amenable for mass applications [24]. These include growth by chemical vapour deposition (CVD, segregation by heat treatment of carbon-containing substrates, and liquid phase exfoliaton. In fact, most of these methods date back several decades [24]. The current interest in graphene has pushed these early approaches to large yields, controlled growth and large areas, and made it possible in just six years to go from micrometre-sized flakes to near-mass-production of layer controlled samples [24]. Various methods have been devised and categorized into "top-down" and "bottom-up" processes.

Top-down approaches commence with an existing form of the bulk material and process it to create the final product [25]. This approach may be cost efficient, depending on the material used. In general, it is limited to a lab scale and has limited quality control. In this approach, graphene or altered graphene sheets are produced by separation, peeling, cleaving, or exfoliation of graphite or its derivatives (graphite oxide (GO) and graphite fluoride (GF)) [25]. Since this approach involves great investment and produces relatively low yields, the need remains for mass scaled-up processes to economically address the needs of industries [25]. Various mechanical processes have been involved in producing high-quality, defect-free graphene: mechanical exfoliation of graphite, sonication, functionalization, electrochemical exfoliation, super acid dissolution of graphite, alkylation of graphene derivatives, chemical reduction of aqueous/organically treated graphene oxide (GO), thermal exfoliation, and chemical reduction of GO [25].

The bottom-up approach consists of standard techniques such as epitaxial growth using metallic substrates by means of CVD or organic synthesis, which depend on the choice of precursor chemicals and thermal degradation and decomposition of the SiC [25]. Several other processes, such as arc discharge, chemical conversion, CO reduction, CNT unzipping, and self-organization of surfactants have also been tried for synthesis of graphene and its derivatives [25]. Of all these processes, CVD and epitaxial growth, which produce bantam quantities of flawless graphene sheets with larger size, may in future be attractive for mass-scale graphene production, in contrast to mechanical cleaving [25]. Using CVD and epitaxial methods, graphene sheets and their way into fundamental research with a multitude of applications ranging from electronics to polymeric nanocomposites [25].

Mechanical Exfoliation is the first process used by Noveselov *et al.* to produce high-quality single crystal graphene monolayers [26]. For this method, a high tack tape (Nitto™ tape) is used to peel thin flakes from a bulk graphite sample [26]. Further peeling reduces the thickness of the flakes until they are finally captured on a surface. Initially, the samples of single crystal material obtained in this way were only a few tens of microns in size. It is now possible to produce millimeter sized flakes using this technique [26]. The Figure 13 shows the Mechanical exfoliation process of graphene using scotch tape from HOPG (highly oriented pyrolytic graphite).

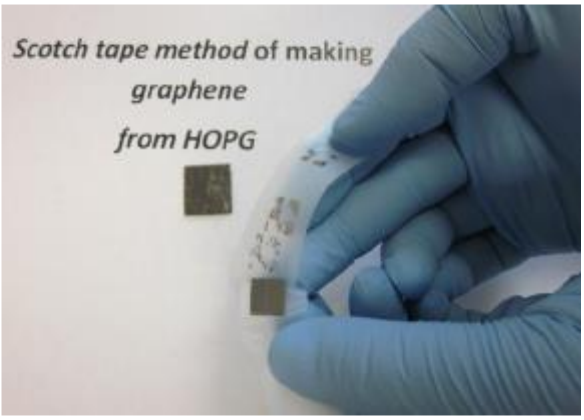


Figure 13 - Mechanical exfoliation process of graphene using scotch tape from HOPG [27].

At present, chemical conversion of graphite to graphene oxide has emerged to be a viable route to afford graphene-based single sheets in considerable quantities. Graphite oxide (GO) is usually synthesized through the oxidation of graphite using oxidants including concentrated sulfuric acid, nitric acid and potassium permanganate based on Hummers method [27]. The reduction of GO allows a regeneration of graphitic structure through dehydration and deoxygenating processes, enabling to restore the conductivity of materials. The reduction of GO can be performed by several methods: chemical methods using reducing agents such as hydrazine, hydrogen plasma, dimethyl hydrazine, hydroquinone, sodium borohydride, ascorbic acid, alcohols, strong alkalis solutions, electrochemical methods, thermal methods and methods are using UV. The process of GO reduction is very important, because it allows obtaining reaction products with similar properties to that of graphene. However, the reduced GO shows significant structural differences when compared with graphene. Nevertheless, it is important to note that the purpose of this method is obtaining graphene with similar mechanical and conductive properties to graphene obtained by "scotch tape" method. The structural defects applied during the oxidation graphite process lead to the removal of carbon atoms of aromatic structure of the carbon plans, thereby creating nanometric zones of impossible discontinuity to recover, through the reduction process.

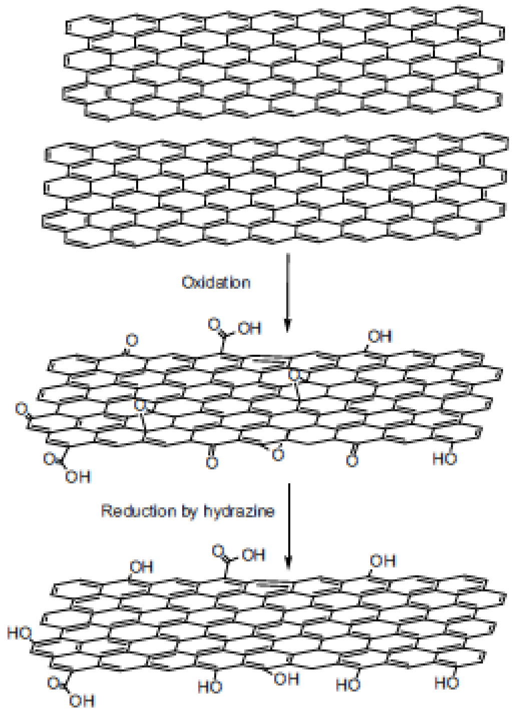


Figure 14 - Oxidation of graphite to graphene oxide and reduction to reduced graphene oxide [27].

Graphite can be produced on SiC surface by annealing SiC surface using ultra-high vacuum (UHV) which is a most used method by semiconductor industry because graphite are synthesized on SiC substrates and could be used immediately. During the heating of SiC substrate under UHV, silicon atoms sublimate from substrate. With the removal of silicon atoms, the arrangement of carbon atoms will take place to form graphene layers. The annealing time and temperature could influence the number of graphene layer. Producing graphite through ultrahigh vacuum (UHV) annealing of SiC surface has been an attractive approach especially for semiconductor industry because the products are obtained on SiC substrates and requires no transfer before processing devices [27]. When SiC substrate is heated under UHV, silicon atoms sublimate from the substrate. The removal of Si leaves surface carbon atoms to rearrange into graphene layers. The thickness of graphene layers depends on the annealing time and temperature. The formation of ''few-layer graphene'' (FLG) typically requires few minutes annealing of the SiC surface at temperature around 1200°C [27]. The main advantage of graphene grown on SiC substrates is that no transfer is needed for device processing. Also the size of the graphene sheet can be as large as the substrate which is another benefit for device processing. Epitaxial Graphene has superlative electronic properties, and therefore has the potential to replace silicon for the next generation ICs and ultra-fast (100 GHz to THz frequencies) high performance electronic devices. EG is the most promising candidate for graphene-based electronics as it can be directly grown on SiC semiconductor substrate without any need for its transfer (unlike in the case of CVD graphene on metal substrates). The advantages of epitaxial growth technique are its compatibility with the present day Complementary metal–oxide–semiconductor (CMOS) technology and its scalability, which can help in realizing the ultimate dream of ushering in new era of graphene-based electronics.

The following figure shows 2 different configurations to produce graphene. Picture 15a shows SiC wafer in UHV: Sublimed silicon is not confined, causing rapid, out of equilibrium graphene growth, while figure 15b shows The CCS method: sublimed Si gas is confined in a graphite enclosure so that growth occurs in near thermodynamic equilibrium. Growth rate is controlled by the enclosure aperture (leak), and the background gas pressure [28].

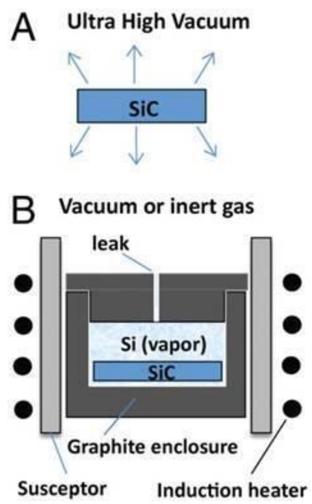


Figure 15 - Silicon sublimation from the SiC. (a) SiC wafer in UHV: Sublimed silicon is not confined, causing rapid, out of equilibrium graphene growth. (b) The CCS method: sublimed Si gas is confined in a graphite enclosure so that growth occurs in near thermodynamic equilibrium. Growth rate is controlled by the enclosure aperture (leak), and the background gas pressure [28].

CVD provides an inexpensive and readily accessible method for producing single-layer and few layer graphene of reasonably high quality [26]. Much success has been obtained in CVD growth of graphene on transition metal substrates such as Ni, Pd, Ru, Ir, and Cu. Growth on copper has recently advanced to such an extent that large area (up to 32" sheets) of material can be produced with good device characteristics including mobility up to 7350 at low temperature and with >90% transmission of light. Recent progress on the growth of graphene on relatively inexpensive polycrystalline Ni and Cu substrates has triggered interest in optimizing growth conditions for large area growth and transfer [26]. The results of growth on Ni foils give mobility values of up to 3650 and half integer quantum hall effect [26]. However, the high temperatures required for this process seem to stem from the high catalytic reduction temperature of hydrocarbons (CVD method) or the high driving energy required for carbon atoms to diffuse into the transition metals (surface segregation method), rather than the actual formation temperature of graphene on the surface of transition metals [29].

Plasma enhanced chemical vapor deposition (PECVD) offers another route of graphene synthesis at a lower temperature compared to thermal CVD [27]. The advantages of the plasma deposition include very short deposition time (<5 min) and a lower growth temperature of 650°C compared to the thermal CVD approach (1000°C) [27]. The growth mechanism involved a balance between the graphene deposition through the surface diffusion of C-bearing growth species from precursor gas and etching caused by atomic hydrogen. The verticality of the graphene sheets, produced through this method, is caused by the plasma electric field direction [27].

Figure 16 demonstrates a schematic of an experimental setup of CVD which is commonly employed to produce single layer graphene by Cu or Ni catalysts [30]. It basically consists of a tube furnace for high temperature heating, a quartz vacuum chamber, a vacuum and pressure control system for the growth condition adjustment, and several mass flow controllers (MFC) to provide carbon source and reactant gases with a necessary flow rate [30].

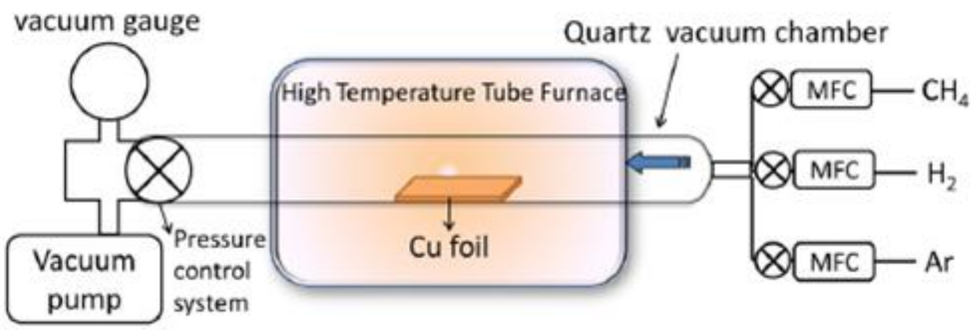


Figure 16 - Schematic of a common setup for chemical vapor deposition of graphene [30].

The current graphene synthesis methods are summarized in Table 5.

Table 5 - A Brief Summary of Graphene Synthesis Methods [30].

Synthesis Method	Brief Description/Remarks
Mechanical Exfoliation	-Using a regular Scoth tape to peel off graphene from HOPG; -Atomic layer of graphene can be seen on ~300 nm SiO¨2 substrates under an optical microscope; -Pristine graphene with highest quality of electrical properties; -The size, thickness and location are uncontrollable, with limited practical applications;
Solution based exfoliation of graphene oxide (GO)	-Graphite powders are initially oxidized by chemical modification (Hummers´method) to be dispersed in solution; -GO are subsequently reduced to graphene by thermal annealing or chemical reducing agents; -Large scale production for bulk applications, such as supercapacitors, composite materials, etc; Significant structural defects and leaving oxygen functional groups on the product.
Epitaxial growth using SiC substrates	-A conversion of SiC substrate to graphene via sublimation of silicon atoms on the surface; -Doe at high temperature (1200ºC) and ultrahigh vacuum condition; -Limited accessibility due to high-end equipment.
CVD growth Graphene	-Most promising inexpensive and feasible method for single layer or multi-layers graphene production; -Using transition metal (Ni, Cu, etc.) substrates or thin films as catalyst; -Rowing carbon source (CH4) and reactant gases (H2) at high temperature (1000ºC) for the nucleation of graphene; -Single layer graphene can usually be obtained on Cu; -Can be scaled up for large area graphene production for practical applications, such as transparent electrode applications.

The price of graphene is linked to its quality, and not all applications require superb material quality [31]. For example, graphene oxide powder (graphene functionalized with oxygen and hydrogen) is inexpensive and has been used to make a conductive graphene paper, for DNA analysis, and for other advanced composite and biotechnology applications [31]. However, the electronic properties of graphene oxide at the moment are not sufficiently good for batteries, flexible touch screens, solar cells, LEDs, smart windows, and other advanced optoelectronic applications [31]. Mechanically exfoliated graphene comes in small, high-quality flakes. The coverage of mechanically exfoliated graphene, however, is only on the order of a few small flakes per square centimetre, not early enough for applications. In addition, the price of such graphene can be on the order of several thousands of dollars per flake. CVD graphene offers sufficient quality for almost any graphene application [31]. The price of CVD graphene is linked to production volume and costs of transferring from the copper substrate, on which it is grown, onto another substrate [31].

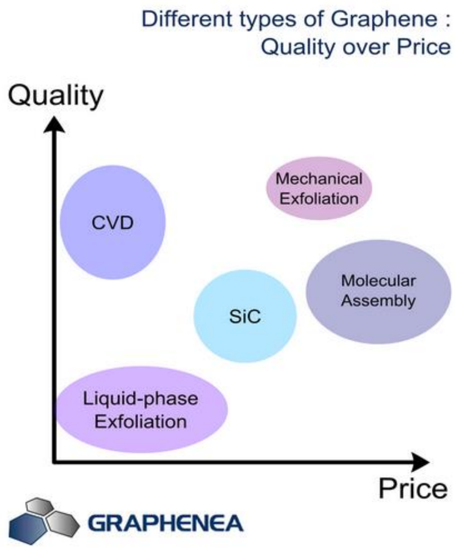


Figure 17 - Different types of graphene synthesis: Quality vs Price [31].

5. An overview of the current nanotechnology application in the SUDOE space industry

The methodology applied in the project in order to feed the cooperation of the stakeholders in the specific area of nanotechnology in the SUDOE space industry, rely on the innovation promotion and the constitution of cooperation's stable networks in the technological field.

Due to the current uncertainties that still exist regarding nanotechnology manipulation, lack of knowledge and information, it's mandatory to have a structured and dedicated methodology to overcome it and in order to achieve the stakeholders' deep involvement.

The CarbonInspired 2.0 project's aim is to capitalize the results from the previous one, disseminating them through the primary target audience: the companies, especially for a deeper awareness of the nanotechnology potential.

Dedicated questionnaires to the industry sector were formulated, being one of the key actions of the project. The construction of a database with detailed data concerning the use of nanotechnology, type of projects, major obstacles, fears and health and environment issues is a primordial goal.

Besides the general company information in order to characterize the sector industry type and the professional category of those who filled the questionnaire, it intends to give a full description of the nanotechnology's current application in the SUDOE space industry and also to understand the gap between the nanotechnology development and its practical utilization in company's context. For that reason, two different categories were defined: nanotechnology's users and non-users, to obtain the major obstacles and concerns of each one.

Nanotechnology user's questions focused on the products' quantity and type and the relevance of the R&D in nanotechnology on the company's innovation. Health and security issues and environmental impact were considered as major concerns regarding the use and manipulation of nanomaterials. The nanotechnology non-user questionnaire section intended to obtain the main reasons for the non-utilization of nanotechnology, especially the major obstacles.

Considering the numerous actions conducted by the consortium to achieve a bigger collaboration among the stakeholders and receptivity of industry for the nanotechnology potential, hundreds of companies were contacted, through virtual and presential channels, to participate in the questionnaires and in the CarbonInspired 2.0 platform and benefits as specialized formation.

Regarding the relevance of their feedback, and as a consequence of this action, 151 answers were achieved from several countries. Most of the answers came from Portugal, Spain and France industry, but also, from U.S.A., Germany, Belgium, U.K. and Moldova Republic. More than 50% are small-medium size companies, with an broad activity sector, mainly in the area of transportation, molding, construction, aerospace, aeronautic, chemistry, materials, food industries, automotive, electronics, biotechnology, environment and health.

One of the goals was to confirm the familiarity of the nanotechnology benefits in industry, where, 61% of the surveyed are familiar with nanotechnology benefits but only 26% are actual nanotechnology's users, as illustrated in Figure 18 and Figure 19.

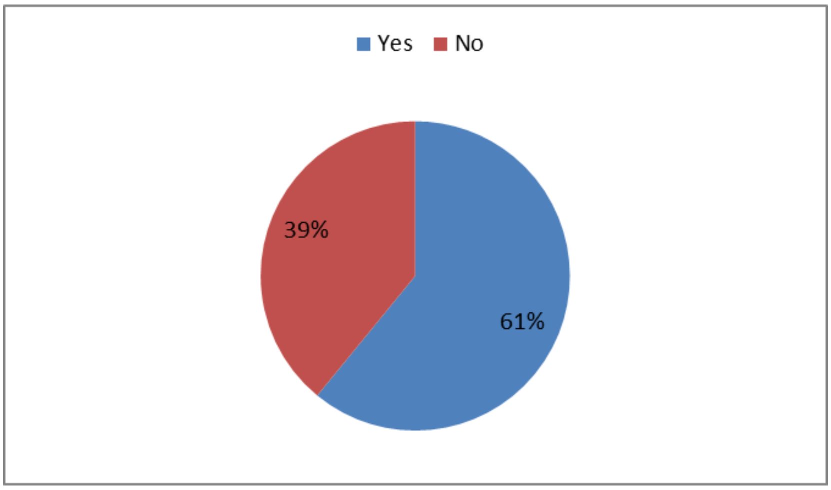


Figure 18 - Familiarity of the benefits of nanotechnology in industry.

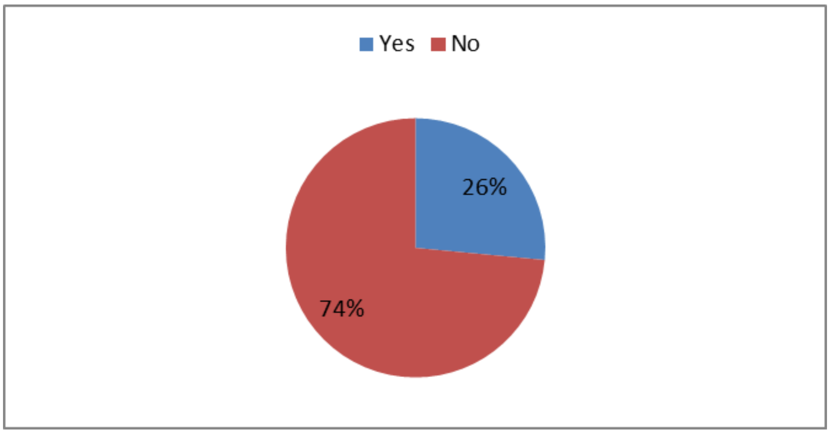


Figure 19 - Familiarity of the benefits of nanotechnology in industry.

Nanotechnology user and non-user considered the lack of information, the lack of knowledge and the high ratio between the investment and profit as obstacles for the nanotechnology usage. Nevertheless, human health and security for nanomaterials manipulation and the environment impact weren't preponderant.

The following figures illustrate the questionnaires answers.

5.1. General information

Total answers amount: 151

- Number of questionnaires in french: 64
- Number of questionnaires in portuguese: 62
- Number of questionnaires in spanish: 20
- Number of questionnaires in english: 5

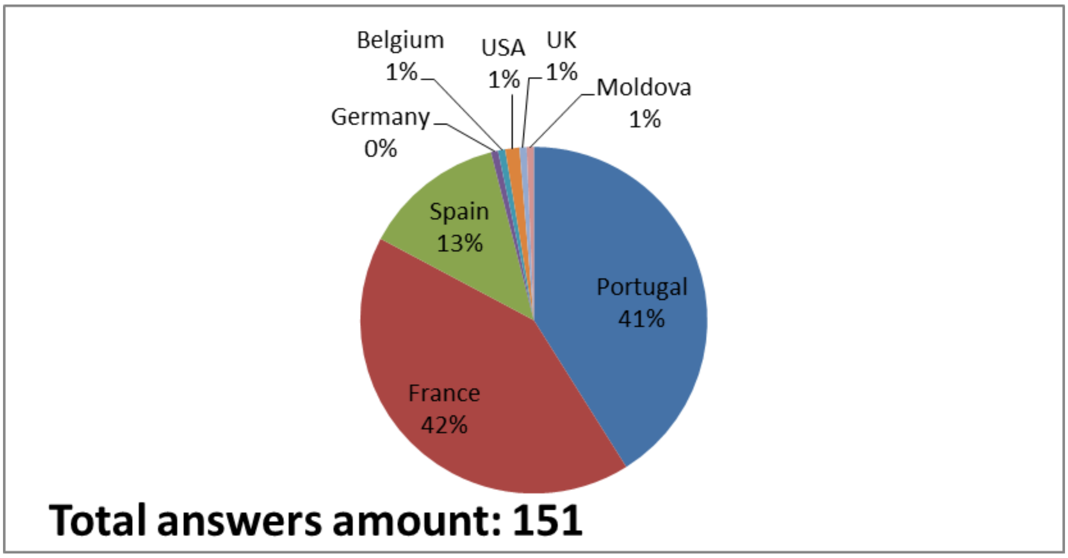


Figure 20: Countries that answered to the questionnaires

5.2. General company characterization

- **Professional position in the company of the person that completed the inquiry**

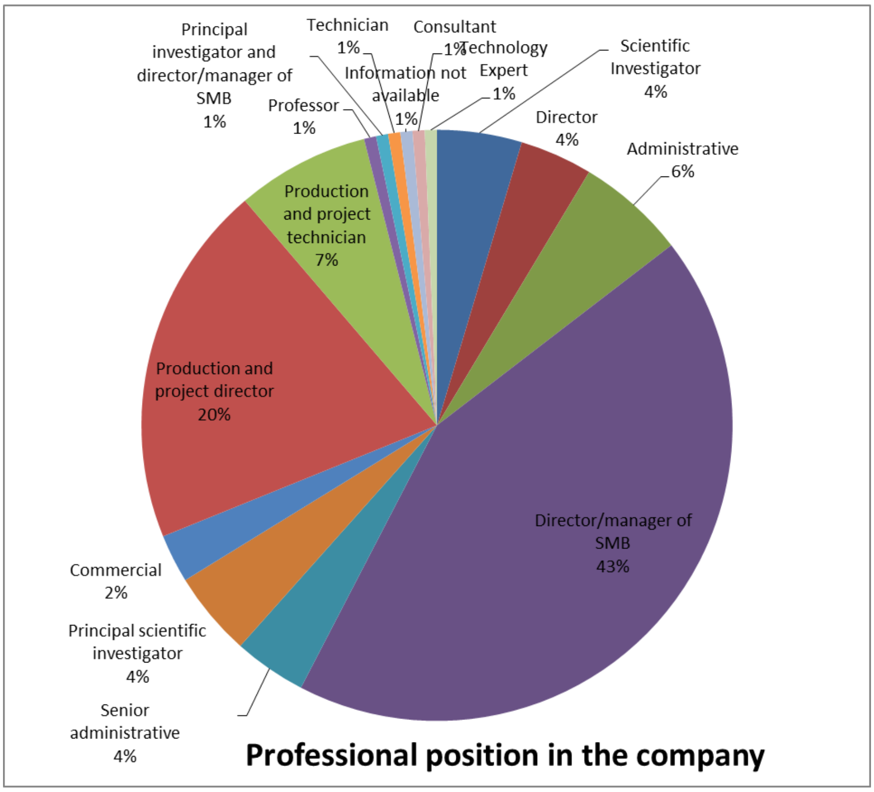


Figure 21: Professional position in the company

- **Company activity sector**

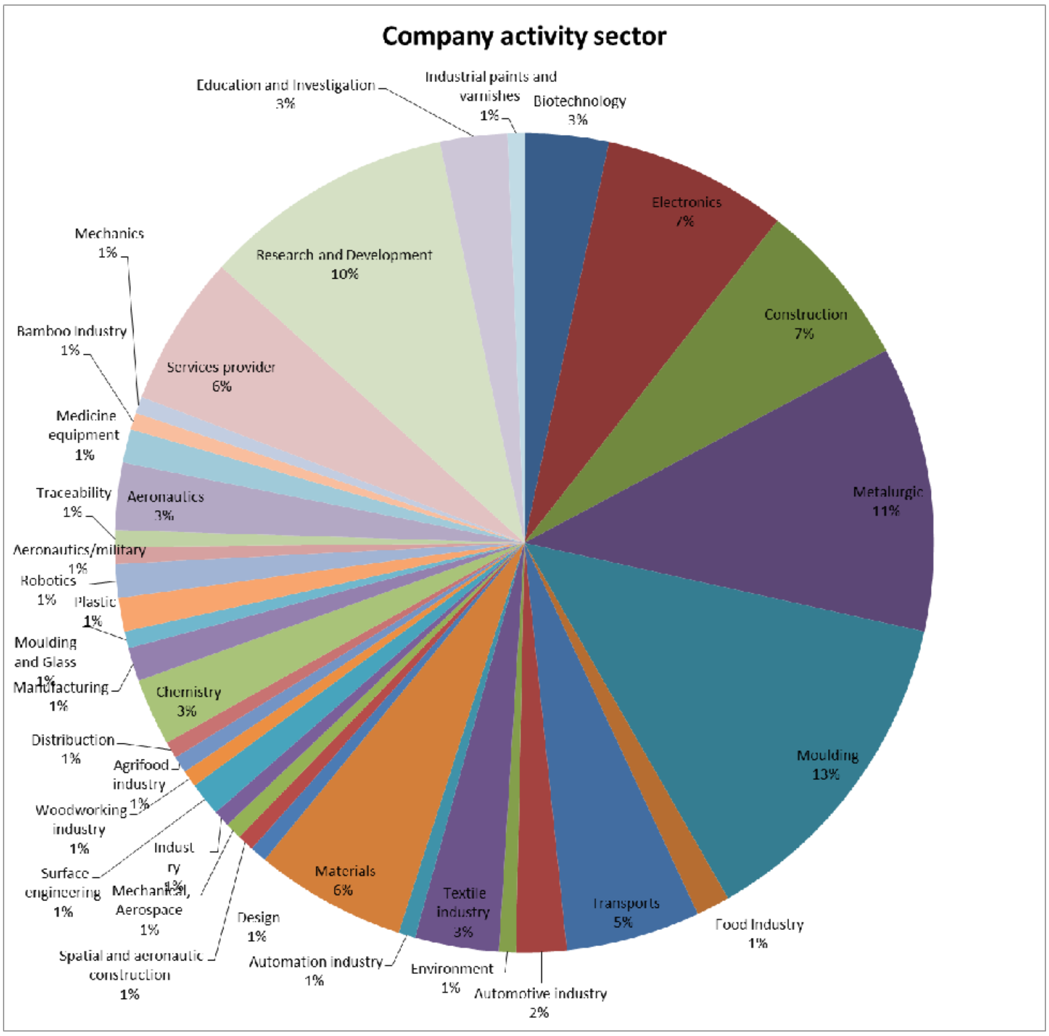


Figure 22: Company activity sector

- **Company type**

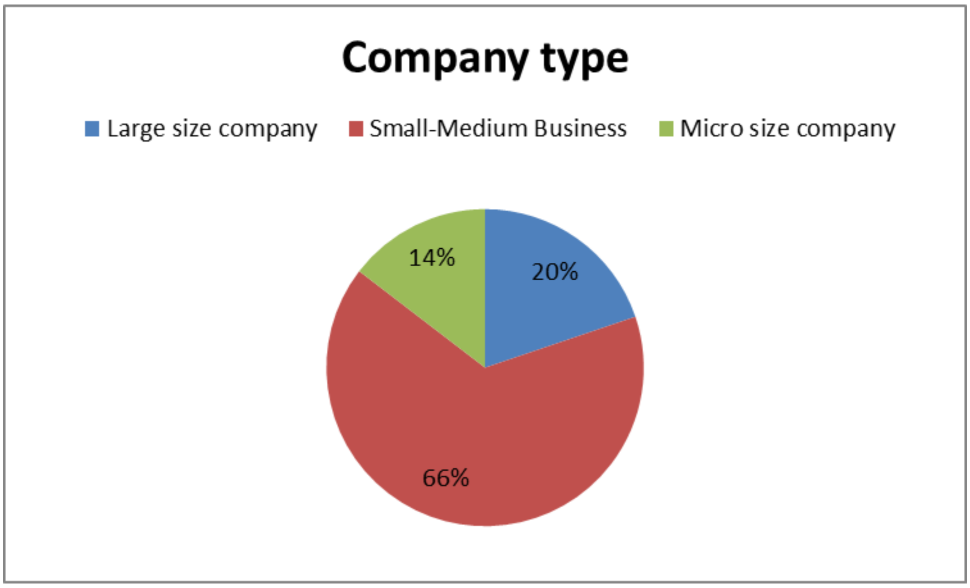


Figure 23: Company type

5.3. Nanotechnology user

Total nanotechnology company users: 40

- **Company type**

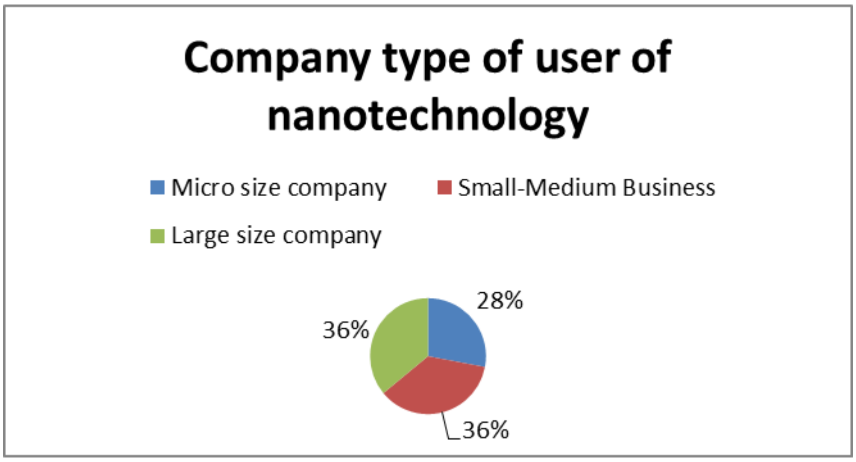


Figure 24: Company type of user of nanotechnology

- **Activity sector – nanotechnology user**

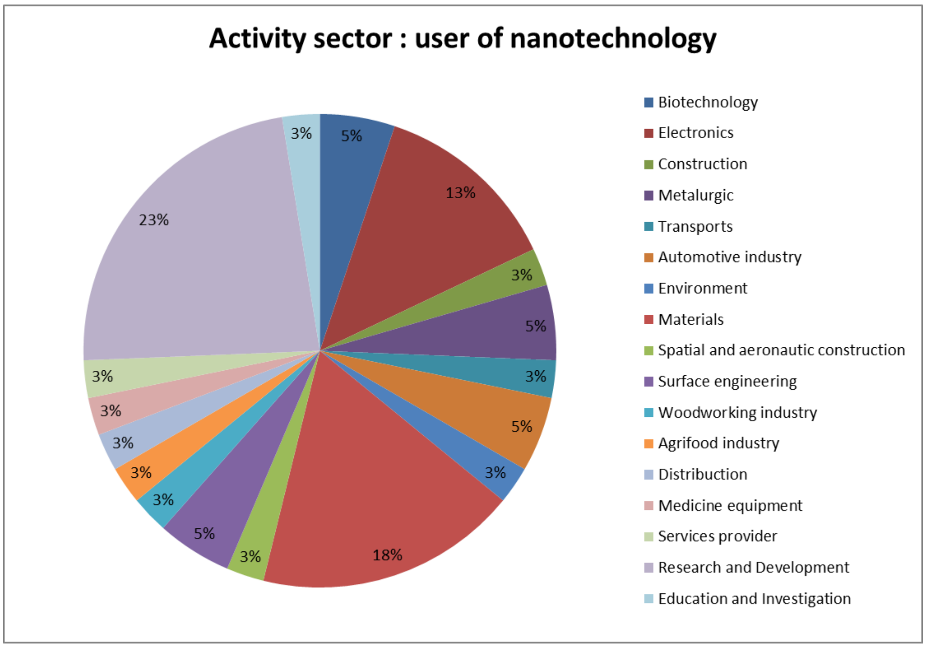


Figure 25: Activity sector - nanotechnology user

- **Category classification company, as a user of nanotechnology**

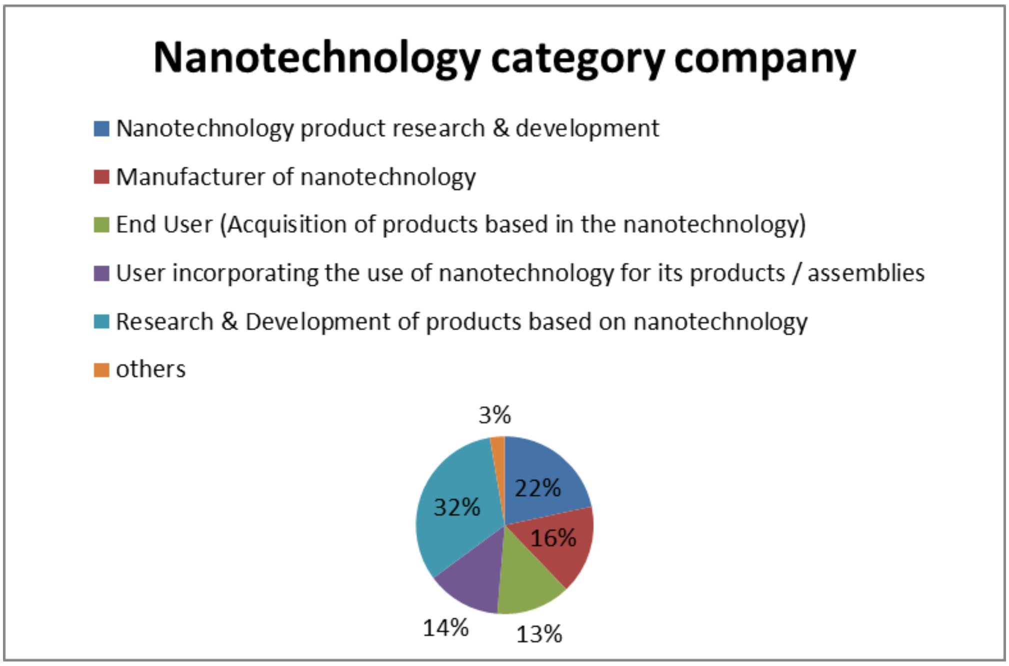


Figure 26: Company type of user of nanotechnology

- **Number of products in the market using nanotechnology**

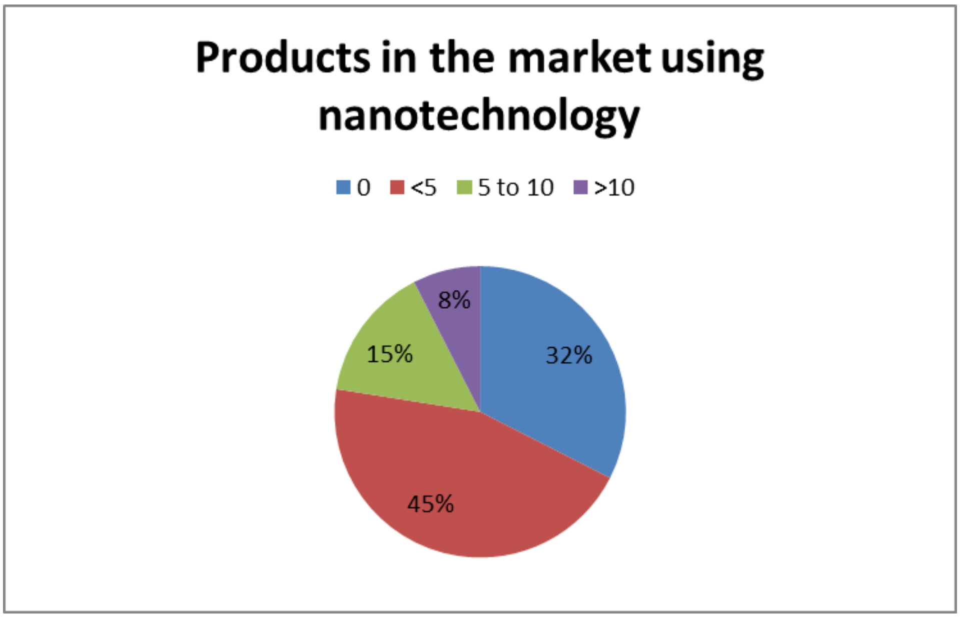


Figure 27: Number of products in the market

- **Research and development (R&D) relevance in nanotechnology in your company**

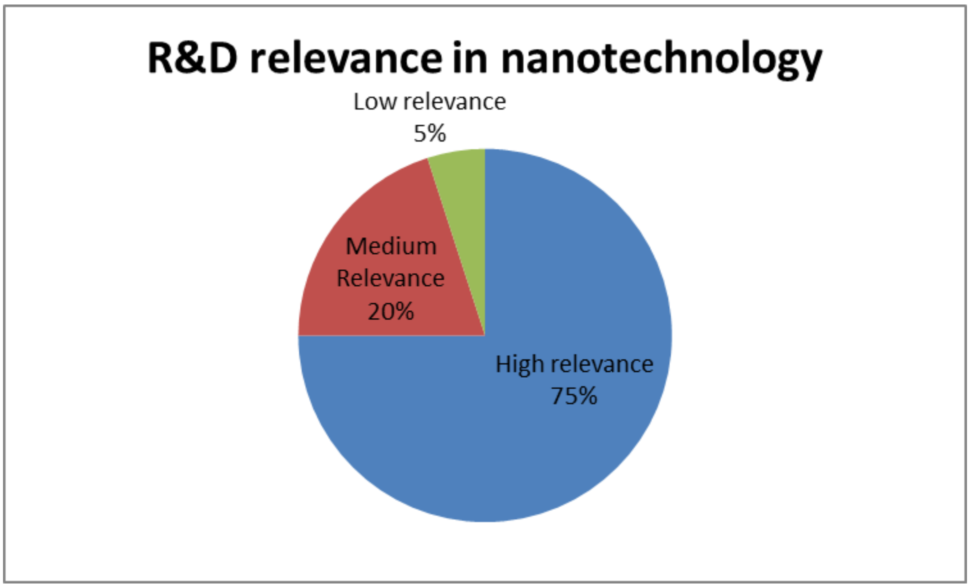


Figure 28: R&D relevance in nanotechnology in the company

- **Type of R&D**

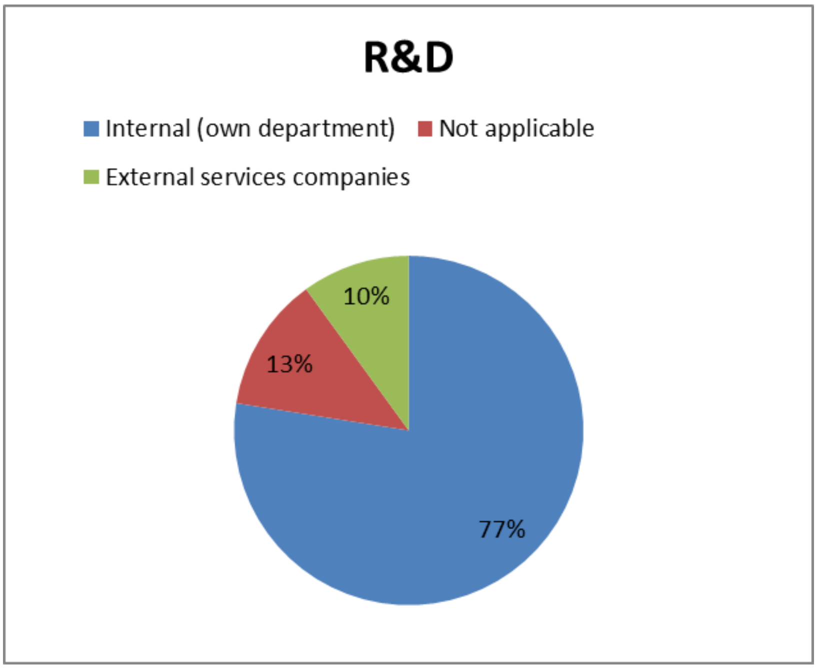


Figure 29: Type of R&D

- **Number of employees using specific personal protective equipment for nanotechnology**

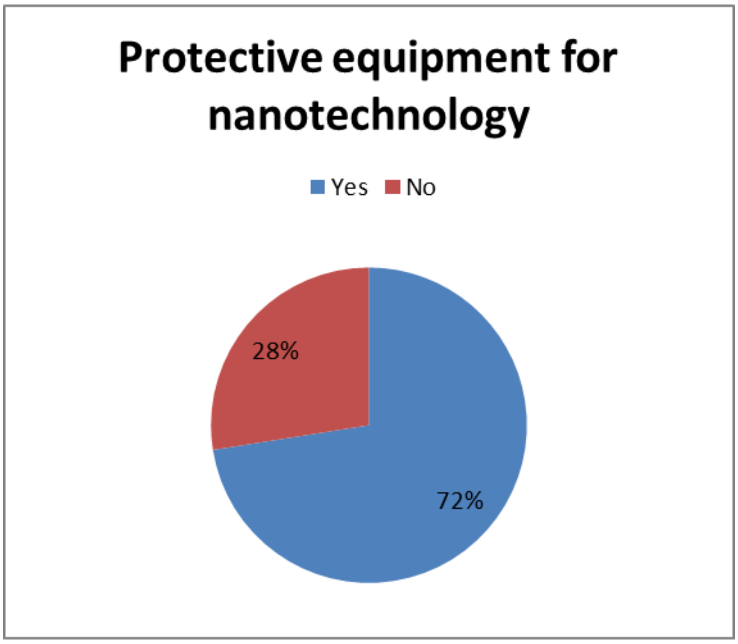


Figure 30: Protective equipment for nanotechnology

- **Major difficulties in implementing nanotechnology**

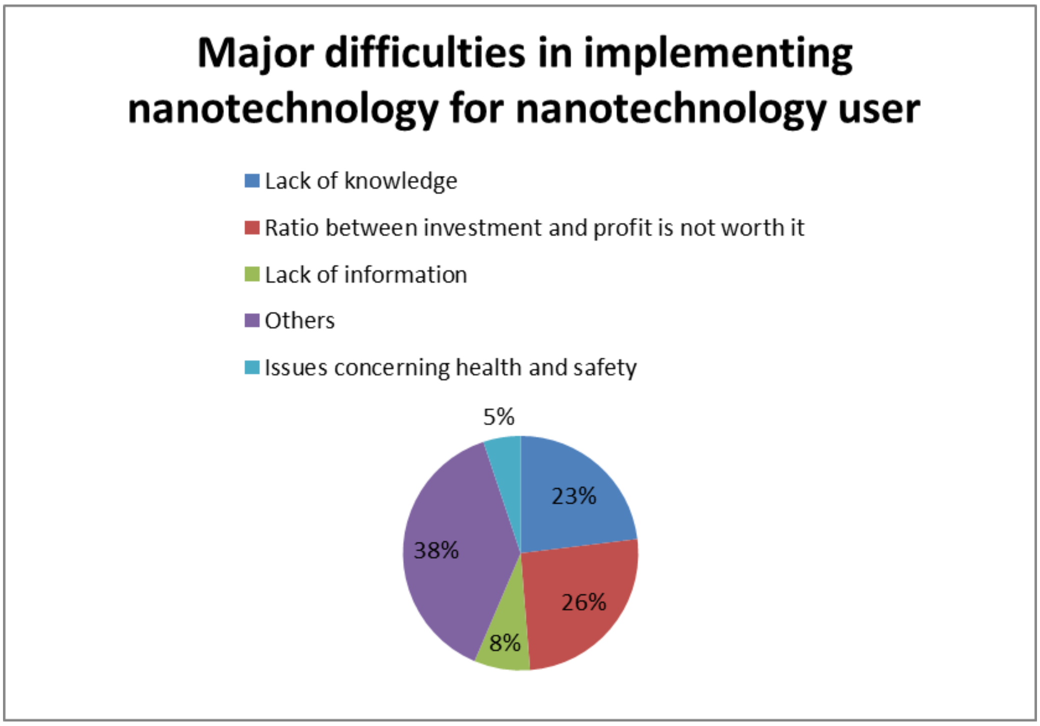


Figure 31: Major difficulties in implementing nanotechnology (nanotechnology user)

- **Expectations to continue using nanotechnology in the future**

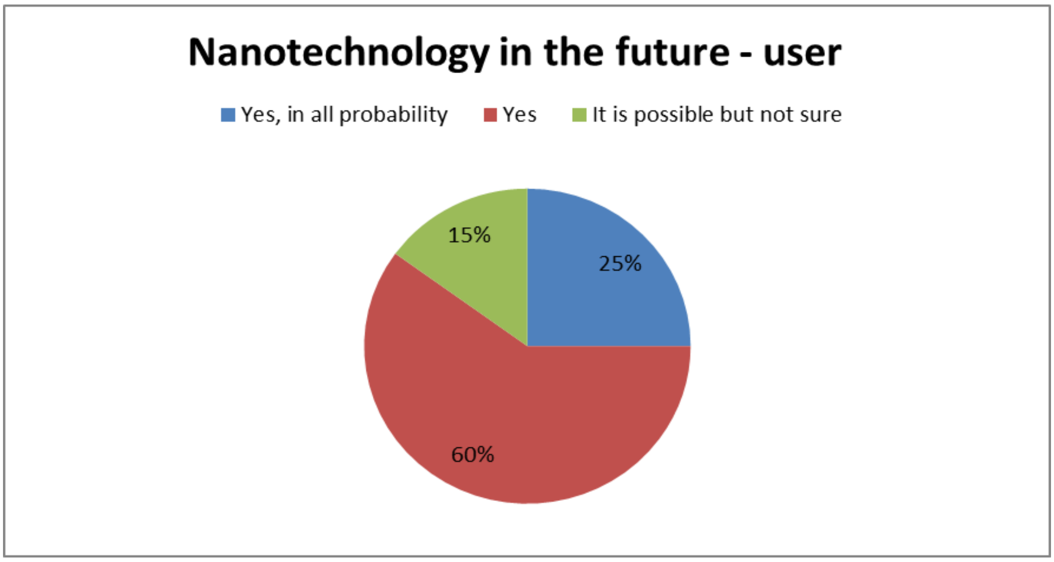


Figure 32: Nanotechnology usage in the future for actual users

5.4. Non-nanotechnology user

- **Investing in technological innovation using nanotechnology intention**

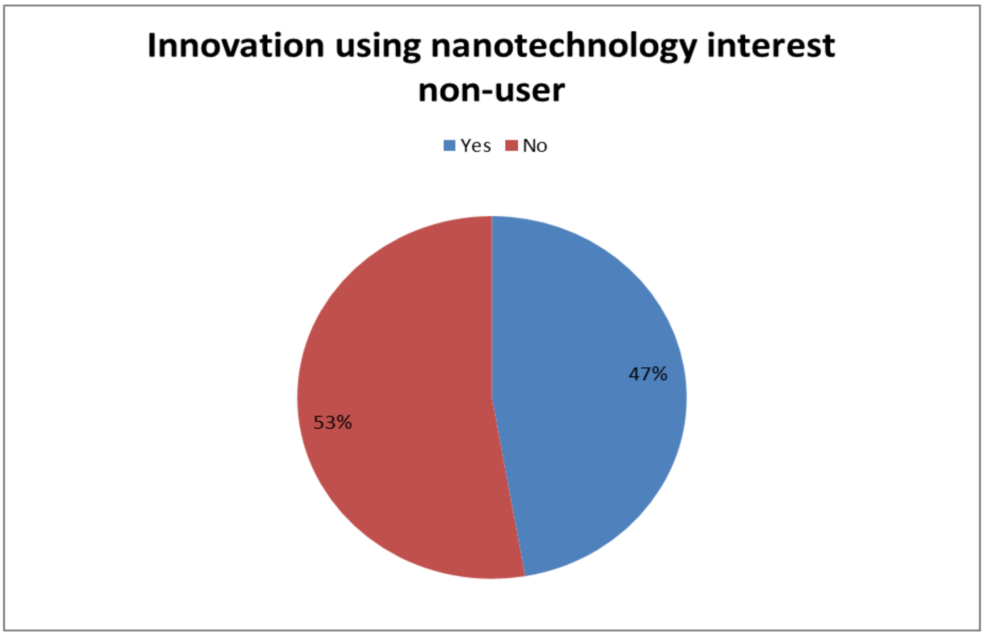


Figure 33: Investing in technological innovation using nanotechnology intention

- **Major obstacles for nanotechnology usage: actual non-users**

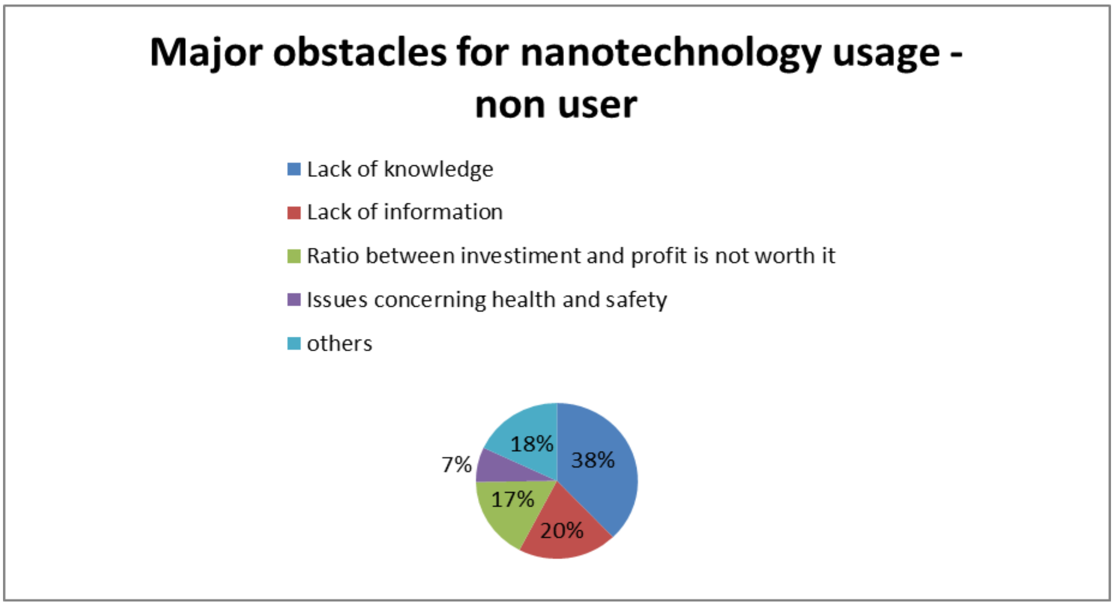


Figure 34: Major obstacles for nanotechnology usage: actual non-users

6. Industrial applications of nanotechnology in industry

The strength of nanotechnology lies in bringing together apparently discrepant areas of science to create new knowledge and expertise. The European research enterprise aims to facilitate that interaction between disciplines as well as between academia and industry to promote technological innovation.

In table 6, an overview of different applications is presented, as referenced by Rittner [32].

Table 6 - Overview of different applications [32].

Electronic, optoelectronic magnetic applications	Biomedical, pharmaceutical, cosmetic applications	Energy, catalytic, structural applications
Optical fibers	Antimicrobials	Automotive catalyst
Phosphors	Biodetection and labeling	Membranes
Quantum optical devices	Biomagnetic separations	Fuel Cells
Multilayer capacitors	Drug delivery	Photocatalysts
Magnetic fluid seals and recording media	MRI contrast agents	Propellants
Electroconducting coatings	Orthopedics/Implants	Scratch-resistant coatings
Chemical polishing	Sunscreens	Structural ceramics
Mechanical polishing	Thermal spray coatings	Solar cells

Nanoscience evolution has been enormous. However, it's possible to obtain references in a near past concerning applications. In next sub-sections the current key and potential short and long-term applications of nanomaterials are presented. Most current applications represent evolutionary developments of existing technologies, as for example the reduction in size of electronic devices.

One of the EU programme's key goals is the scale-up of nanotechnology-based processes to pilot-line production.

Nanotechnology has the potential to improve other areas of industrial production, as well as catalysts, moving towards added-value innovative and sustainable processes that use less energy and raw materials. As well as harnessing nanotechnology in existing industrial processes, there is also a growing need to produce nanomaterials themselves on an industrial scale. Integral to this is the safe handling of nanomaterials and the safety of products throughout their entire lifecycle.

The impact of nanotechnology is staggeringly broad in this context, ranging from the production of electrochromic eyewear [33] all the way through to the use of smart magnetic particles for separation and extraction in biotechnology, food and pharmaceutical applications [34]. Other pilot-line projects aim to incorporate nanoparticles into papermaking [35] and nanomaterial-based fluid lubricants [36].

Meanwhile, other research efforts are focusing on a broad sweep of products and processes from life-saving antimicrobial textiles [37] to metal-nanoparticle coatings conveying high temperature resistance on gas and steam turbines, aircraft engines, boilers, waste incinerators and fire protection materials.

Nanomaterials could also provide a solution to the problem of metal corrosion, which affects many sectors and costs some 3%-4% of GDP worldwide a year. Nanostructured coatings could offer corrosion resistance to high-precision mechanical parts, aircraft brake systems and gas-handling components [38], while coatings for steel parts based on nanoceria, nanoclay and conductive polymers could avoid currently used toxic and hazardous compounds [39]. Texturing surfaces on the nanoscale either physically or chemically can bring other unique properties. By creating a regularly roughened surface, the so-called lotus effect ensures that dirt and water just run off. Italian automaker Fiat is already exploring these water-hating (or superhydrophobic) surfaces for car wing mirrors, while glass-makers are actively pursuing self-cleaning windows. Nanotextured surfaces even hold promise for prolonging the life and efficiency of medical devices.

Meanwhile, composite materials – incorporating novel carbon materials like nanotubes or fibres – promise lighter aircraft, improved fuel economy and reduced emissions. Nanocomposites and coatings based on polyester resins and nanoclays provide another set of useful properties – fire retardency. Adding nanoparticles to thermoplastic polymers improves resistance to fire without resorting to halogen-based retardents, which have raised health and environmental concerns over the production of toxic compounds if they do ignite.

Carbon-based nanocomposites could also find application in diverse areas from antistatic packaging for electronic goods to scaff olds for tissue engineering. Adding carbon nanotubes to thermoplastics holds promise for new composites for the automotive, rail, space, civil engineering and biomedical sectors as well [40, 41]. Different filler and matrix choices can yield radically different materials. For example, wrapping sugar molecules – or polysaccharides – embedded with nanoparticles around cellulose material yields a rather different bio-based smart composite that could find use in medical or electronic devices where its flame resistance, conductivity, antimicrobial activity and barrier properties are vital [42]. Basing composites on natural fibres and biopolymers could bring sustainability to numerous sectors, including automotives where such materials are alternatives to traditional plastic materials used for door panels, dashboards and other internal fittings [43], as well as household appliances [44].

Even the most traditional of materials like stone and cement are getting a nanoscale makeover. Nanocoatings are being developed to help in the conservation of stone buildings [45] and fibre-reinforced concrete is being advanced from its position as a ‘dirty’ material emitting nearly a ton of carbon dioxide for every ton produced to a cleaner, more sustainable one.

Another project aims to create a nanoscale ‘foam’ core coated with a nanoclay fibre-reinforced cement ‘skin’, which can be produced in a low-energy extrusion process, minimising the use of environmentally unfriendly additives.

Nanomaterials are also proving their worth as exceedingly fine sieves to clean up water and separate gases. The nanosized pores in polymer- or silicon-based membranes can be used to trap unwanted elements from water [46] or separate gases like hydrogen and carbon dioxide in industrial processes [47]. One of the potentially most useful applications of these ultra thin membranes is in a process known as electro dialysis, where industrial waste material (usually salts) is removed from wastewater streams [48].

To serve new industrial applications with the large-scale quantities of nanomaterials needed, new manufacturing processes are required. Much effort is being directed at developing reliable means of producing various nanomaterials on a large scale, from inorganic nanotubes and ceramics to carbon-based nanomaterials and nanostructured metal alloys. Research activities are looking at cutting-edge materials like graphene, for example, which holds promise for a number of fields [49]. EU-backed projects are exploring roll-based chemical vapour deposition of graphene [50] and mass production of carbon nanotubes using wafer-scale equipment developed for the semiconductor chip industry [51].

6.1. Current applications in the market

Nanoscale materials, as mentioned above, have been used for many decades in several applications and are already present in a wide range of products, including mass-market consumer ones. Among the most known is glass for windows which are coated with titanium oxide nanoparticles that react to sunlight to break down dirt. When water hits the glass, it spreads evenly over the surface, instead of forming droplets, and runs off rapidly, taking the dirt, off with it [52].

Nanotechnologies are also used by automotive industry to reinforce certain properties of car bumpers and to improve the adhesive properties of paints. Other uses of nanotechnologies in consumer products include [52, 53]:

- Sunglasses

For protective and antireflective ultra thin polymer coatings, and also scratch-resistant coatings based on nanocomposites that are transparent, ultra-thin, simple to care for and well suited for daily use, being reasonably priced.

- Textiles

They can incorporate nanotechnology to make practical improvements to such properties as windproofing and waterproofing, preventing wrinkling or staining and guarding against electrostatic discharges. Windproof and waterproof properties of a ski jacket, for example, are obtained not by a surface coating of the jacket but by the use of nanofibers. Given that low-cost countries are capturing an ever-increasing share of clothes manufacturing, high-cost regions are likely to focus on high-tech clothes with additional benefits for users that nanotech can help implement. Future projects include clothes with additional electronic functionalities, the so-called ”smart clothes” or ”wearable electronics”. These could include sensors to monitor body functions or release drugs in the required amounts, self-repairing mechanisms or even access to the Internet.

- Sports equipment

An example of high-performance ski wax, which produces a hard and fast-gliding surface, is already in use. The ultra-thin coating lasts longer than conventional waxing systems. Tennis rackets with carbon nanotubes have increased torsion and flex resistance. The rackets are more rigid than current carbon rackets and pack more power. Long-lasting tennis-balls are made by coating the inner core with clay polymer nanocomposites, with twice the lifetime of conventional balls.

- Sunscreens and cosmetics

Customers like products that are translucent because they suggest purity and cleanliness, and L'Oréal discovered that when lotions are ground down to 50 or 60 nm, they let light through. For sunscreens, mineral nanoparticles (such as titanium dioxide) offer several advantages. Traditional chemical UV protection suffers from its poor long-term stability, but titanium dioxide nanoparticles have a comparable UV protection property as the bulk material, but lose the cosmetically undesirable whitening as the particle size is decreased. For anti-wrinkle creams, a polymer capsule is used to transport active agents like vitamins.

Nanosized titanium dioxide and zinc oxide are currently used in some sunscreens, as they absorb and reflect ultraviolet (UV) rays and yet are transparent to visible light and so are more appealing to the consumer [53].

Nanosized iron oxide is present in some lipsticks as a pigment although not being allowed in Europe. The use of nanoparticles in cosmetics has raised a number of concerns about consumer safety [53].

- Televisions

Carbon nanotubes could be in use by late 2006 according to Samsung16. Manufacturers expect these "field effect displays," (FED) to consume less energy than plasma or liquid crystal display (LCD) sets and combine the thinness of LCD and the image quality of traditional cathode ray tubes (CRT). The electrons in an FED are fired through vacuum at a layer of phosphorescent glass covered with pixels. But the electron source is only 1 to 2 mm from the target glass instead of 60cm with CRT, and, instead of one electron source, the electron gun, there are thousands. FED contain less electronics than LCD and can be produced in a wide range of sizes. Toshiba, for example, will offer screen sizes of at least 50 inches, around 130 cm

- Composites

Materials that combine one or more separate components and which are designed to exhibit overall the best properties of each component. This multi-functionality applies not only to mechanical properties, but extends to optical, electrical and magnetic ones. Currently, carbon fibres and bundles of multi-walled CNTs are used in polymers to control or enhance conductivity, with applications such as antistatic packaging. The use of individual CNTs in composites is a potential long-term application. A particular type of nanocomposite is where nanoparticles act as fillers in a matrix; for example, carbon black used as a filler to reinforce car tires. However, particles of carbon black can range from tens to hundreds of nanometres in size, so not all carbon black falls within our definition of nanoparticles.

- Clays

Containing naturally occurring nanoparticles have long been important as construction materials and are undergoing continuous improvement. Clay particle based composites – containing plastics and nano-sized flakes of clay – are also finding applications such as use in car bumpers.

- Coatings

With a thickness controlled at the nano- or atomic scale have been in routine production for some time, for example in MBE or metal oxide CVD for optoelectonic devices, or in catalytically active and chemically functionalized surfaces. Recently developed applications include the self-cleaning window, which is coated in highly activated titanium dioxide, engineered to be highly hydrophobic (water repellent) and antibacterial, and coatings based on nanoparticulate oxides that catalytically destroy chemical agents as described by Royal Society 2004. Wear and scratch-resistant hard coatings are significantly improved by nanoscale intermediate layers (or multilayers) between the hard outer layer and the substrate material. The intermediate layers give good bonding and graded matching of elastic and thermal properties, thus improving adhesion. A range of enhanced textiles, such as breathable, waterproof and stain resistant fabrics, have been enabled by the improved control of porosity at the nanoscale and surface roughness in a variety of polymers and inorganics.

- Tougher and harder cutting tools

Made of nanocrystalline materials, such as tungsten carbide, tantalum carbide and titanium carbide, are more wear and erosion-resistant, and last longer than their conventional (large-grained) counterparts. They are finding applications in the drills used to bore holes in circuit boards.

6.2. Short and medium-term applications

- Paints

Incorporating nanoparticles in paints can improve their performance, for example by making them lighter and giving them different properties. Thinner paint coatings (‘lightweighting’), used for example on aircraft, would reduce their weight, which could be beneficial to the environment. However, the whole life cycle of the aircraft needs to be considered before overall benefits can be claimed. It may also be possible to substantially reduce solvent content of paints, with resulting environmental benefits. New types of fouling resistant marine paint could be developed and are urgently needed as alternatives to tributyl tin (TBT), now that the ecological impacts of TBT have been recognized. Anti-fouling surface treatment is also valuable in process applications such as heat exchange, where it could lead to energy savings. If they can be produced at sufficiently low cost, fouling-resistant coatings could be used in routine duties such as piping for domestic and industrial water systems. It remains speculation whether very effective anti-fouling coatings could reduce the use of biocides, including chlorine.

Other new, and more medium to long-term, application for nanoparticles might lies in paints that change colour in response to variations in temperature or chemical environment, or paints that have reduced infra-red absorptivity and therefore reduce heat loss.

Concerns about the health and environmental impacts of nanoparticles may require the need for the durability and abrasion behaviour of nano-engineered paints and coatings to be addressed, so that abrasion products take the form of coarse or microscopic agglomerates rather than individual nanoparticles.

- Remediation

The potential of nanoparticles to react with pollutants in soil and groundwater and transform them into harmless compounds is being researched. In one pilot study the large surface area and high surface reactivity of iron nanoparticles were exploited to transform chlorinated hydrocarbons (some of which are believed to be carcinogens) into less harmful end products in groundwater (Zhang 2003). It is also hoped that they could be used to transform heavy metals such as lead and mercury from bioavailable forms into insoluble forms. Serious concerns have been raised over the uncontrolled release of nanoparticles into the environment.

- Fuel Cells

Engineered surfaces are essential in fuel cells, where the external surface properties and the pore structure affect performance. The hydrogen used as the immediate fuel in fuel cells may be generated from hydrocarbons by catalytic reforming, usually in a reactor module associated directly with the fuel cell. The potential use of nano-engineered membranes to intensify catalytic processes could enable higher-efficiency, small-scale fuel cells. These could act as distributed sources of electrical power. It may eventually be possible to produce hydrogen locally from sources other than hydrocarbons, which are the feedstocks of current attention.

- Displays

The huge market for large area, high brightness, flat-panel displays, as used in television screens and computer monitors, is driving the development of some nanomaterials. Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride synthesized by sol–gel techniques (a process for making ceramic and glass materials, involving the transition from a liquid ‘sol’ phase to a solid ‘gel’ phase) are candidates for the next generation of light-emitting phosphors. CNTs are being investigated for low voltage field-emission displays; their strength, sharpness, conductivity and inertness make them potentially very efficient and long-lasting emitters.

- Batteries

With the growth in portable electronic equipment (mobile phones, navigation devices, laptop computers, remote sensors), there is great demand for lightweight, high-energy density batteries. Nanocrystalline materials synthesized by sol–gel techniques are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than conventional ones. Nickel–metal hydride batteries made of nanocrystalline nickel and metal hydrides are envisioned to require less frequent recharging and to last longer because of their large grain boundary (surface) area.

- Fuel additives

The expanded set of tools which has been made available to researchers through advances in nanotechnology is being used to create novel fuel additives which aim to improve combustion cleanliness in engines [54]. Research is underway into the addition of nanoparticulate ceria (cerium oxide) to diesel fuel to improve fuel economy by reducing the degradation of fuel consumption over time (Oxonica 2003).

For example, F2-21® eeFuel® is a highly concentrated fuel additive utilizing high-tech liquid nanotechnology. Inside the fuel tank, F2-21® eeFuel® builds an exceptionally stable three dimensional lattice structure consisting of sub-microscopic nano-clusters, all evenly distributed within the fuel [55]. These F2-21 nano-clusters are physically, chemically, or catalytically active depending on the stage of the combustion cycle [55]

- Catalysts

In general, nanoparticles have a high surface area, and hence provide higher catalytic activity. Nanotechnologies are enabling changes in the degree of control in the production of nanoparticles, and the support structure on which they reside. It is possible to synthesise metal nanoparticles in solution in the presence of a surfactant to form highly ordered monodisperse films of the catalyst nanoparticles on a surface. This allows more uniformity in the size and chemical structure of the catalyst, which in turn leads to greater catalytic activity and the production of fewer by products.

It may also be possible to engineer specific or selective activity. These more active and durable catalysts could find early application in cleaning up waste streams. This will be particularly beneficial if it reduces the demand for platinum-group metals, whose use in standard catalytic units is starting to emerge as a problem, given the limited availability of these metals.

- Carbon nanotube composites

CNTs have exceptional mechanical properties, particularly high tensile strength and light weight. An obvious area of application would be in nanotube reinforced composites, with performance beyond current carbon-fibre composites. One current limit to the introduction of CNTs in composites is the problem of structuring the tangle of nanotubes in a well-ordered manner so that use can be made of their strength.

Another challenge is generating strong bonding between CNTs and the matrix, to give good overall composite performance and retention during wear or erosion of composites. The surfaces of CNTs are smooth and relatively unreactive, and so tend to slip through the matrix when it is stressed. One approach that is being explored to prevent this slippage is the attachment of chemical side-groups to CNTs, effectively to form ‘anchors’. Another limiting factor is the cost of production of CNTs. However, the potential benefits of this light, high strength material in numerous applications for transportation are such that significant further research is likely to appear.

- Lubricants

Nanospheres of inorganic materials could be used as lubricants, in essence by acting as nanosized 'ball bearings'. The controlled shape is claimed to make them more durable than conventional solid lubricants and wear additives. Whether the increased financial and resource cost of producing them is offset by the longer service life of lubricants and parts remains to be investigated. It is also claimed that these nanoparticles reduce friction between metal surfaces, particularly at high normal loads. If so, they should find their first applications in high-performance engines and drivers; this could include the energy sector as well as transport. There is a further claim that this type of lubricant is effective even if the metal surfaces are not highly smooth. Again, the benefits of reduced cost and resource input for machining must be compared against production of nanolubricants. In all these applications, the particles would be dispersed in a conventional liquid lubricant; design of the lubricant system must therefore include measures to contain and manage waste.

- Magnetic materials

It has been shown that magnets made of nanocrystalline yttrium–samarium–cobalt grains possess unusual magnetic properties due to their extremely large grain interface area (high coercivity can be obtained because magnetization flips cannot easily propagate past the grain boundaries). This could lead to applications in motors, analytical instruments like magnetic resonance imaging (MRI), used widely in hospitals, and microsensors. Overall magnetisation, however, is currently limited by the ability to align the grains' direction of magnetisation.

Nanoscale-fabricated magnetic materials also have applications in data storage. Devices such as computer hard disks depend on the ability to magnetize small areas of a spinning disk to record information. If the area required to record one piece of information can be shrunk in the nanoscale (and can be written and read reliably), the storage capacity of the disk can be improved dramatically. In the future, the devices on computer chips which currently operate using flows of electrons could use the magnetic properties of these electrons, called spin, with numerous advantages.

Recent advances in novel magnetic materials and their nanofabrication are encouraging in this respect.

- Medical implants

Current medical implants, such as orthopedic implants and heart valves, are made of titanium and stainless steel alloys, primarily because they are biocompatible. Unfortunately, in some cases these metal alloys may wear out within the lifetime of the patient. Nanocrystalline zirconium oxide (zirconia) is hard, wear resistant, bio-corrosion resistant and bio-compatible. It therefore presents an attractive alternative material for implants. It and other nanoceramics can also be made as strong, light aerogels by sol–gel techniques.

Nanocrystalline silicon carbide is a candidate material for artificial heart valves primarily because of its low weight, high strength and inertness.

- Machinable ceramics

Ceramics are hard, brittle and difficult to machine. However, with a reduction in grain size to the nanoscale, ceramic ductility can be increased. Zirconia, normally a hard, brittle ceramic, has even been rendered superplastic (for example, able to be deformed up to 300% of its original length). Nanocrystalline ceramics, such as silicon nitride and silicon carbide, have been used in such automotive applications as high-strength springs, ball bearings and valve lifters, because they can be easily formed and machined, as well as exhibiting excellent chemical and high-temperature properties.

They are also used as components in high-temperature furnaces. Nanocrystalline ceramics can be pressed into complex net shapes and sintered at significantly lower temperatures than conventional ceramics.

- Water purification

Nano-engineered membranes could potentially lead to more energy-efficient water purification processes, notably in desalination by reverse osmosis. Again, these applications would represent incremental improvements in technologies that are already available. They would use fixed nanoparticles, and are therefore distinct from applications that propose to use free nanoparticles.

- Military battle suits

Enhanced nanomaterials form the basis of a state of- the-art 'battle suit' that is being developed by the Institute of Soldier Nanotechnologies at Massachusetts Institute of Technology, USA (MIT 2004). A short-term development is likely to be energy-absorbing materials that will withstand blast waves; longer-term are those that incorporate sensors to detect or respond to chemical and biological weapons (for example, responsive nanopores that 'close' upon detection of a biological agent). There is speculation that developments could include materials which monitor physiology while a soldier is still on the battlefield, and uniforms with potential medical applications, such as splints for broken bones.

- Electronics and communications

Recording using nanolayers and dots, flat-panel displays, wireless technology, new devices and processes across the entire range of communication and information technologies, factors of thousands to millions improvements in both data storage capacity and processing speeds and at lower cost and improved power efficiency compared to present electronic circuits

- Chemicals and materials

Catalysts that increase the energy efficiency of chemical plants and improve the combustion efficiency (thus lowering pollution emission) of motor vehicles, super-hard and tough (i.e., not brittle) drill bits and cutting tools, "smart" magnetic fluids for vacuum seals and lubricants.

- Pharmaceuticals, healthcare, and life sciences

Nanostructured drugs, gene and drug delivery systems targeted to specific sites in the body, bio-compatible replacements for body parts and fluids, self-diagnostics for use in the home, sensors for labs-on-a-chip, material for bone and tissue regeneration.

- Manufacturing

Precision engineering based on new generations of microscopes and measuring techniques, new processes and tools to manipulate matter at an atomic level, nanopowders that are sintered into bulk materials with special properties that may include sensors to detect incipient failures and actuators to repair problems, chemical-mechanical polishing with nanoparticles, self-assembling of structures from molecules, bio-inspired materials and biostructures.

- Energy technologies

New types of batteries, artificial photosynthesis for clean energy, quantum well solar cells, safe storage of hydrogen for use as a clean fuel, energy savings from using lighter materials and smaller circuits

- Space exploration

Lightweight space vehicles, economic energy generation and management, ultrasmall and capable robotic systems

- Environment

Selective membranes that can filter contaminants or even salt from water, nanostructured traps for removing pollutants from industrial effluents, characterisation of the effects of nanostructures in the environment, maintenance of industrial sustainability by significant reductions in materials and energy use, reduced sources of pollution, increased opportunities for recycling

- National security

Detectors and detoxifiers of chemical and biological agents, dramatically more capable electronic circuits, hard nanostructured coatings and materials, camouflage materials, light and self-repairing textiles, blood replacement, miniaturized surveillance systems.

- Computer chips

The dominant role of miniaturisation in the evolution of the computer chip is reflected in the fact that the ITRS roadmap defines a manufacturing process standard – a technology node – in terms of a length. The current 130 nm technology node that produces the Intel Xeon processor defines the size of the DRAM (dynamic random access memory) half-pitch (half the distance between two adjacent metal wires in a memory cell).

This is a requirement on the lithography, process technology and metrology needed to manufacture a working device to this tolerance. As a comparison, the 1971 Intel 4004 chip used 10,000 nm technology; the chips of 2007 and 2013 will require 65nm and 32nm technology, respectively. In the broadest sense, computer chips in current manufacture are therefore already using nanotechnologies and have been so doing for over 20 years. Furthermore, it is not simply the DRAM half-pitch that is on the nanometer scale. All the technology that goes into the research, metrology and production of chips has been working, in some cases, at the sub-nanometre atomic level. The variety of tools that support the IT industry includes computer modelling of advanced devices and materials atom by atom, microscopies that can image single atoms, metrologies that can define the absolute position of a single atomic defect over a 30cm diameter wafer (the substrate used for computer chips), thin-film growth processes that can produce layers of material with atomic precision, and lithographies that can 'write' features, such as the DRAM cell, with an accuracy of sub-10nm.

- Information storage

A technology that has necessarily developed in tandem with IT is that of memory for data storage. This can be divided into two quite different types: solid-state memory such as DRAM that a processor chip would use or flash memory for storing images in a digital camera; and disk-based memory such as the magnetic hard drives as found in all computers. Solid-state memory essentially uses the same processes and technology as the computer chip, with very similar design rules and a similar emphasis on packing more memory into a given area to increase total memory per device. The development of the hard disk drive, however, has taken a quite different route in evolution as it is based on reading and writing information magnetically to a spinning disk. It is therefore primarily mechanical, or more strictly electro-mechanical, and presents quite different technical challenges. Once again, however, the importance of length scales is paramount as the ideal disk drive is one that has the minimal physical size with a massive ability to store data. This is reflected in the evolution of the disk drive over the past 50 years. The first magnetic hard drive was developed by IBM in 1956 and required fifty 24 inch disks to store five megabytes (million bytes) of data. In 1999 IBM introduced a 73gigabyte (thousand million bytes) drive that could fit inside a personal computer; that is, over 14,000 times the available data storage in a device less than one thousandth the size of the 1956 drive. Although the individual bits of magnetic information that are written onto the disk drive to give it the high-density storage are currently smaller than 100 nm, the constraints related to this nanotechnology on other aspects of the drive require fabrication of components with even greater precision. The importance of this nanotechnology in the related compact disk (CD) and digital versatile disk (DVD) drives that are now commonplace is equally ubiquitous.

- Optoelectronics

The other crucial element of the IT revolution, optoelectronics, relates to devices that rely on converting electrical signals to and from light for data transmission, for displays for optical-based sensing and, in the future, for optical-based computing. Technology in this sector is strongly associated with those described above, and relies substantially on the tools developed there. Although some optoelectronic devices do not depend so critically on miniaturisation as computer chips do, there is nevertheless a similar trend towards miniaturisation, with some existing components, such as quantum-well lasers and liquid crystal displays, requiring nanometre precision in their fabrication.

6.3. Current and near past research projects in nanotechonology

6.3.1. *Nanoelectronics*

Over the last fifty years, semiconducting materials – primarily silicon – have enabled a revolution in ICT, being an example the FP7 ICT GRAND project assessing graphene nanoribbons for CMOS processing and on-chip integration. Heating is a problem at the macroscale too for high-tech industries reliant on large-scale computing. It can take as much energy to cool as it does to run a data centre. But nanotechnology can help.

A new liquid coolant using engineered nanoparticles, which could be up to 40% more efficient than conventional coolants, is being developed as part of a the NanoHex FP7 project, that aims to develop and optimise safe processes for the production of high performance nanofluid coolants for use in industrial heat management, applied and recycled. The recent developments in the design and synthesis of nanoscale building blocks as active elements in opto- or bio-electronic devices with tailored electronic functionality have the potential to open up new horizons in nanoscience and also revolutionize multi-billion dollar markets across multiple technology sectors including healthcare, printable electronics, and security. Ligand-stabilized inorganic nanocrystals (~2-30 nm core diameters) and functional organic molecules are attractive building blocks due to their size dependent opto-electronic properties, the availability of low-cost synthesis processes and the potential for formation of ordered structures via (bio) molecular recognition and self-assembly. Harnessing the complementary properties of both nanocrystals and functional molecules thus represents a unique opportunity for generation of new knowledge and development of new classes of high knowledge-content materials with specific functionality tailored for key applications, e.g., printable electronics, biosensing or energy conversion in the medium term, and radically new information and signal processing paradigms in the long term. Self-assembly and self-organisation processes offer the potential to achieve dimensional control of novel multifunctional materials at length scales not accessible to conventional top-down technologies based on lithography. The SOI-HITS intends to develop sensors with built-in electronic interface that will be designed to work in harsh high temperature environments. Initially, efforts are looking to improve CMOS technology using novel semiconducting materials with advantages over silicon such as germanium and III-V compound semiconductors [2, 56].

But silicon, in the form of nanowires thousands of times smaller than the diameter of a human hair, could continue to be the material of choice for transistors. In the move to sub-22 nm nodes, interest is turning to novel carbon materials such as nanotubes, molecular wires and graphene, whose novel electronic properties have already made it a prime candidate for beyond-CMOS switches and interconnects with feature sizes down to just 5 nm [2, 57, 58]. Interconnects, which link together devices on a chip, are crucial to operating speed. Historically, interconnects were fabricated from aluminium, but as the number of transistors has increased, wiring has switched to copper. But with the density of interconnects increasing still further, new options are required. Carbon nanotubes are among the most promising alternatives under investigation that could be cost effective and easy to implement on an industrial scale [2, 59]. They could also help solve one of the other major issues facing chip designers, local heating from the close proximity of many individual devices [2, 60]. Future devices will need to dissipate heat better and employ ultra-low power transistors [2, 61]. Computer memory, which comes in two forms – primary or volatile memory (RAM, DRAM, cache) for providing information fast and secondary or non-volatile memory ROM, flash, magnetic storage, hard and optical disks) for program and data storage, will require new magnetic materials.

Regardless of type, all memory devices store information as a binary code using tiny magnetic grains, which can be either magnetised (denoting ‘1’) or unmagnetised (0). Each storage unit or ‘bit’ comprises around 100-600 grains, which are now typically just 10 nm in size. Going smaller than this will make it increasingly difficult if not impossible to separate signals from noise, so new data storage concepts are needed. One promising option is spintronics, where the ‘up’ or ‘down’ spin of an electron is used to store information instead [29]. Graphene and single-walled carbon nanotubes are compelling candidates for such spintronic devices [30], as are magnetic nanowires, which could take memory into three-dimensions to provide ultra-high density information storage.

Despite the many advantages, current silicon-based electronic manufacturing methods are expensive, energy-intensive and time-consuming. But the integration of new materials and processes could change that.

Organic materials, for example, could enable roll-to-roll manufacturing of flexible electronic and photonic devices, with many benefits in lower production costs and novel applications. Flexible, transparent organic electronics could provide low power displays for e-readers or electronic newspapers, as well as RFID tags and easy-to-use sensors for health and environmental monitoring.

Organic solar cells, meanwhile, could harvest light at lower levels earlier in the day and for most of the year, as well as being integrated into a variety of devices and objects from windows or building facades all the way through to clothing that could recharge small electronic items. Meanwhile, nanoscale materials also herald a new generation of ultra-sensitive, reliable and easy-to-use sensors for healthcare and environmental monitoring. Graphene, for example, can be ideal for highly responsive and durable gas sensors detecting toxic pollutants such as carbon monoxide and dioxide, hydrogen sulphide and ethanol even in very low concentrations. Tiny precision-fabricated machines, known as micro- and nano-electromechanical systems (MEMS, NEMS), could also provide a route to low-cost and low-power sensors for a range of mass-market applications, as well as environmental monitoring and biological sensing. This kind of physical sensor features a suspended beam as small as a nanowire, which vibrates at a particular frequency.

When a target gas molecule, DNA or protein lands on the sensor, the mass of the vibrating wire is altered, producing a change in signal that can be detected.

But the reach of nanoelectronic materials does not end here. Novel nanomaterials and architectures could yield tiny lithium-ion batteries for microelectronic devices and biomedical micro-machines, lighter more flexible overhead power transmission lines, more affordable and efficient solid state LEDs or even a bridge to the biological world, providing implantable devices able to control neuronal signaling and help in the treatment of spinal cord lesions or neurodegenerative diseases.

In Plastic C nanoelectronics is a forefront research area with cross fertilization between the materials science, chemistry, physics, nanotechnology, and engineering communities as detailed in [62] with relevant applications in mechanically flexible SWNT thin-film transistors, carbon nanotube-based printed electronics, electronic textile ("wearable electronics"), multifunctional and responsive elastomers, artificial skin and muscle, flexible gas sensors and plastic solar panels. Nanomaterials can be used not only to manipulate electrons, but also single photons of light, improving a generation of lasers, light sources, optical fibres and detectors as in FAST-DOT 7FP project. Gold is still particularly valued because it works well in visible and near infrared light, ideal for improving photovoltaics, displays, and as part of sensing and detection devices for medicine, biological research and environmental monitoring, as the new generation of low cost, reliable and highly efficient ultra-short pulse broadband lasers could be made possible by using novel semiconductor nanostructure clusters. Novel Quantum Dot (QD) structures and devices have been designed, fabricated and evaluated by the project consortium, detailed theoretical models have been developed for the simulation of QD mode-locked lasers, and novel operating regimes for the mode-locked lasers have been identified. Nanophotonics could also provide a solution to the problem of communication on and between computer chips [63]. Just like the optical fibres that bring digital information to our homes at high speed, light could also relay information around computer chips more readily than an electrical signal. To achieve this, tiny optical interconnects will be needed in the form of self-assembled nanocrystals or nanowires, along with photonic crystals to guide light around sharp corners. Using optical interconnects has the added advantage of consuming much less power.

But one of the more intriguing potential applications of nanophotonics lies in information processing. Because of the ability to manipulate both electronics and photons, nanophotonic devices could serve as a basis for the massively parallel processing of high volumes of information such as from the Large Hadron Collider at CERN, for example, or radar data from traffic monitoring systems.

6.3.2. *Nanomedicine*

There are differences in the definition of nanomedicine. While the US National Nanotech Initiative clearly refers to the nanoscale, the European Science Foundation and the European Technology Platform on Nanomedicine do not refer to it. Alternatively, it stands that nanomedicine is defined as the application of nanotechnology to health [64]. Despite the differences in the terminology, it's possible to refer several applications and projects in this area of nanotechnology in health area. In [65], nanotechnology in medicine is reinforced by unique features such as surface to mass ratio that is much larger than that of other particles, their quantum properties and their abilities to adsorb and carry other compounds such as drugs, probes and protein. Specifically healthcare and life science applications are becoming the most challenging and growing area for nanotechnology based systems and solutions. Nanostructured drugs and delivery systems targeted to specific sites in the body, biocompatible nanomaterials for replacement of dam-aged body parts, innovative bone and tissue reengineering technologies and reliable and cost effective lab-on-a chip biosensors for cancer diagnosis are just a few examples of high value added by nanotechnology for applications in medicine [66].

Implementing advances in nanotechnology and biology in the medical and clinical area will help Europe support its ageing population, which is putting an increasing burden on care networks and the economy. One person in five of the current world population is over 65, a proportion that is set to grow to one in four over the next two decades. The implications are startling: one in three of the population is likely to develop cancer, with currently over 3.2 million cases diagnosed and 1.7 million cancer-related deaths recorded every year in Europe alone. Nanotechnology could transform future cancer treatment, as well as that for a whole host of other chronic and debilitating conditions of old age including cardiovascular disease, rheumatoid and osteo-arthritis, neurodegenerative disorders (Alzheimer's and Parkinson's), improving patient outcomes, reducing long-term social care costs and making healthcare more affordable. Photoluminescent, magnetic and optical properties of nanomaterials to develop super-sensitive, high-throughput clinical, laboratory and point-of-care devices for testing body fluids or cancerous tissue are also a potential area of future development [67].

Cancer-related deaths are often the result of metastases, where the original cancer cells have spread beyond the original tumour site, rather than the primary disease itself. So, parallel projects are focusing on detecting these breakaway disease-bearing cells, (known as circulating tumour cells or CTCs), to give clinicians a low-cost, minimally invasive insight into disease progression and patient response to treatment. Neurodegenerative conditions or dementia, which affect well over 6 million people in Europe with a further 1.4 million cases added each year, present a similar set of problems.

Reliable diagnosis is complex and time-consuming, requiring both psychological testing and brain imaging. But tiny semiconducting quantum dots labelled with antibody biomarkers could provide a much earlier diagnosis via a simple blood test, an approach that could be less onerous for patients and more cost-effective for healthcare providers. Once a basic diagnosis has been made, techniques like magnetic resonance imaging (MRI), X-ray computed tomography (CT) and positron emission tomography (PET) are commonly used to track the progress of disease and monitor the effects of treatment. Tiny magnetic particles of gadolinium are already in use as a contrast agent to improve the quality of information gathered by MRI scans. Taking this approach to the nanoscale could not only improve resolution – potentially down to the level of a single cell – but bring other advantages as well.

Using targeted agents to both identify diseased tissue and deliver pharmacologically active treatments triggered by light, heat or a magnetic field is a new approach known as 'theranostics'. The combination of existing, well-established techniques like MRI and ultrasound with engineered nanoscale delivery and monitoring agents is a very attractive option, which is being pursued as a joint priority area by the EU. One of the 25 or so projects in this effort is exploring the use of ultrasound to create localized pressure or high temperature at a disease site to trigger the release of drugs from nanocarriers.

Magnetic nanoparticles are also ideal carriers for tumour targeting agents and anticancer drugs to transport treatment to precisely where it is needed. An external magnetic field can guide the particles into place and then induce local heating to unzip the agents or drugs33. Another novel approach being pursued is the use of super-fast laser pulses to initiate ablation of cancer cells via noble metal nanoparticles [68].

As far as the patient is concerned, targeted drug delivery promises less invasive treatment with minimized side effects. Particularly in cancer care, reducing the often severe side effects of chemotherapy would be a significant boon for patients, while also reducing unnecessary hospitalizations. The approach could also allow higher local doses to be administered, improving treatment outcomes without increasing side effects. Though straightforward in concept, the practice is demanding, requiring delivery entities that can hold different therapeutic agents, move across barriers like the blood-brain barrier (BBB), recognize a target and deliver a cargo [69].

This revolutionary approach is also being taken to tackle another major health issue facing Europe – diabetes. There are currently 30 million diabetics across the region, but the number is expected to grow to around 50 million by 2025.

As well as potentially devastating effects on patients – including cardiovascular disease, kidney failure, neuropathy, lower limb amputation and blindness – the condition costs European care providers some EUR 50 billion a year. One EU project is focusing on the cause of diabetes, the decline in insulin-producing b-cells, using MRI to diagnose and quantify the disease, as well as deliver therapies. Nanoscale delivery agents could also enable drugs to reach parts of the body that would otherwise be difficult or impossible. For example, treating diseases like Alzheimer's and Parkinson's requires drug molecules to cross the BBB. The fine, thread-like nature of carbon nanotubes could be ideal for piercing the BBB to deliver drugs [70, 71] or worming into tumour cells [72]. If nanoparticles could facilitate the transport of drugs to the brain, it could help address dementia, which affects some 24 million individuals worldwide.

As well as delivering drugs, nanoparticles can also provide a means to attack tumours in novel ways. In an emerging approach known as hyperthermia, magnetic nanoparticles are used to induce local heating at the site of a tumour and destroy diseased tissue [73]. Nanoparticles are simply injected into the body and directed to the tumour site by an external magnetic field via MRI, for example, offering a much less invasive treatment for small, non-defined tumours than conventional surgical approaches.

Nanotechnology could also take medicine in another exciting new direction – assisting the body to repair itself. By bringing together smart nanoscale biomaterials and advanced cell therapy, the body's own self-repair mechanisms can be harnessed to mend, regenerate or replace damaged tissues or organs. Nanostructured or nanopatterned biomaterials serve as intelligent scaffolds that initiate, stimulate and direct the growth of new tissue into the required shape with the correct function. Using nanotextured scaffolds or templates with the right cues, stem cells can be given a growth plan to regenerate tissue. EU research efforts are taking this approach to establish new classes of biomaterials that bridge the gap between the highly complex architecture of the human body and the cruder efforts offered by cell culture [74]. Other efforts are using nanopatterned scaffolds or surfaces to direct the growth of replacement cardiac tissues [75, 76], bone and cartilage [77, 78] and even skin [79].

Many tissue-related injuries have devastating consequences, particularly spinal cord injuries, which affect millions of people worldwide and are hard to treat. Nanofibres are being explored to direct and encapsulate neural stem cells transplanted into the spine to repair the damage and regenerate tissue [80], while neuronal networks are also being grown on nanopatterned surfaces [81]. Implantable devices, made out of biocompatible materials, are also under development to deliver local electrical stimuli to promote nerve regeneration, sense inflammation and control the immune response.

Meanwhile, a better understanding of the physical operation of the body on the nanoscale, bringing together a whole host of disciplines from cognitive science to engineering to cell biology, is heralding a new generation of robotic devices, which will transform the lives of those with physical or visual disabilities. Using sensors based on nanoelectromechanical system (NEMS) arrays and hybrid bio-NEMS, one EU backed project is developing a touch-sensitive robotic finger [82]. Not only could such a robotic system assist the disabled, it could also be used for space exploration, extreme environments or product testing. Nanostructured materials are also being used to make tactile screens to help the visually impaired read complex mathematical equations or graphical images [82].

Other examples are the nanomaterial-based sensors for detection of disease by volatile organic compounds [83], a new diagnosis frontier reviewed on [84] as well in [85] comprehensive review, the current state-of-the art of nanomaterials for cancer diagnosis and treatment is presented. Emerging possibilities and future concepts are discussed as well.

In a clinically relevant review [86], tuberculosis is analyzed, as being a major public health concern worldwide. In this paper, the role and significance of nanoparticle based drug delivery systems are discussed for targeting tuberculosis, including strains that are drug resistant with conventional methods, as well in [87], summarizes the impact of nanotechnology on the diagnosis and treatment of Alzheimer's disease, ranging from circulating amyloid "sinks" to NP-based bio barcodes and many other recent advances, without neglecting potential pitfalls, side effects and safety issue and in the field of dentistry [88].

The [89] describes the utility of tetragonal nano-zirconia (t-ZrO2) to remove trace levels of 134Cs and 137Cs isotope contaminants from 125I solution obtained from neutron irradiation of natural Xe target. A careful scrutiny of the adsorption parameters of t-ZrO2 was considered worthwhile investigating to arrive at the optimum conditions to perform the purification as well as concentration of 125I solution. The procedure proposed here in provides 125I of acceptable purity and radioactive concentration for clinical application.

6.3.3. *Nanobiotechnology*

Where nanotechnology meets biology on the scale of proteins, DNA and cells, revolutionary scientific tools and new applications in nanomedicine and the self-assembly of materials are within reach. Here biological processes are being used in the short-term to inform nanomedicine and biotechnology, while longer-term efforts are mimicking nature to create nanoscale machines like molecular motors.

Nanobiotechnology is providing a variety of new tools for biological research at the single molecule and cellular level. For example, nanoscale porous materials are being explored for DNA sequencing, with the potential for simpler and more accurate detection. Meanwhile, nanostructured materials can also give an insight into how bacteria interact with their physical surroundings [90, 91]. In the long run, a better understanding of the factors affecting bacterial growth could inform the development of much-needed new antibiotics. A more immediate and practical application is the prevention of bacterial build-up on surfaces. Known as 'biofilms', these bacterial buildups can be extremely problematic in healthcare, where their presence on surgical implants or catheters can cause infection. But nanoscale coatings based on plastic-like polymers that release zinc, silver or copper ions during use have the potential to curtail bacterial attachment and prevent buildup.

One of the more science fiction-like goals of this field is the development of molecular machines capable of carrying out complex tasks at the nanoscale. Research efforts are focusing on biomolecular motors [92] and DNA nanomachines based on interlinked ring structures called catenanes or dumbbellshaped molecules known as rotaxanes [93]. Such tiny machines could carry out biosensing tasks, circuit assembly for nanoscale electronic devices or even act as artificial muscles. Meanwhile, taking inspiration from magnetotactic bacteria, researchers are creating magnetite nanoparticle-based nanorobots that can 'swim' in a magnetic field [94]. But friction can be a major problem at such a small scale, so researchers are turning to carbon nanotubes and graphene to get around this sticky problem [95].

Other efforts in nanobiotechnology remain firmly rooted in the present with solutions for intelligent, sustainable food packaging [96], membranes for filtering and purification, and devices for assessing food safety and quality. Making screening methods for foodstuffs quicker, easier, more reliable and cheaper could help avoid situations such as the recent UK scandal involving horse meat. One EU project, for example, is using activated nanostructure sensors to develop monitoring systems able to detect pathogens, drug residues or fraudulent material in milk [97].

The NANOFORBIO 7FP relies on the detection of single proteins, which is crucial for the genomic screening of hereditary diseases. Meanwhile, in a parallel effort, the project is exploring how bacteria respond to being squeezed by a nanostructured physical environment. The study is pushing the boundaries of basic science, but could ultimately yield a radically new approach to antibiotics.

In EMBEK1 is being developed surface coatings for implants and dressing material on which the development of bacteria is hardly possible. These antimicrobial films could be applied to medical devices such as catheters, wound dressings and personal care items.

In biotechnology field, a wide variety applications can be reviewed, for example, in [98-100].

6.3.4. *Energy and Environment*

Silicon thin film devices currently show limited conversion efficiencies, but radical new synthesis routes could improve this problem [101]. Alternatively, other thin-film materials, like cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) are moving into commercial production. CIGS has many advantages, but commercialization continues to lag behind because costly and complex vacuum-based deposition processes are required. New vacuum-free and environmentally friendly production routes to CIGS solar cells are, therefore, a high priority [102, 103]. Meanwhile, the already-promising properties of CdTe could be boosted through nanostructuring [104]. Solar cells based on plastic and solution processable inorganic materials provide another route to cost-effective production, but require a paradigm shift improvement in device performance [105]. Hybrid polymer-inorganic devices that use organic dyes to facilitate energy conversion – known as dye-sensitized solar cells – offer perhaps the greatest hope of improvements in efficiency. But adding semiconducting quantum dots to polymer-based solar cells could also boost performance [106]. While much of the impetus here is to move away from traditional silicon-based solar cells, silicon could still provide a route to cost effective photovoltaics if nanocrystals could be harnessed in hybrid devices [107]. By reducing the amount of silicon used, costs can be cut while still exploiting the material's high conversion efficiency and low environmental impact. Simultaneously, research efforts are also investigating other routes to high-efficiency, low-cost solar cells using semiconducting nanowires [108, 109], the plasm on effect [110] and semiconductor quantum dots for light harvesting [111].

As well as improving renewable energy technologies, new materials are urgently needed that boost energy efficiency and capture energy that would otherwise go to waste. Thermoelectric devices require no fuel and have no moving parts, but can recapture or 'harvest' energy that would otherwise be lost, for example from the flue gases venting from power plants to vehicle exhaust [112]. Embedding nanoparticles in thermoelectric alloys could create nanocomposites able to perform efficient waste heat recovery from high-temperature industrial processes and automotive engines [113]. Regular arrays of silicon-germanium nanowires and quantum dots, or superlattices, could even harvest excess heat from microelectronic chips to provide a small-scale on-chip energy sources [114]. As well as on-chip sustainable energy generation, the set-up could lead to thermoelectric generators for domestic or industrial use.

Concerns over local air quality and global warming have focused attention on emissions from road transport. An alternative to gasoline is urgently needed to tackle these issues. In the short-term, battery-powered hybrid and plug-in electric vehicles are already on the market but serious improvements in these technologies are required for mainstream adoption. Further down the road, hydrogen offers a like-for-like replacement fuel for gasoline, but major challenges remain in its storage, production and delivery.

6.4. Potential applications in several sectors

Following the descriptions above, and separating the applications per broad areas, in this section, potential industrial applications are presented in order to obtain emergent opportunities of nanotechnology in the industrial sector [52].

6.4.1. *Nanomedicine sector*

Medical and life-science applications may prove to be the most lucrative markets for nanotechnologies, with "lab-on-a-chip" devices already being manufactured and animal testing and early clinical trials starting on nanotechniques for drug delivery. However, the long product approval processes typical of the domain may mean that the health benefits to users and economic benefits to companies will take longer to realise than in other domains. Nanotech's promise comes from the fact that nanoscale devices are a hundred to ten thousand times smaller than human cells and are similar in size to large biological molecules ("biomolecules") such as enzymes and receptors. For example, haemoglobin, the molecule that carries oxygen in red blood cells, is approximately 5 nm in diameter, DNA 2.5, while a quantum dot is about the same size as a small protein (<10 nm) and some viruses measure less than 100 [nm]. Devices smaller than

50 nm can easily enter most cells, while those smaller than 20 nm can move out of blood vessels as they circulate through the body.

Because of their small size, nanoscale devices can readily interact with biomolecules on both the surface of cells and inside of cells. By gaining access to so many areas of the body, they have the potential to detect disease and deliver treatment in new ways. Nanotechnology offers the opportunity to study and interact with cells at the molecular and cellular scales in real time, and during the earliest stages of the development of a disease. And since nanocomponents can be made to share some of the same properties as natural nanoscale structures, it is hoped to develop artificial nanostructures that sense and repair damage to the organism, just as naturally-occurring biological nanostructures such as white blood cells do.

Cancer research illustrates many of the medical potentials of nanotechnologies in the longer term. It is hoped that nanoscale devices and processes will help to develop [115]:

• Imaging agents and diagnostics that will allow clinicians to detect cancer in its earliest stages;

• Systems that will provide real-time assessments of therapeutic and surgical efficacy for accelerating clinical translation;

• Multifunctional, targeted devices capable of bypassing biological barriers to deliver multiple therapeutic agents directly to cancer cells and those tissues in the microenvironment that play a critical role in the growth and metastasis of cancer;

• Agents that can monitor predictive molecular changes and prevent precancerous cells from becoming malignant;

• Novel methods to manage the symptoms of cancer that adversely impact quality of life;

• Research tools that will enable rapid identification of new targets for clinical development and predict drug resistance.

➢ Drug delivery

This may be the most profitable application of nanotechnology in medicine, and even generally, over the next two decades. Drugs need to be protected during their transit through the body to the target, to maintain their biological and chemicals properties or to stop them damaging the parts of the body they travel through. Once a drug arrives at its destination, it needs to be released at an appropriate rate for it to be effective.

This process is called encapsulation, and nanotechnology can improve both the diffusion and degradation characteristics of the encapsulation material, allowing the drug to travel efficiently to the target and be released in an optimal way. Nanoparticle encapsulation is also being investigated for the treatment of neurological disorders to deliver therapeutic molecules directly to the central nervous system beyond the blood-brain barrier, and to the eye beyond the blood-retina barrier. Applications could include Parkinson’s, Huntington’s chorea, Alzheimer’s, ALS and diseases of the eye.

➢ Repair and replacement

Damaged tissues and organs are often replaced by artificial substitutes, and nanotechnology offers a range of new biocompatible coatings for the implants that improves their adhesion, durability and lifespan. New types of nanomaterials are being evaluated as implant coatings to improve interface properties. For example, nanopolymers can be used to coat devices in contact with blood (e.g. artificial hearts, catheters) to disperse clots or prevent their formation. Nanomaterials and nanotechnology fabrication techniques are being investigated as tissue regeneration scaffolds. The ultimate goal is to grow large complex organs. Examples include nanoscale polymers moulded into heart valves, and polymer nanocomposites for bone scaffolds.

Commercially viable solutions are thought to be 5 to 10 years away, given the scientific challenges related to a better understanding of molecular/cell biology and fabrication methods for producing large threedimensional scaffolds.

Nanostructures are promising for temporary implants, e.g. that biodegrade and do not have to be removed in a subsequent operation. Research is also being done on a flexible nanofiber membrane mesh that can be applied to heart tissue in open-heart surgery. The mesh can be infused with antibiotics, painkillers and medicines in small quantities and directly applied to internal tissues.

Subcutaneous chips are already being developed to continuously monitor key body parameters including pulse, temperature and blood glucose. Another application uses optical microsensors implanted into subdermal or deep tissue to monitor tissue circulation after surgery, while a third type of sensor uses MEMS (microelectromechanical system) devices and accelerometers to measure strain, acceleration, angular rate and related parameters for monitoring and treating paralysed limbs, and to improve the design of artificial limbs. Implantable sensors can also work with devices that administer treatment automatically if required, e.g. fluid injection systems to dispense drugs. Initial applications may include chemotherapy that directly targets tumors in the colon and are programmed to dispense precise amounts of medication at convenient times, such as after a patient has fallen asleep.

Sensors that monitor the heart’s activity level can also work with an implantable defibrillator to regulate heartbeats.

➢ Hearing and vision

Nano and related micro technologies are being used to develop a new generation of smaller and potentially more powerful devices to restore lost vision and hearing. One approach uses a miniature video camera attached to a blind person’s glasses to capture visual signals processed by a microcomputer worn on the belt and transmitted to an array of electrodes placed in the eye. Another approach uses of a subretinal implant designed to replace photoreceptors in the retina. The implant uses a microelectrode array powered by up to 3500 microscopic solar cells.

For hearing, an implanted transducer is pressure-fitted onto a bone in the inner ear, causing the bones to vibrate and move the fluid in the inner ear, which stimulates the auditory nerve. An array at the tip of the device uses up to 128 electrodes, five times higher 16 than current devices, to simulate a fuller range of sounds. The implant is connected to a small microprocessor and a microphone in a wearable device that clips behind the ear. This captures and translates sounds into electric pulses transmitted by wire through a tiny hole made in the middle ear.

6.4.2. *Food and Agriculture sector*

Nanotechnology is rapidly converging with biotech and information technology to radically change food and agricultural systems. Over the next two decades, the impacts of nano-scale convergence on farmers and food could even exceed that of farm mechanisation or of the Green Revolution according to some sources such as the ETC group [116]. Food and nutrition products containing nano-scale additives are already commercially available. Likewise, a number of pesticides formulated at the nano-scale are on the market and have been released in the environment. According to Helmut Kaiser Consultancy, some 200 transnational food companies are currently investing in nanotech and are on their way to commercialising products [117]. The US leads, followed by Japan and China.

Companies not associated with food production in the public mind are already supplying nano-enabled ingredients to the industry. BASF, for example, exploits the fact that many vitamins and other substances such as carotinoids are insoluble in water, but can easily be mixed with cold water when formulated as nanoparticles. Many lemonades and fruit juices contain these specially formulated additives, which can also be used to provide an”attractive” color [118]. Expected breakthroughs in crop DNA decoding and analysis could enable agri-firms to predict, control and improve agricultural production. And with technology for manipulating the molecules and atoms of food, the food industry would have a powerful method to design food with much greater capability and precision, lower costs and improved sustainability. The combination of DNA and nanotechnology research could also generate new nutrition delivery systems, to bring active agents more precisely and efficiently to the desired parts of the human body.

Nanotechnology will not only change how every step of the food chain operates but also who is involved. The most cited nano-agricultural developments are:

- Nanoseeds: In Thailand, scientists at Chiang Mai University's nuclear physics laboratory have rearranged the DNA of rice by drilling a nano-sized hole through the rice cell's wall and membrane and inserting a nitrogen atom. So far, they've been able to change the colour of the grain, from purple to green;

- Nanoparticle pesticides: Monsanto, Syngenta and BASF are developing pesticides enclosed in nanocapsules or made up of nanoparticles. The pesticides can be more easily taken up by plants if they're in nanoparticle form; they can also be programmed to be ”time-released”;

- Nanofeed for Chickens: With funding from the US Department of Agriculture (USDA), Clemson University researchers are feeding bioactive polystyrene nanoparticles that bind with bacteria to chickens as an alternative to chemical antibiotics in industrial chicken production;

- Nano Ponds: One of the USA’s biggest farmed fish companies, Clear Spring Trout, is adding nanoparticle vaccines to trout ponds, where they are taken up by fish;

- ”Little Brother”: The USDA is pursuing a project to cover farmers’ fields and herds with small wireless sensors to replace farm labour and expertise with a ubiquitous surveillance system;

- Nano foods: Kraft, Nestlé, Unilever and others are employing nanotech to change the structure of food – creating ”interactive” drinks containing nanocapsules that can change colour and flavour (Kraft) and spreads and ice creams with nanoparticle emulsions (Unilever, Nestlé) to improve texture. Others are inventing small nanocapsules that will smuggle nutrients and flavours into the body (what one company calls ”nanoceuticals”);

- Nano packaging: BASF, Kraft and others are developing new nanomaterials that extend food shelf life and signal when a food spoils by changing colour.

- Food safety: Scientists from the University of Wisconsin have successfully used single bacterial cells to make tiny bio-electronic circuits, which could in the future be used to detect bacteria, toxins and proteins [119].

Nanosensors can work through a variety of methods such as by the use of nanoparticles tailor-made to fluoresce different colors or made from magnetic materials can selectively attach themselves to food pathogens. Handheld sensors employing either infrared light or magnetic materials could then note the presence of even minuscule traces of harmful pathogens. The advantage of such a system is that literally hundreds and potentially thousands of nanoparticles can be placed on a single nanosensor to rapidly, accurately and affordably detect the presence of any number of different bacteria and pathogens. A second advantage of nanosensors is that given their small size they can gain access into the tiny crevices where the pathogens often hide, and nanotechnology may reduce the time it takes to detect the presence of microbial pathogens from two to seven days down to a few hours and, ultimately, minutes or even seconds [120].

6.4.3. *Semiconductors and computing sector*

The computer industry is already working on a nanoscale. Although the current production range is at 90 nm, 5 nm gates have been proven in labs, although they cannot be manufactured yet. By 2010, world-wide, about $300 billion worth of semiconductor production are nanotechnology-based (including nanocomponents such as nanolayers, nanoscale treated materials, or other nanostructures) and by 2015, about $500 billion. Because nanotechnology can reduce its basic features, CMOS will continue being used for a decade or more. The intermediate future will have CMOS married to a generation of nanodevices as yet undefined, because there are many alternatives, and it is still too early to tell which will prevail. One solution could consider hybrid structures, exploiting the advantages of today’s CMOS technology (integration and scaling of transistors and high functionality on a small support) with off-chip optoelectronic interconnects to overcome the throughput bottlenecks [121]. Towards 2015, semiconductor development priorities will change, as the focus shifts from scaling and speed to system architecture and integration, with user specific applications for bio-nanodevices, the food industry and construction applications. Another trend is the convergence between IT, nanotechnology, biotechnology and cognitive sciences. The higher speeds at which information will be disseminated will change how we work with computers, and also perhaps how we deal with things like damaged nerves, possibly by developing direct interfaces with the nervous system and electronic circuits, so-called neuromorphic engineering, where signals are directly transmitted from a human organism to a machine. The actual technologies employed are hard to predict. Currently there exist at least four interrelated technical barriers to nanoscale manufacturing:

- How to control the assembly of 3-D heterogeneous systems, including alignment, registration and interconnection at 3-D and with multiple functionalities;

- How to handle and process nanoscale structures in a high-rate/high-volume manner without compromising beneficial nanoscale properties;

- How to test nanocomponents' long-term reliability, and detect, remove or prevent defects and contamination;

- Metrology. At present, using an electron microscope, it is possible to get depth of field, sufficient resolution or low energy (important so as not to damage certain components), but not all three at once. Failure analysis is another metrology issue: how to get a real 3-D view of the structure and defects that may develop during processing or use.

At present, technology front runners include spin electronics, molecular electronics, biocomponents, quantum computing, DNA computing, etc. However, the history of technology teaches that sudden upsets that could change everything are to be expected. As recently as 1998, limited use was predicted for giant magneto resistance introduced by IBM. But within two years it replaced all equivalent hard disk reading technologies and their extensive production facilities. The technique exploits the electron's spin to produce novel interconnect and device structures, giving rise to the name "spintronics" [122]. Spin is present in all electrons, and manipulating spin would use conventional solid-state semiconductor and metal materials, without the problems associated with nanotubes or molecules. Spin packets have a long lifetime and high mobility in semiconductors, making them attractive for transmitting information in the chip, within the silicon, without using a metal. One major problem with spintronics is that when a magnet heats up, it ceases being ferromagnetic, a condition necessary to exploit the electron spin. It is also difficult to control the ferromagnetic force or direction.

Assuming these problems can be solved, promising applications for spintronics includes MRAM (magnetic random access memory), high-speed non-volatile memory architecture and logic devices like the spin field effect transistor (spin FET), which consumes less power and operates faster than its conventional counterpart.

Chip makers are already working at around 100 nm, but this is essentially a ”shrinking” of conventional technologies to make them smaller, and this is now reaching its limits. Miniaturisation into much smaller scales will run into problems caused by quantum phenomena, such as electrons tunnelling through the barriers between wires, so an alternative to transistor technology must be found, one whose components will exploit quantum effects rather suffer from them. The first generation of nanocomputers will have components that behave according to quantum mechanics, but their algorithms will probably not involve quantum mechanics. If quantum mechanics could be used in the algorithms as well, the computer would be enormously more powerful than any classical scheme, but such developments are unlikely in the foreseeable future [123].

In the meantime, research is in progress to manipulate molecules to carry out calculations. In "chemical computing", a series of chemical reactions, e.g. of DNA, corresponds to a computation, with the final products of the reactions representing the answer. With this technique, many calculations can be carried out in parallel, but each step requires a long time, and can be very expensive because of the cost of the chemicals used.

A second approach is to use molecules as the ”host” for nuclear spins that form the quantum bits (qubits) in a nuclear magnetic resonance-based computer. However, this approach may not be able to scale up to a computationally useful number of qubits. The most promising approach is thought to be molecular electronics, using a molecule or group of molecules in a circuit. Bit densities for molecular logic and memory components could be on the order of a terabit/cm2. Switching speeds could get down into the range of a few picoseconds (1000 times faster than current DRAM)

6.4.4. *Textile sector*

The textile industry could be affected quite significantly by nanotechnology, with some estimates talking of a market impact of hundreds of billions of dollars over the next decade. Nanoscience has already produced stain- and wrinkle-resistant clothing, and future developments will focus on upgrading existing functions and performances of textile materials; and developing ”smart” textiles with unprecedented functions such as:

- sensors and information acquisition and transfer;
- multiple and sophisticated protection and detection;
- health-care and wound-healing functions;
- self-cleaning and repair functions.

This last function illustrates how nanotechnology could impact areas outside its immediate application.

US company Nano-Tex is already marketing its NanoCare stain- and wrinkle-resistant technology, and NanoFresh (to freshen sports clothing) is expected soon. Scientists at the Hong Kong Polytechnic University have built a nano layer of particles of titanium dioxide, a substance that reacts with sunlight to break down dirt and other organic material. This layer can be coated on cotton to keep the fabric clean. Clothes simply need to be exposed to natural or ultraviolet light for the cleaning process to begin. Once triggered by sunlight, clothing made out of the fabric will be able to rid itself of dirt, pollutants and micro-organisms. The whole laundry industry would be affected if the technology proves to be economically viable.

Research involving nanotechnology to improve performances or to create new functions is most advanced in nanostructured composite fibers employing nanosize fillers such as nanoparticles (clay, metal oxides, carbon black), graphite nanofibers (GNF) and carbon nanotubes (CNT). The main function of nanosize fillers is to increase mechanical strength and improve physical properties such as conductivity and antistatic behaviours. Being evenly distributed in polymer matrices, nanoparticles can carry load and increase the toughness and abrasion resistance; nanofibers can transfer stress away from polymer matrices and enhance tensile strength of composite fibers. Additional physical and chemical performances imparted to composite fibers vary with specific properties of the nanofillers used. Although some of the filler particles such as clay, metal oxides, and carbon black have previously been used as microfillers in composite materials for decades, reducing their size into nanometer range have resulted in higher performances and generated new market interest.

- Carbon Nanofibers and Carbon Nanoparticles

Carbon nanofibers and carbon black nanoparticles are among the most commonly used nanosize filling materials. Carbon nanofibers can effectively increase the tensile strength of composite fibers due to their high aspect ratio, while carbon black nanoparticles can improve abrasion resistance and toughness. Both have high chemical resistance and electric conductivity.

- Clay Nanoparticles

Clay nanoparticles or nanoflakes possess electrical, heat and chemical resistance and an ability to block UV light. Composite fibers reinforced with clay nanoparticles exhibit flame retardant, anti-UV and anticorrosive behaviours.

- Metal Oxide Nanoparticles

Certain metal oxide nanoparticles possess photocatalytic ability, electrical conductivity, UV absorption and photooxidising capacity against chemical and biological species. Research involving these nanoparticles focuses on antimicrobial, self-decontaminating and UV blocking functions for both military protection gear and civilian health products.

- Carbon Nanotubes

Potential applications of CNTs include conductive and high-strength composite fibers, energy storage and energy conversion devices, sensors, and field emission displays. One CNT fiber already exhibits twice the stiffness and strength, and 20 times the toughness of steel wire of the same weight and length. Moreover, toughness can be four times higher than that of spider silk and 17 times greater than Kevlar fibers used in bullet-proof vests, suggesting applications in safety harnesses, explosion-proof blankets, and electromagnetic shielding.

- Nanotechnology in Textile Finishing

Nanoscale emulsification, through which finishes can be applied to textile material in a more thorough, even and precise manner provide an unprecedented level of textile performance regarding stain-resistant, hydrophilic, anti-static, wrinkle resistant and shrink proof properties.

Nanosize metal oxide and ceramic particles have a larger surface area and hence higher efficiency than larger size particles, are transparent, and do not blur the color and brightness of the textile substrates. Fabric treated with nanoparticles Ti02 and MgO replaces fabrics with active carbon, previously used as chemical and biological protective materials. The photocatalytic activity of Ti02 and MgO nanoparticles can break down harmful chemicals and biological agents.

Finishing with nanoparticles can convert fabrics into sensor-based materials. If nanocrystalline piezoceramic particles are incorporated into fabrics, the finished fabric can convert exerted mechanical forces into electrical signals enabling the monitoring of bodily functions such as heart rhythm and pulse if they are worn next to skin.

- Self-assembled Nanolayers

In the longer-term future, self-assembled nanolayer (SAN) coating may challenge traditional textile coating. Research in this area is still in the very early stages, but the idea is to deposit a coating less than one nanometer thick on the textile, and then to vary the number of successive nanolayers to modulate the desired physical properties of the finished article.

6.4.5. *Energy sector*

Breakthroughs in nanotechnology could provide technologies that would contribute to world-wide energy security and supply. A report published by Rice University (Texas) in February 2005 identified numerous areas in which nanotechnology could contribute to more efficient, inexpensive, and environmentally sound technologies than are readily available [124]. Although the most significant contributions may be to unglamorous applications such as better materials for exploration equipment used in the oil and gas industry or improved catalysis, nanotechnology is being proposed in numerous energy domains, including solar power; wind; clean coal; fusion reactors; new generation fission reactors; fuel cells; batteries; hydrogen production, storage and transportation; and a new electrical grid that ties all the power sources together. The main challenges where nanotechnology could contribute are:

- Lower the costs of photovoltaic solar energy tenfold;

- Achieve commercial photocatalytic reduction of CO2 to methanol;

- Create a commercial process for direct photoconversion of light and water to produce hydrogen;

- Lower the costs of fuel cells between tenfold and a hundredfold and create new, sturdier materials;

- Improve the efficiency and storage capacity of batteries and supercapacitors between tenfold and a hundredfold for automotive and distributed generation applications;

- Create new lightweight materials for hydrogen storage for pressure tanks, liquid hydrogen vessels, and an easily reversible hydrogen chemisorption system;

- Develop power cables, superconductors or quantum conductors made of new nanomaterials to rewire the electricity grid and enable long-distance, continental and even international electrical energy transport, also reducing or eliminating thermal sag failures, eddy current losses and resistive losses by replacing copper and aluminium wires;

- Develop thermochemical processes with catalysts to generate hydrogen from water at temperatures lower than 900˚C at commercial costs;

- Create superstrong, lightweight materials that can be used to improve energy efficiency in cars, planes and in space travel; the latter, if combined with nanoelectronics based robotics, possibly enabling space solar structures on the moon or in space;

• Create efficient lighting to replace incandescent and fluorescent lights;

• Develop nanomaterials and coatings that will enable deep drilling at lower costs to tap energy resources, including geothermal heat, in deep strata;

• Create CO_2 mineralization methods that can work on a vast scale without waste streams.

Solving these challenges will take many years, but commercial and public research institutes are already exploiting nanotechnology for energy applications. Bell Labs, for example, is exploring the possibility of producing a microbattery that would still work 20 years after purchase by postponing the chemical reactions that degrades traditional batteries. The battery is based on a Bell Labs discovery that liquid droplets of electrolyte will stay in a dormant state atop microscopic structures called "nanograss" until stimulated to flow, thereby triggering a reaction producing electricity [125]. Other researchers hope to dispense with batteries completely by developing nanotubes-based ”ultra” capacitors powerful enough to propel hybrid-electric cars. Compared with batteries, ultracapacitors can put out much more power for a given weight, can be charged in seconds rather than hours, and can function at more extreme temperatures. They're also more efficient, and they last much longer. Photovoltaics are another area where nanotech is already providing products that could have a significant impact.

Three US-based solar cell start-ups (Nanosolar, Nanosys and Konarka Technologies), and corporate players including Matsushita and STMicroelectronics are striving to produce photon-harvesting materials at lower costs and in higher volumes than traditional crystalline silicon photovoltaic cells [126]. Nanosolar has developed a material of metal oxide nanowires that can be sprayed as a liquid onto a plastic substrate where it selfassembles into a photovoltaic film. A roll-to-roll process similar to high-speed printing offers a high-volume approach that does not require high temperatures or vacuum equipment. Nanosys intends its solar coatings to be sprayed onto roofing tiles. And Konarka is developing plastic sheets embedded with titanium dioxide nanocrystals coated with light-absorbing dyes.

The company acquired Siemens' organic photovoltaic research activities, and Konarka's recent $18 million third round of funding included the world's first- and fifth-largest energy companies, Electricité de France and ChevronTexaco. If nanotech solar fabrics could be applied to, e.g., buildings and bridges, the energy landscape could change in important ways. Integrated into the roof of a bus or truck, they could split water via electrolysis and generate hydrogen to run a fuel cell. Losers would include current photovoltaic-cell makers and battery manufacturers who failed to react to the new challenge. Such developments however depend on solving a number of fundamental problems at the nanoscale, but researchers are making fast progress using nanoscale design, include accelerating the kinetics of reactions through catalysis, separating the products at high temperature, and directing products to the next reaction step.

7. Nanofluids potential industrial applications

Nowadays, the working fluids became obsolete, due to low thermal conductivity when compared with metals. All efforts to maximize the thermal properties (i.e. increase the contact surface or even creating turbulence) are always limited by operant fluid conduction capacity. In the century XIX, it arises the development of suspensions of solid particles in liquids, however only with development of nanotechnology was initiated using of other fluids. In 1995, Choi *et al.* [127] mixed nanoparticles of solid metals with liquids, calling this mix of nanofluids.

Nanofluids are dilute liquid suspensions of nanoparticles with at least one of their principal dimensions smaller than 100 nm. From previous investigations, nanofluids have been found to possess enhanced thermophysical properties such as thermal conductivity, thermal diffusivity, viscosity and convective heat transfer coefficients compared to those of base fluids like oil or water [128].

Nanofluids can be used for a wide variety of industries, ranging from transportation to energy production and in electronics systems like microprocessors, Micro-Electro-Mechanical Systems (MEMS) and in the field of biotechnology. Recently, the number of companies that observe the potential of nanofluids technology and their focus for specific industrial applications is increasing. In the transportation industry, nanocars, GM and Ford, among others are focusing on nanofluids research projects [129-132].

Nanofluids can be used to cool automobile engines and welding equipment and to cool high heat-flux devices such as high power microwave tubes and high-power laser diode arrays. A nanofluid coolant could flow through tiny passages in MEMS to improve its efficiency. The measurement of nanofluids critical heat flux (CHF) in a forced convection loop is useful for nuclear applications. If nanofluids improve chiller efficiency by 1%, a saving of 320 billionkWh of electricity or an equivalent 5.5 million barrels of oil per year would be realized in the US alone. Nanofluids find potential for use in deep drilling application. A nanofluid can also be used for increasing the dielectric strength and life of the transformer oil by dispersing nanodiamond particles [132, 133].

Kostic reported that nanofluids can be used in following specific areas [134]:

- Heat-transfer nanofluids;
- Tribological nanofluids;
- Surfactant and coating nanofluids;
- Chemical nanofluids;
- Process/extraction nanofluids;
- Environmental (pollution cleaning) nanofluids;
- Bio- and pharmaceutical-nanofluids;

• Medical nanofluids (drug delivery and functional tissue–cell interaction).

7.1. Heat transfer applications

7.1.1. *Industrial cooling applications*

Routbort *et al.* [135] started a project in 2008 that employed nanofluids for industrial cooling that could result in great energy savings and resulting emissions reductions. For U.S. industry, the replacement of cooling and heating water with nanofluids has the potential to conserve 1 trillion Btu of energy. For the U.S. electric power industry, using nanofluids in closed loop cooling cycles could save about 10–30 trillion Btu per year (equivalent to the annual energy consumption of about 50,000–150,000 households). The associated emissions reductions would be approximately 5.6 million metric tons of carbon dioxide; 8,600 metric tons of nitrogen oxides; and 21,000 metric tons of sulfur dioxide.

For Michelin North America tire plants, the productivity of numerous industrial processes is constrained by the lack of facility to cool the rubber efficiently as it is being processed. This requires the use of over 2 million gallons of heat transfer fluids for Michelin's North American plants. It is Michelin's goal in this project to obtain a 10% productivity increase in its rubber processing plants if suitable water-based nanofluids can be developed and commercially produced in a cost-effective manner.

Han *et al.* [136] have used phase change materials as nanoparticles in nanofluids to simultaneously enhance the effective thermal conductivity and specific heat of the fluids. As an example, a suspension of indium nanoparticles (melting temperature, 157˚C) in polyalphaolefin has been synthesized using a one-step, nanoemulsification method.

The fluid's thermophysical properties, that is, thermal conductivity, viscosity, specific heat and their temperature dependence were experimentally measured. The observed melting-freezing phase transition of the indium nanoparticles significantly augmented the fluid's effective specific heat.

This work is one of the few to address thermal diffusivity; similar studies allow industrial cooling applications to continue without thorough understanding of all the heat transfer mechanisms in nanofluids.

7.1.2. *Smart fluids*

In this new age of energy awareness, our lack of abundant sources of clean energy and the widespread dissemination of battery operated devices, (such as cellphones and laptops), have reinforced the necessity for a smart technological handling of energetic resources. Nanofluids have been demonstrated to be able to handle this role in some instances as a smart fluid.

In a paper published in the March 2009 issue of Physical Review Letters, Donzelli *et al.* [137] showed that a particular class of nanofluids can be used as a smart material working as a heat-valve to control the flow of heat. The nanofluid can be readily configured either in a "low" state, where it conducts heat poorly, or in a "high" state, where the dissipation is more efficient. To leap the chasm to heating and cooling technologies, the researchers will have to show more evidence of a stable operating system that responds to a larger range of heat flux inputs.

7.1.3. *Nuclear reactors*

Kim *et al.* [138, 139] at the Nuclear Science and Engineering Department of the Massachusetts Institute of Technology (MIT), performed a study to assess the feasibility of nanofluids in nuclear applications by improving the performance of any water-cooled nuclear system that is heat removal limited. Possible applications include pressurized water reactor (PWR) primary coolant, standby safety systems, accelerator targets, plasma divertors, and so forth [140]. In a pressurized water reactor (PWR) nuclear power plant system, the limiting process in the generation of steam is the critical heat flux (CHF) between the fuels rods and the water—when vapor bubbles that end up covering the surface of the fuel rods conduct very little heat as opposed to liquid water. Using nanofluids instead of water, the fuel rods become coated with nanoparticles such as alumina, which actually push newly formed bubbles away, preventing the formation of a layer of vapor around the rod and subsequently increasing the CHF significantly.

After testing in MIT's Nuclear Research Reactor, preliminary experiments have shown promising success where it is seen that PWR is significantly more productive. The use of nanofluids as a coolant could also be used in emergency cooling systems, where they could cool down overheat surfaces more quickly leading to an improvement in power plant safety.

Some issues regarding the use of nanofluids in a power plant system include the unpredictability of the amount of nanoparticles that are carried away by the boiling vapor. One another concern is related to the extra safety measures that have to be taken in the disposal of the nanofluid. The application of nanofluid coolant to boiling water reactors (BWR) is predicted to be minimal because nanoparticle carryover to the turbine and condenser would raise erosion and fouling concerns.

From Jackson's study [141] it was observed that considerable enhancement in the critical heat flux can be achieved by creating a structured surface from the deposition of nanofluids. If the deposition film characteristics (such as the structure and thickness) can be controlled it may be possible to increase the CHF with little decrease in the heat transfer.

Whereas the nanoparticles themselves cause no significant difference in the pool-boiling characteristics of water, the boiling of nanofluids shows promise as a simple way to create an enhanced surface. The use of nanofluids in nuclear power plants seems like a potential future application [140]. Several significant gaps in knowledge are evident at this time, including the demonstration of the nanofluid thermal-hydraulic performance at prototypical reactor conditions and the compatibility of the nanofluid chemistry with the reactor materials.

Another possible application of nanofluids in nuclear systems is the alleviation of postulated severe accidents during which the core melts and relocates to the bottom of the reactor vessel. If such accidents were to occur, it is desirable to retain the molten fuel within the vessel by removing the decay heat through the vessel wall. This process is limited by the occurrence of CHF on the vessel outer surface, but analysis indicates that the use of nanofluid can increase the in-vessel retention capabilities of nuclear reactors by as much as 40% [142].

Many water-cooled nuclear power systems are CHF limited, but the application of nanofluid can greatly improve the CHF of the coolant so that there is a bottom-line economic benefit while also raising the safety standard of the power plant system.

7.1.4. *Extraction of geothermal power and other energy sources*

The world's total geothermal energy resources were calculated to be over 13000 ZJ in a report from MIT (2007) [143].

In 2009 only 200 ZJ were extractable, however, with technological improvements, over 2,000 ZJ could be obtained and supply the world's energy needs for several millennia. When extracting energy from the earth's crust that varies in length between 5 to 10 km and temperature between 500˚C and 1000˚C, nanofluids can be employed to cool the pipes exposed to such high temperatures. When drilling, nanofluids can serve in cooling the machinery and equipment working in high friction and high temperature environment. As a "fluid superconductor," nanofluids could be used as a working fluid to extract energy from the earth core and processed in a PWR power plant system producing large amounts of work energy. In the sub-area of drilling technology, so fundamental to geothermal power, improved sensors and electronics cooled by nanofluids capable of operating at higher temperature in down hole tools, and revolutionary improvements utilizing new methods of rock penetration cooled and lubricated by nanofluids will lower production costs. Such improvements will enable access to deeper, hotter regions in high grade formations or to economically acceptable temperatures in lower-grade formations. In the sub-area of power conversion technology, improving heat-transfer performance for lower-temperature nanofluids, and developing plant designs for higher resource temperatures to the supercritical water region would lead to an order of magnitude (or more) gain in both reservoir performance and heat-to power conversion efficiency.

Tran *et al.* [144] funded by the United States Department of Energy (USDOE), performed research targeted at developing a new class of highly specialized drilling fluids that may have superior performance in high temperature drilling. This research is applicable to high pressure high temperature drilling, which may be pivotal in opening up large quantities of previously unrecoverable domestic fuel resources. Commercialization would be the bottleneck of progress in this sub-area.

7.2. Automotive applications

Engine oils, automatic transmission fluids, coolants, lubricants, and other synthetic high-temperature heat transfer fluids found in conventional truck thermal systems — radiators, engines and heating, ventilation and air-conditioning (HVAC) systems in general — have inherently poor heat transfer properties.

These could benefit from the high thermal conductivity offered by nanofluids that resulted from addition of nanoparticles [145, 146].

7.2.1. *Nanofluid coolant*

In looking for ways to improve the aerodynamic designs of vehicles, and subsequently the fuel economy, manufacturers must reduce the amount of energy needed to overcome wind resistance on the road. At high speeds, approximately 65% of the total energy output from a truck is expended in overcoming the aerodynamic drag. This fact is partly due to the large radiator in front of the engine positioned to maximize the cooling effect of oncoming air.

The use of nanofluids as coolants would allow for smaller size and better positioning of the radiators. Owing to the fact that there would be less fluid due to the higher efficiency, coolant pumps could be shrunk and truck engines could be operated at higher temperatures allowing for more horsepower while still meeting stringent emission standards.

Argonne researchers, Singh *et al.* [147] have determined that the use of high-thermal conductive nanofluids in radiators can lead to a reduction in the frontal area of the radiator by up to 10%. This reduction in aerodynamic drag can lead to a fuel savings of up to 5%. The application of nanofluid also contributed to a reduction of friction and wear, reducing parasitic losses, operation of components such as pumps and compressors, and subsequently leading to more than 6% fuel savings. It is conceivable that greater improvement of savings could be obtained in the future.

In order to determine whether nanofluids degrade radiator material, they have built and calibrated an apparatus that can emulate the coolant flow in a radiator and are currently testing and measuring material loss of typical radiator materials by various nanofluids. Erosion of radiator material is determined by weight loss-measurements as a function of fluid velocity and impact angle.In their tests, they observed no erosion using nanofluids made from base fluids ethylene and tri-cloroethylene gycols with velocities as high as 9m/s and at 90˚– 30˚ impact angles.

Through preliminary investigation, it was determined that copper nanofluid produces a higher wear rate than the base fluid and this is possibly due to oxidation of copper nanoparticles. A lower wear and friction rate was seen for alumina nanofluids in comparison to the base fluid. Some interesting erosion test results from Singh *et al.* [147] are shown in Tables 1 and 2.

Shen *et al.* [148] researched the wheel wear and tribological characteristics in wet, dry and minimum quantity lubrication (MQL) grinding of cast iron. Water-based alumina and diamond nanofluids were applied in the MQL grinding process and the grinding results were compared with those of pure water. Nanofluids demonstrated the benefits of reducing grinding forces, improving surface roughness, and preventing burning of the workpiece. Contrasted to dry grinding, MQL grinding could considerably lower the grinding temperature.

More research must be conducted on the tribological properties using nanofluids of a wider range of particle loadings as well as on the erosion rate of radiator material in order to help develop predictive models for nanofluid wear and erosion in engine systems. Future research initiatives involve nanoparticles materials containing aluminum and oxide-coated metal nanoparticles. Additional research and testing in this area will assist in the design of engine cooling and other thermal management systems that involve nanofluids.

Future engines that are designed using nanofluids cooling properties would be able to run at more optimal temperatures allowing for increased power output. With a nanofluids engine, components would be smaller and weigh less allowing for better gas mileage, saving consumers money and resulting in fewer emissions for a cleaner environment.

7.2.2. *Nanofluid in fuel*

The aluminum nanoparticles, produced using a plasma arc system, are covered with thin layers of aluminum oxide, owing to the high oxidation activity of pure aluminum, thus creating a larger contact surface area with water and allowing for increased decomposition of hydrogen from water during the combustion process.

During this combustion process, the alumina acts as a catalyst and the aluminum nanoparticles then serve to decompose the water to yield more hydrogen. It was shown that the combustion of diesel fuel mixed with aqueous aluminum nanofluid increased the total combustion heat while decreasing the concentration of smoke and nitrous oxide in the exhaust emission from the diesel engine [149, 150].

7.2.3. *Brake and other vehicular nanofluids*

As vehicle aerodynamics is improved and drag forces are reduced, there is a higher demand for braking systems with higher and more efficient heat dissipation mechanisms and properties such as brake nanofluid.

A vehicle's kinetic energy is dispersed through the heat produced during the process of braking and this is transmitted throughout the brake fluid in the hydraulic braking system. If the heat causes the brake fluid to reach its boiling point, a vapor-lock is created that retards the hydraulic system from dispersing the heat caused from braking. Such an occurrence will in turn cause a brake malfunction and poses a safety hazard in vehicles. Since brake oil is easily affected by the heat generated from braking, nanofluids with enhanced characteristics maximize performance in heat transfer as well as remove any safety concerns.

Copper-oxide brake nanofluid (CBN) is manufactured using the method of arc-submerged nanoparticle synthesis system (ASNSS). Essentially this is done by melting bulk copper metal used as the electrode which is submerged in dielectric liquid within a vacuum-operating environment and the vaporized metals are condensed in the dielectric liquid [149, 150].

Aluminum-oxide brake nanofluid (AOBN) ismade using the plasma charging arc system. This is performed in a very similar fashion to that of the ASNSS method. The aluminum metal is vaporized by the plasma electric arc at a high temperature and mixed thoroughly with the dielectric liquid [149, 150]

CBN has a thermal conductivity 1.6 times higher than that of the brake fluid designated DOT3, while AOBN's thermal conductivity is only 1.5 times higher than DOT3. This enhanced thermal conductivity optimizes heat transmission and lubrication.

CBN and AOBN both have enhanced properties such as a higher boiling point, higher viscosity and a higher conductivity than that of traditional brake fluid (DOT3). By yielding a higher boiling point, conductivity and viscosity, CBN and AOBN reduce the occurrence of vapor-lock and offer increased safety while driving.

In the nanofluid research applied to the cooling of automatic transmissions, [151], dispersed CuO and Al_2O_3 nanoparticles into engine transmission oil. The experimental setup was the transmission of a four-wheel drive vehicle. The transmission had an advanced rotary blade coupling, where high local temperatures occurred at high rotating speeds. Temperature measurements were taken on the exterior of the rotary-blade-coupling transmission at four engine operating speeds (range from 400 to 1600 rpm), and the optimum composition of nanofluids with regard to heat transfer performance was studied. The results indicated that CuO nanofluids resulted in the lowest transmission temperatures both at high and low rotating speeds. Therefore, the use of nanofluid in the transmission has a clear advantage from the thermal performance viewpoint. As in all nanofluid applications, however, consideration must be given to such factors as particle settling, particle agglomeration, and surface erosion.

In automotive lubrication applications [152], surface-modified nanoparticles stably dispersed in mineral oils were shown to be effective in reducing wear and enhancing load-carrying capacity. Results from a research project involving industry and academia points to the use of nanoparticles in lubricants to enhance tribological properties such as load-carrying capacity, wear resistance, and friction reduction between moving mechanical components. Such results are promising for enhancing heat transfer rates in automotive systems through the use of nanofluids.

7.3. Electronic applications

Nanofluids are used for cooling of microchips in computers and elsewhere. They are also used in other electronic applications which use microfluidic applications.

7.3.1. *Cooling of microchips*

A principal limitation on developing smaller microchips is the rapid heat dissipation. However, nanofluids can be used for liquid cooling of computer processors due to their high thermal conductivity.

It is predicted that the next generation of computer chips will produce localized heat flux over 10MW/m2, with the total power exceeding 300W. In combination with thin film evaporation, the nanofluid oscillating heat pipe (OHP) cooling system will be able to remove heat fluxes over 10MW/m2 and serve as the next generation cooling device that will be able to handle the heat dissipation coming from new technology [153, 154].

In order to observe the oscillation, researchers had to modify the metal pipe system of the OHP to use glass or plastic for visibility. However, since OHP systems are usually made of copper, the use of glass or plastic changes the thermal transfer properties of the system and subsequently altering the performance of the system and the legitimacy of the experimental data [153, 154].

So as to obtain experimental data while maintaining the integrity of the OHP system, in [155], employed neutron imaging to study the liquid flow in a 12-turn nanofluid OHP. As a consequence of the high intensity neutron beam from an amorphous silicon imaging system, they were able to capture dynamic images at 1/30th of a second. The nanofluid used was composed of diamond nanoparticles suspended in water. Even though nanofluids and OHPs are not new discoveries, combining their unique features allows for the nanoparticles to be completely suspended in the base liquid increasing their heat transport capability. Since nanofluids have a strong temperature-dependent thermal conductivity and they show a nonlinear relationship between thermal conductivity and concentration, they are high performance conductors with an increased CHF. The OHP takes intense heat from a high-power device and converts it into kinetic energy of fluids while not allowing the liquid and vapor phases to interfere with each other since they flow in the same direction.

Ma *et al.* [153, 154] introduced diamond nanoparticles into high performance liquid chromatography (HPLC) water. The movement of the OHP keeps the nanoparticles fromsettling and thus improving the efficiency of the cooling device. At an input power of 80W, the diamond nanofluid decreased the temperature difference between the evaporator and the condenser from 40.9˚C to 24.3˚C.

However, as the heat input increases, the oscillating motion increases and the resultant temperature difference between the evaporator and condenser does not continue to increase after a certain power input. This phenomenon inhibits the effective thermal conductivity of the nanofluid from continuously increasing. However, at its maximum power level of 336W, the temperature difference for the nanofluid OHP was still less than that for the OHP with pure water. Hence, it has been shown that the nanofluid can significantly increase the heat transport capability of the OHP.

Lin *et al.* [156] investigated nanofluids in pulsating heat pipes by using silver nanoparticles, and discovered encouraging results. The silver nanofluid improved heat transfer characteristics of the heat pipes. Nguyen *et al.* [157] investigated the heat transfer enhancement and behavior of Al2O3-water nanofluid with the intention of using it in a closed cooling system designed for microprocessors or other electronic devices. The experimental data supports that the inclusion of nanoparticles into distilled water produces a significant increase of the cooling convective heat transfer coefficient. At a given particle concentration of 6.8%, the heat transfer coefficient increased as much as 40% compared to the base fluid of water. Smaller Al_2O_3 nanoparticles also showed higher convective heat transfer coefficients than the larger ones.

Further research of nanofluids in electronic cooling applications will lead to the development of the next generation of cooling devices that incorporate nanofluids for ultrahigh-heat-flux electronic systems.

7.3.2. *Microscale fluidic applications*

The manipulation of small volumes of liquid is necessary in fluidic digital display devices, optical devices, and microelectromechanical systems (MEMS) such as lab-on-chip analysis systems. This can be done by electrowetting, or reducing the contact angle by an applied voltage, the small volumes of liquid. Electrowetting on dielectric (EWOD) actuation is one very useful method of microscale liquid manipulation. Vafaei *et al.*, [158], discovered that nanofluids are effective in engineering the wettability of the surface and possibly of surface tension. Using a goniometer, it was observed that even the addition of a very low concentration of bismuth telluride nanofluid dramatically changed the wetting characteristics of the surface. Concentrations as low as 3×10^{-6} increased the contact angle to over 40˚, distinctly indicating that the nanoparticles change the force balance in the vicinity of the triple line.

7.4. Biomedical applications

7.4.1. *Nanodrug delivery*

Most bio-MEMS studies were done in academia in the 1990s, while recently commercialization of such devices has started. Examples include an electronically activated drug delivery microchip [159]; a controlled delivery system via integration of silicon and electroactive polymer technologies; a MEMS-based DNA sequencer developed in [160]; and arrays of in-plane and out-ofplane hollow micro-needles for dermal/transdermal drug delivery [161, 162] as well as nanomedicine applications of nanogels or gold-coated nanoparticles [163]. An objective of the advanced endeavors in developing integrated micro- or nano-drug delivery systems is the interest in easily monitoring and controlling target-cell responses to pharmaceutical stimuli, to understand biological cell activities, or to enable drug development processes.

While conventional drug delivery is characterized by the "high-and-low" phenomenon, microdevices facilitate precise drug delivery by both implanted and transdermal techniques. This means that when a drug is dispensed conventionally, drug concentration in the blood will increase, peak and then drop as the drug is metabolized, and the cycle is repeated for each drug dose. Employing nanodrug delivery (ND) systems, controlled drug release takes place over an extended period of time. Thus, the desired drug concentration will be sustained within the therapeutic window as required.

A nanodrug-supply system, that is, a bio-MEMS, was introduced in [164]. Their principal concern was the conditions for delivering uniform concentrations at the microchannel exit of the supplied nanodrugs. A heat flux which depends on the levels of nanofluid and purging fluid velocity was added to ascertain that drug delivery to the living cells occurs at an optimal temperature, that is, 37˚C. The added wall heat flux had also a positive influence on drug-concentration uniformity. In general, the nano-drug concentration uniformity is affected by channel length, particle diameter and the Reynolds number of both the nanofluid supply and main microchannels. Since the transport mechanisms are dependent on convection— diffusion, longer channels, smaller particle diameters as well as lower Reynolds numbers are desirable for best, that is, uniform drug delivery.

7.4.2. *Cancer therapeutics*

There is a new initiative which takes advantage of several properties of certain nanofluids to use in cancer imaging and drug delivery. This initiative involves the use of iron-based nanoparticles as delivery vehicles for drugs or radiation in cancer patients. Magnetic nanofluids are to be used to guide the particles up the bloodstream to a tumor with magnets. It will allow doctors to deliver high local doses of drugs or radiation without damaging nearby healthy tissue, which is a significant side effect of traditional cancer treatment methods. In addition, magnetic nanoparticles are more adhesive to tumor cells than non malignant cells and they absorb much more power than microparticles in alternating current magnetic fields tolerable in humans; they make excellent candidates for cancer therapy.

Magnetic nanoparticles are used because as compared to other metal-type nanoparticles, these provide a characteristic for handling and manipulation of the nanofluid by magnetic force [165]. This combination of targeted delivery and controlled release will also decrease the likelihood of systemic toxicity since the drug is encapsulated and biologically unavailable during transit in systemic circulation.

The nanofluid containing magnetic nanoparticles also acts as a super-paramagnetic fluid which in an alternating electromagnetic field absorbs energy producing a controllable hyperthermia. By enhancing the chemotherapeutic efficacy, the hyperthermia is able to produce a preferential radiation effect on malignant cells [166].

There are numerous biomedical applications that involve nanofluids such as magnetic cell separation, drug delivery, hyperthermia, and contrast enhancement in magnetic resonance imaging. Depending on the specific application, there are different chemical syntheses developed for various types of magnetic nanofluids that allow for the careful tailoring of their properties for different requirements in applications. Surface coating of nanoparticles and the colloidal stability of biocompatible water-based magnetic fluids are the two particularly important factors that affect successful application [167, 168].

Nanofluids could be applied to almost any disease treatment techniques by reengineering the nanoparticles' properties. In their study, the nanoparticles were laced with the drug docetaxel to be dissolved in the cells' internal fluids, releasing the anticancer drug at a predetermined rate. The nanoparticles contain targeting molecules called aptamers which recognize the surface molecules on cancer cells preventing the nanoparticles from attacking other cells. In order to prevent the nanoparticles from being destroyed by macrophages—cells that guard against foreign substances entering our bodies—the nanoparticles also have polyethylene glycol molecules. The nanoparticles are excellent drug delivery vehicles because they are so small that living cells absorb them when they arrive at the cells' surface.

For most biomedical uses the magnetic nanoparticles should be below 15 nm in size and stably dispersed in water. A potential magnetic nanofluid that could be used for biomedical applications is one composed of FePt nanoparticles.

This FePt nanofluid possesses an intrinsic chemical stability and a higher saturation magnetization making it ideal for biomedical applications. However, before magnetic nanofluids can be used as drug delivery systems, more research must be conducted on the nanoparticles containing the actual drugs and the release mechanism.

7.4.3. *Cryopreservation*

Conventional cryopreservation protocols for slow-freezing or vitrification involve cell injury due to ice formation/cell dehydration or toxicity of high cryoprotectant (CPA) concentrations, respectively. In the study [169], they developed a novel cryopreservation technique to achieve ultra-fast cooling rates using a quartz micro-capillary (QMC). The QMC enabled vitrification of murine embryonic stem (ES) cells using an intracellular cryoprotectant concentration in the range used for slowing freezing (1–2 M). More than 70% of the murine ES cells post-vitrification attached with respect to non-frozen control cells, and the proliferation rates of the two groups were alike. Preservation of undifferentiated properties of the pluripotent murine ES cells post-vitrification cryopreservation was verified using three different types of assays.

These results indicate that vitrification at a low concentration (2 M) of intracellular cryoprotectants is a viable and effective approach for the cryopreservation of murine embryonic stem cells.

2.4.4 Nanocryosurgery

Cryosurgery is a procedure that uses freezing to destroy undesired tissues. This therapy is becoming popular because of its important clinical advantages.

Although it still cannot be regarded as a routine method of cancer treatment, cryosurgery is quickly becoming as an alternative to traditional therapies.

Simulations were performed in [170] on the combined phase change bioheat transfer problems in a single cell level and its surrounding tissues, to explicate the difference of transient temperature response between conventional cryosurgery and nanocryrosurgery. According to theoretical interpretation and existing experimental measurements, intentional loading of nanoparticles with high thermal conductivity into the target tissues can reduce the final temperature, increase the maximum freezing rate, and enlarge the ice volume obtained in the absence of nanoparticles.

Additionally, introduction of nanoparticle enhanced freezing could also make conventional cryosurgery more flexible in many aspects such as artificially interfering in the size, shape, image and direction of ice ball formation. The concepts of nanocryrosurgery may offer new opportunities for future tumor treatment.

With respect to the choice of particle for enhancing freezing, magnetite (Fe_3O_4) and diamond are perhaps the most popular and appropriate because of their good biological compatibility. Particle sizes less than 10 µm are sufficiently small to start permitting effective delivery to the site of the tumor, either via encapsulation in a larger moiety or suspension in a carrier fluid. Introduction of nanoparticles into the target via a nanofluid would effectively increase the nucleation rate at a high temperature threshold.

7.4.4. Sensing and imaging

Colloidal gold has been used for several centuries now, be it as colorant of glass ("Purple of Cassius") and silk, in medieval medicine for the diagnosis of syphilis or, more recently, in chemical catalysis, non-linear optics, supramolecular chemistry,molecular recognition and the biosciences. Colloidal gold is often referred to as the most stable of all colloids. Its history, properties and applications have been reviewed extensively. For a thorough and up-todate overview the paper by Daniel and Astruc [171] and the references cited therein may be consulted. As stated in the introduction, no attempt is made here to review the use of colloids which are also nanofluids. An increase of colloids which are nanofluids is expected in this category.

7.5. Other applications

Nanofluid Detergent. Nanofluids do not behave in the same manner as simple liquids with classical concepts of spreading and adhesion on solid surfaces [172-174]. This fact opens up the possibility of nanofluids being excellent candidates in the processes of soil remediation, lubrication, oil recovery and detergency. Future engineering applications could abound in such processes. Wasan and Nikolov, [175], of Illinois Institute of Technology in Chicago were able to use reflected-light digital video microscopy to determine the mechanism of spreading dynamics in liquid containing nanosized polystyrene particles. They were able to demonstrate the two dimensional crystal-like formation of the polystyrene spheres in water and how this enhances the spreading dynamics of a micellar fluid at the three-phase region.

8. CarbonInspired 2.0 consortium demonstrators/prototypes for industrial potential application

Within the technical development of the project, five prototypes where developed to effectively demonstrate the applicability and functionality of nanoparticles and nanomaterials: 1) coating based on nanoparticles for maritime components; auto heating seat device; water detoxification system; heating paint for aeronautic application; and nanodiamond coatings of microinjection molding cavities.

8.1. Coating based on nanoparticles for maritime components

Engineered structures such as ships and marine platforms, as well as offshore rigs and jetties, are under constant attack from the marine environment, needing protection from the influences of the marine environment elements, such as saltwater, biological species and temperature fluctuations [176].

An epoxy coating based on nanoparticles for maritime components has been developed by AIMPLAS to overcome biofouling and corrosion created by a wide range of exposure conditions in marine structure.

The coating development started with the selection of a commercial epoxy suitable for maritime conditions. Then, several commercial available nanoparticles such as ZnO, SiO_2 were selected and submitted to chemical modifications, to improve the compatibility with the epoxy matrix and to promote biofouling effects. After the latter, the hardener was added to the resin and the final mixture was applied to metallic test parts. Samples were introduced in an oven to carry out a suitable curing step. To reproduce the real conditions of the maritime environment, a volume of seawater was used and an inoculum of microalgae was introduced to generate an unfavorable medium. Seawater, microorganisms, light intensity, air contributing and room temperature were the conditions controlled. The samples were submerged in test medium and the exposure was conducted during 45 days. Visual evaluations and microscopy analysis were performed pointing out the growth of microalgae and others organisms. During testing, most of the coated samples demonstrate their antifouling properties, not showing evidence of the presence of algae or other organism deposits in the surface. On the other hand, reference sample without coating, showed corrosion pits and additional defects.

Epoxy coating based on nanoparticles could be a solution to increase the performance of maritime components, due to synergistic effect created by different nanoparticles and the antifouling system resulting in a combination of properties such as hydrophobicity, large surface area of nanomaterials, roughness and anticorrosion. It is important to refer that the antifouling system can be considered a non-toxic approach, without including biocide components according to current regulations.

Figure 35 - Evolution of test pieces and medium after 45 days.

8.2. Auto heating seat device

Textiles are ideal substrates for the integration of novel properties and functions to enhance the user comfort and the environment, since they are universal interfaces. They provide a versatile structure for the incorporation of novel functionalities with value added. Nanotechnology can be used to enhance textiles attributes, such as fabric softness, durability, breathability, water repellency, fire retardant, anti-microbial properties, and the like in fibers, yarns, and fabrics.

An auto heating seat device has been developed by CTAG, creating a homogenous heating along the seat surface, has showed in Figure 36.

In a first step, the physical mixing of acrylic resin, commercial solution of MWCNTs, additives and metallic fillers was performed. The acrylic resin was used to ensure the durability of the electro-heating textile, while the additives were used to prevent the re-aggregation of the nanoparticles, improving the conductivity level and optimizing the nanoparticles concentration. The metallic fillers were used to improve the thyrotrophic properties of the final mixture. Then, for a correct impregnation of the mixture, it was deposited on a PES/cotton substrate, and dry in a lab drier at a controlled temperature. After this, thermal measurements were done and a comparative study between the produced prototype and a conventional electric resistances seat, concluding that the application of nanomaterials directly in the textile allow a homogeneous distribution of heat flow. The prototype reaches a thermal leap up to 30ºC, working within the security range to be used in humid environments or outside, with no hazardousness for the user. Moreover, the obtained heat is uniform among the whole seat surface, increasing the comfort and achieving the desired thermal sensation. It is also important to refer that there isn’t loss of physical properties due to rigidity increments.

8.3. Water detoxification system

Textile industry is one of the most water and chemical intensive industries worldwide due to the fact that 200400 litres of water are needed to produce 1 kg of textile fabric in textile factories. The water used in this industry is almost entirely discharged as waste. Moreover, the loss of dye in the effluents of textile industry can reach up to 75%. It was considered that the removal of color from wastewaters is more important than the removal of other organic colorless chemicals. Decolorization of effluent from textile dyeing and finishing industry was regarded important because of aesthetic and environmental concerns [177].

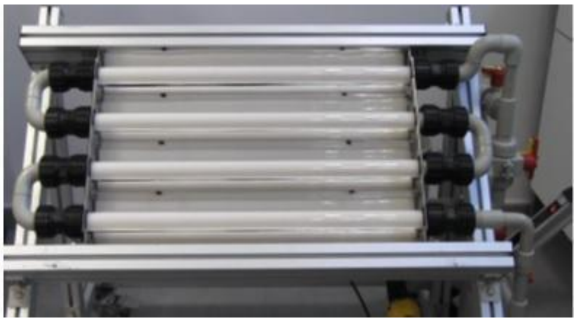
Nowadays, nanoparticles and nanomaterials are being used for water and wastewater treatment: adsorption, membranes, photocatalysis, disinfection and microbial control and sensing and monitoring [178]. Recent studies have demonstrated that heterogeneous photocatalysis is the most efficient technique in the degradation of colored chemicals. It can completely degrade the organic pollutants into harmless inorganic substances like CO_2, H_2O. Photocatalysis is defined as the acceleration of a photoreaction in the presence of a catalyst TiO_2 is the most widely used semiconductor photocatalyst for wastewater treatment due to its low toxicity and cost, chemical stability and abundance as raw material. The basic mechanism of TiO_2 photocatalysis is well known. UV irradiation induces the formation of electron–hole pairs, whose charge carriers react with H_2O, $OH^–$, and O_2 to produce hydroxyl radicals (•OH) and superoxide radical anions (O_2•–), which in turn induce decomposition of almost all organic molecules on the TiO_2 surface.

In semiconductor photocatalysis of industrial wastewater treatment, there are different parameters affecting the efficiency of treatment. These parameters include mass of catalyst, dye concentration, pH, light intensity, addition of oxidizing agent, temperature and type of photocatalyst. It is important to mention, that from an engineering point of view the immobilization of TiO_2 onto support is preferable compare to the slurry system as to avoid costly and difficult separation and the recycling of the photocatalyst. Among the supports studied in bibliography are silica gel, glass fibers, zeolites, glass surfaces, polymeric supports and ceramic materials [179].

IK4-TEKNIKER has employed a photocatalytic reactor from Ecosystem for the detoxification of coloured solutions. The photoreactor, showed in figure 37, possesses 4 tubes of borosilicate glasses, which allows the UV radiation to pass, with 32 mm diameter, 1.4 mm thichness and 750 mm length. The tubes have a CPC aluminium panel to allow the light to reflect improving the efficiency of the mechanism.

The nanoparticles coupled with UV or solar light can remove 100% of the color of the water and the 75 % of the TOC. Furthermore, it was showed that TiO_2 photocatalyst is much more effective in the form of nanoparticles than in bulk powders; they can be supported onto different substrates, such as glass fibers and sepiolites, in order to expedite the separation of the catalyst and avoid the leaching of the nanoparticles to the environment; and that the photocatalysis with TiO_2 can use sunlight with light sensitivity, avoiding the high costs of UV lamps and electrical energy.

NanoTiO_2 powders, used in direct dispersion into the coloured solution, have shown highly efficient in the photocatalytic detoxification of colored wastewater. A solution with 10 mg/L of an azodye methylene orange has been decoulorized with a 1 g/L of TiO_2 NP suspended in an aqueous solution with pH=2.7 after 90 min of reaction, when the process use UV radiation. Furthermore, the 60% of the total organic carbon was removed for the solution. One of the main advantages of using the photocatalytic process is that it can work with UV radiation or using sunlight with light sensitivity, reducing the high costs of UV lamps and electrical energy. Combining nanoparticles with sunlight, after 120 min of reaction the 100% of the color was eliminated and 70% of the total organic carbon was removed for the solution.

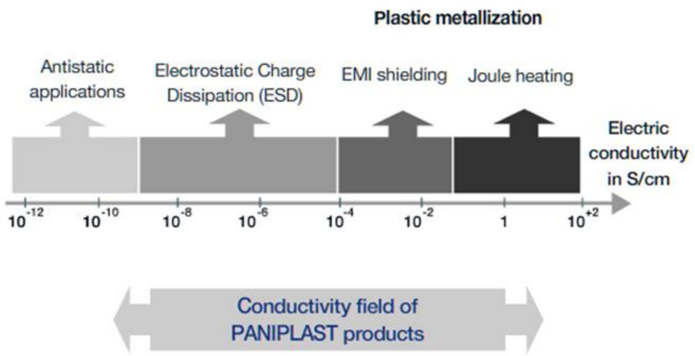



8.4. Heating paint for aeronautic application

The aeronautics industry is an asset for Europe's economy, representing a pinnacle of manufacturing, employing large numbers of highly skilled people, spinning out technology to other sectors and yielding consistently large balance-of-payments benefits [180].

The first glance of the benefit of nanotechnology in the aeronautics industry is in the viability to have lighter materials without compromising strength and other mechanical properties. Nevertheless, it will also benefit from electronics and displays with low power consumption, new sensors, paints, etc. A particular request from the sector is the development of de-icing devises, to overcome the problems of ice forming on sensors and aeronautic components. De-icing is not only of interest to the designers of electrical wires and telecommunication networks; it indeed interests other sectors, such as those related to aerial, sea and rail transportation [181].

For those up-mentioned reasons, RESCOLL and ADERA jointly developed an innovative technology to meet the needs of the market. A heating paint, based on conductive polymers such as polyaniline has been developed. The technology used is based on the technology PANIPLAST patented by RESCOLL. Figure 38 presents a schematic representation of the conductivity field of PANIPLAST products. Polyaniline (PANI) is an intrinsically conductive nanostructured polymer with low cost, low density, and compatibility with common binders (acrylic or urethane dispersion). The PANI was synthesized and incorporated into an aqueous based paint by mixing. This mixture results in an electrical conducting paint that will heat up due to Joule effect.



After formulating the paint with the conductive polymer, an electrical conductivity up to 1S/cm is reached. The practical application of the paint shows a very homogeneous heating, a quick and an efficient deicing, with temperature close to +15°C, where the ambient temperature was close to -15°C.

Finally this technology allows obtaining good results using lightweight materials and an inexpensive process. Moreover, this process can be applied in large surfaces as well as small surfaces. Figure 39 show the heating paint applied in an airplane wind.

8.5. Nanodiamond coatings of microinjection moulding cavities

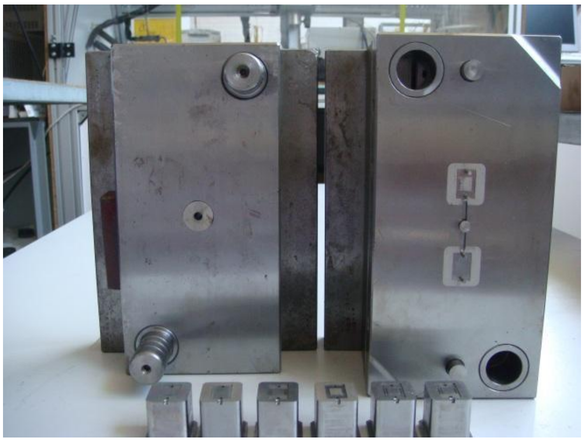
Microelectromechanical systems (MEMS) has advanced to a mature stage of quantity production, practical applications and expanding to many new areas of exploration and research [182]. MEMS became practical once they could be fabricated using modified semiconductor device fabrication technologies, normally used to make electronics. These include molding and plating, wet and dry etching, electro discharge machining (EDM), and other technologies capable of manufacturing small devices. To assist the development of MEMS, it is therefore necessary to produce micro components, polymeric for instance, with a high degree of accuracy and precision.

Microinjection moulding can be used to replicate such components. Nevertheless, the technology still faces challenges that differ from the ones of conventional injection. High shear heating is known to occur in the polimeric flow through microcavities and may significantly contribute an increase of the wear of the microimpression, compromising both the tool life service and the overall quality of the molded parts [183, 184].

Nanocrystalline diamond coatings have been applied in microinjection moulding cavities, showed in figure 39, exhibiting high hardness and thermal conduction, and a low friction coefficient, contributing to a higher wear resistance and a better cavity temperatures control, resulting in reduced maintenance needs of the tool and the production of better quality polymeric parts.

Before the diamond is deposited on the steel molding tool, a thin film of chromium nitride (CrN) is deposited to serve as an interlayer, because diamond cannot be directly applied in the ferrous substrate. Then, the molding block is submitted to a pre-treatment, for the initial nucleation enhancement and finally placed in the hot-filament chemical vapor deposition reactor. The resulting coating is a homogeneous and coalescent film, with diamond crystals of about 100 nm average. Raman spectroscopy was used to evaluate the quality and the characteristics of film.

The use of the coated molding tools showed that there is a positive influence of the diamond coating on the polymeric flow, especially when the melt temperature is low, leading to enhanced controlled processing condition. Furthermore, it is speculated that the diamond coating can act as a heat transfer buffer, weakening the influence of the heat transfer mechanism on the polymer/mould interface at the flow stage, allowing less aggressive design of the temperature control system and increase the performance of the microinjection moulding.



9. Environmental impact and health issues concerning nanotechnology

Despite the enormous growth of nanotechnology and its relevance, the uncertainty inherent of a "new" technology subsists, especially due to the scarce of information and studies regarding the impact on health and on the environment. This is seen as a limiting factor to a broader incorporation of nanotechnology in industry.

The use of nanomaterials in different consumer and commercial applications raises questions about the potential risks that might arise if people or the environment becomes exposed to nanomaterials during their manufacture, use, or disposal. As nanomaterials come in a variety of forms, based on both their chemical composition and their physical structure, the environmental, health, and safety risks may differ [185, 186].

The European Commission, through the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), identify and manage risks linked to the substances imported, manufactured and marketed. Only recently it is developing efforts to address nanomaterials directly[1]. Regarding the workplace exposure management, the European Agency for Safety and Health at Work (OSHA) published several contents regarding occupational risks and prevention in the healthcare sector [187] and maintenance work [188] as well as good practices in the management of these materials [189]. In the United States, the National Institute for Occupational Safety and Health (NIOSH) recently released recommended exposure limits to individuals working with carbon nanotubes [185]. Several European Union industrial sectors are covered by specific regulations that also regard nanomaterials [190]: Waste Electrical and Electronic Equipment (WEEE) - Directive 2012/19/EU (electronic waste management); Restriction of the use of certain hazardous substances (RoHS) - Directive 2011/65/EU (hazardous substances in electrical and electronic equipment usage); Commission Regulation 169/2011 (authorization of diclazuril as a feed for guinea fowls); Commission Regulation 10/2011 (plastic materials and articles intended to come into contact with food); Commission Regulation 1223/2009 (on cosmetic products); and Commission Regulation 528/2012 (making available on the market and use of biocidal products).

Despite the efforts that have been developed, the lack of information and knowledge about safety and health risks and environmental impact of nanomaterials are still present and it is mandatory to protect all the involved, providing detailed and specific data. Schulte et al. [191] suggested five criterion actions that should be practiced by the stakeholders at the business and societal levels, to a responsible nanotechnology development. These include:

1. Anticipate, identify, and track potentially hazardous nanomaterials in the workplace;
2. Assess workers' exposures to nanomaterials;
3. Assess and communicate hazards and risks to workers;
4. Manage occupational safety and health risks;

[1] http://ec.europa.eu/enterprise/sectors/chemicals/reach/nanomaterials/index_en.htm

5. Foster the safe development of nanotechnology and realization of its societal and commercial benefits.

Although there is much to do in this field, two different situations must be noted: the manipulation of the nanoparticles and nanomaterials; and the end use of a product containing nanoparticles and nanomaterials. Attention must be paid to the first situation.

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