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Industrial applications of nanoparticles – a prospective overview

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Abstract

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. Despite the development in this area, there are some obstacles to a greater impact of nanotechnology in industry. The lack of information concerning this scientific area, the possibility of adverse impacts of nanotechnology on the environment, human health, safety and sustainability, are still a challenge. This article intends to briefly the prototypes being developed with in the CarbonIspired 2.0 consortium, given with them examples of practical applications, security issues and market challenges in order to an effective collaboration between the academies, research centers and the industrial sector.

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Keywords: Nanoparticles; Nanomaterials; Regulation; Prototypes; Health & Safety

1. Introduction

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

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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].

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.

In this article, a summary review of nanoparticles and nanomaterials used in major industrial sectors will be address and the prototypes being developed with in the CarbonIspired 2.0 consortium will be highlighted, providing examples of practical applications, security issues and market.

2. 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 notion very used is nanostructured nanoparticles, consisting of particles with structural features smaller than 100 nm, which may influence their physical, chemical and/or biological properties [3].

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, carbon nanotubes, inorganic nanotubes or biopolymers) and three dimensions at the nanoscale (such as nanoparticles, fullerenes, dendrimers or quantum dots.

Nanomaterials cover a heterogeneous range of materials and with a classification by types not completely clear of controversy. The European Commission presents the following classification, based in various Sustainable and Responsible Investment (SRI) consulting reports [5]:

- Inorganic non-metallic nanomaterials: titanium dioxide (TiO_2), silicon dioxide (SiO_2), zinc oxide (ZnO), aluminum hydroxides and aluminum oxo-hydroxides, diiron trioxide (ferric oxide, hematite, Fe_2O_3), triiron tetraoxide (ferrous-ferric oxide, magnetite,Fe_3O_4), cerium dioxide (CeO_2), zirconium dioxide (ZrO_2), calcium carbonate ($CaCO_3$), barium titanate ($BatiO_3$), barium sulphate ($BaSO_4$), strontium titanate ($SrTiO_3$), strontium carbonate ($SrCO_3$), indium tin oxide (ITO), antimony tin oxide (ATO), disbismuth trioxide (Bi_2O_3), nickel monoxide (NiO) disilver oxide (Ag_2O), aluminium nitride (AlN), silicon nitride (Si_3O_4), titanium nitride (TiN), titanium carbonitride (TiCN), tungsten carbide (WC), tungsten sulphide (WS_2), etc.;
- Metals and Metal alloys: 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), etc.;
- Carbon-based nanomaterials: fullerenes (C_{60}), carbon nanotubes (CNT, SWCNT, MWCNT), carbon nanofibers (CNF), carbon black and graphene flaks;
- Nanopolymers and dendrimers: polymer nanoparticles (e.g. polyalcylbenzenepolydiene nanoparticles PAB-PDM), polymer nanotubes, nanowires and nanorods, polyglycidylmethacrylate (PGMA) fibres, nanocellulose, nanostructured polymer-films (polyalcylthiophene-films, polystyrene-polyethylene oxide

films, acrylic glass Polymethyl methacrylate films, styrene-ethylene-butylene-styrene), polyacrylonitrile nanostructures (PAN), dendrimers;
- Quantum dots;
- Nanoclays;
- Nanocomposites.

However, there are also new types of nanomaterials in development, which are often referred to as “second generation” (targeted drug delivery systems, adaptive structures and actuators), “third generation” (novel robotic devices, 3D-dimensional networks and guided assemblies), and “fourth generation” (molecule-by-molecule design and self-assembly capabilities) nanomaterials [5].

The properties of materials can be different at the nanoscale for two main reasons: the superficial area of nanomaterials is higher, especially if compared with materials at the macroscale, which may result in an increased chemical reactivity and affect mechanical and electric properties; and the quantum effects dominates the behavior of matter at the nanoscale, affecting the optical, electrical and magnetic behavior of materials.

The fundamental properties most often acquired or described to characterize nanomaterials are [6]: size distribution, agglomeration state/dispersion, chemical deposition, crystal structure, surface area and porosity, surface chemistry, surface charge, shape/morphology, dissolution/solubility, physical/chemical properties and methods of synthesis. With this information one may forecast their applicability, toxicity or safety handling procedure. It is based on their intrinsic properties or in the ones obtained by tailoring them with other materials that potential applications are created, to achieve, for example [7]: miniaturization (e.g. of electronic equipment); weight reduction (as a result of an increased material efficiency); and/or improved functionalities of materials (e.g. higher durability, conductivity, thermal stability, solubility, decreased friction).

3. Practical nanomaterials based devices

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.

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.

3.1. 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 [8].

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.

[†] Southwest Europe - (Spain, Portugal and south of France)

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 1 - Evolution of test pieces and medium after 45 days

3.2. 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 2.

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.

Figure 2 - Auto heating seat fabric

3.3. Water detoxification system

Textile industry is one of the most water and chemical intensive industries worldwide due to the fact that 200-400 liters 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 [9].

Nowadays, nanoparticles and nanomaterials are being used for water and wastewater treatment: adsorption, membranes, photocatalysis, disinfection and microbial control and sensing and monitoring [10]. 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 [11].

IK4-TEKNIKER has employed a photocatalytic reactor from Ecosystem for the detoxification of coloured solutions. The photoreactor, showed in figure 3, 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.

NanoTiO_2 powders, used in direct dispersion into the coloured solution, TiO_2 nanoparticles are highly efficient in the photocatalytic detoxification of colored wastewater. 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.

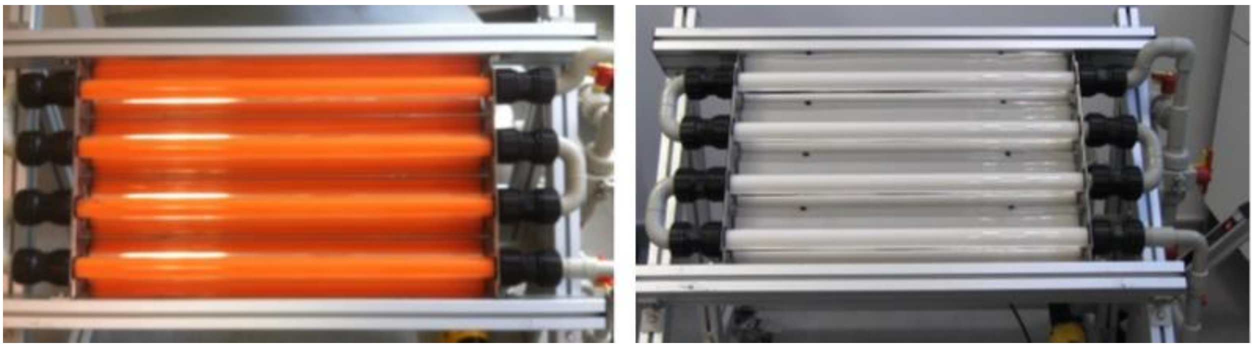

Figure 3 - Photograph of the solution in the reactor before (left) and after (right) the photocatalytic process.

3.4. 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 [12].

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 [13].

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 4 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.

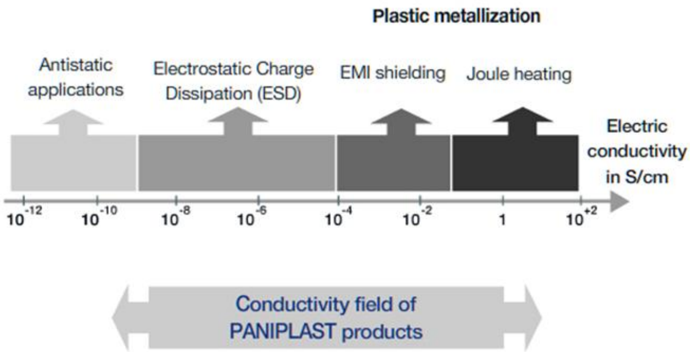

Figure 4 - Schematic representation of the conductivity field of PANIPLAST products

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 5 show the heating paint applied in an airplane wind.

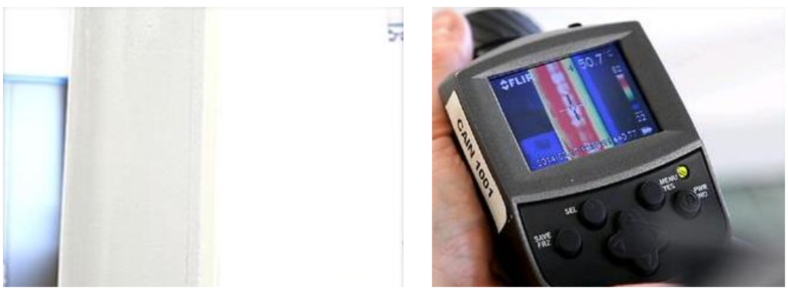

Figure 5 - Heating paint applied in an airplane wind

3.5. 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 [14]. 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 [15, 16].

Nanocrystalline diamond coatings have been applied in microinjection moulding cavities, showed in figure 6, 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.

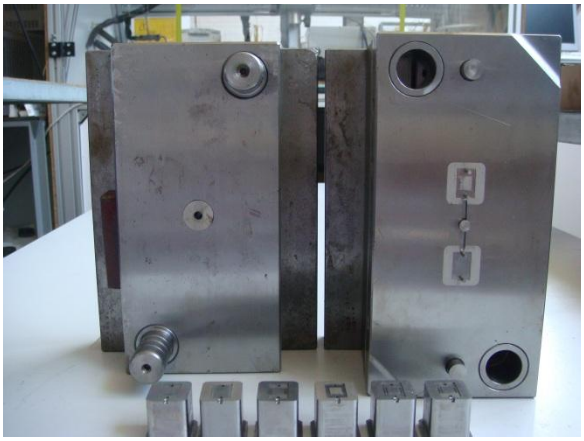

Figure 6 - Mouling tool with diamond coated inserts

4. Health and safety issues and environmental impact of 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 boarder 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 become 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 [17, 18].

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[‡]. 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 [19] and maintenance work [7] as well as good practices in the management of these materials [20]. In the United States, the National Institute for Occupational Safety and Health (NIOSH) recently released recommended exposure limits to individuals working with carbon nanotubes [17]. Several European Union industrial sectors are covered by specific regulations that also regard nanomaterials [21]: 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. [22] 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;
5. Foster the safe development of nanotechnology and realization of its societal and commercial benefits.

Although there is much to do in this field, it must be noted two distinguish situations: the manipulation of the nanoparticles and nanomaterials; and the end use of a product containing nanoparticles and nanomaterials. It is in the first where much attention must be places.

5. Conclusions

Nanotechnology is and will continue to create development and innovation in all different industrial sectors. It is seen as a key enabling technology for a wide range of applications on electronics, healthcare, chemicals, cosmetics, composites, energy, just to cite a few, creating new opportunities for the development of everyday products with enhanced performance, reduced production cost and using less raw material. Despite its development, there are some obstacles to a superior impact of nanotechnology in industry. The lack of information, the possibility of adverse impacts on the environment, human health, safety and sustainability, are still a challenge. A summary

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

review of nanoparticles and nanomaterials used in major industrial sectors have been address and the prototypes being developed with in the CarbonIspired 2.0 consortium presented, providing examples of practical applications, security issues and market.

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