Applications and Opportunities of Nanomaterials in Construction and Infrastructure

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Abstract New and extraordinary physical-chemical properties of materials at nanoscale open up new applications for the building and infrastructure industry such as structural reinforcements, electronic properties and energy harvesting. Therefore the issues and risks associated with the manufacturing of nanomaterials are now of big concern due to the large volumes and typical processing involved in this industry. This paper presents a discussion and selected applications of nanotechnology in the construction and building materials: from metals and alloys, clay and minerals, ceramics, cement and concrete, asphalt, wood and composites, to finishing systems and some of the most used characterization techniques. Besides the progress in some areas, nanotechnology is just emerging in this field, with many challenges and opportunities, problems unsolved and business opportunities. A discussion regarding the potential health issues and risks of using nanomaterials for workers and the potential environment effects is included as well. New images and diagrams are presented and discussed.

Keywords Cement · Concrete · Composites · Asphalt · Clays
Ceramics · Wood · Steel · Characterization · Nanomaterials

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Introduction

The physics and chemistry of nanostructured building materials differ from everyday materials due to quantic effects and due to its high surface area to volume ratio. Typical morphologies in nanomaterials are spheres, cylinders and sheets. These materials have changed the technology in an increasing number of applications, and the construction and building materials industry has also been benefit. In this paper, some of the most significant achievements of nanotechnology in the construction and building materials are discussed, not only in the materials developments but also in the most used characterization techniques. The main goal is to show the progress, tendency, and opportunities in this field, in a context not only useful for students, professors and researchers from engineering and natural sciences, but also for industries starting in nanotechnology, or simply for interested readers without background in nanotechnology.

Regarding the main areas of materials from science to engineering, applications and performance of nanomaterials seem to need more research and development than structure, properties, processing and characterization. This is true since most academic community agree in the high potential of nanomaterials to change significantly many aspects of our future. This is represented in Fig. 1a.

Figure 1b shows the construction and building materials from the present paper, mostly organized by their structure. Metals have metallic bond, ceramics can have ionic and covalent, and composites can have combination of different bond types. All can have secondary bonds too. Including organic materials, such as wood, the building materials can be classified as composites.

Materials in the building and construction industry such as cement and concrete (most used man fabricated material) have had a slow evolution in their science and engineering. Today, nanotechnology is rapidly changing this trend and many scientific and business opportunities appeared. On the other hand, areas such as composites have shown a notable development in the last years, as both

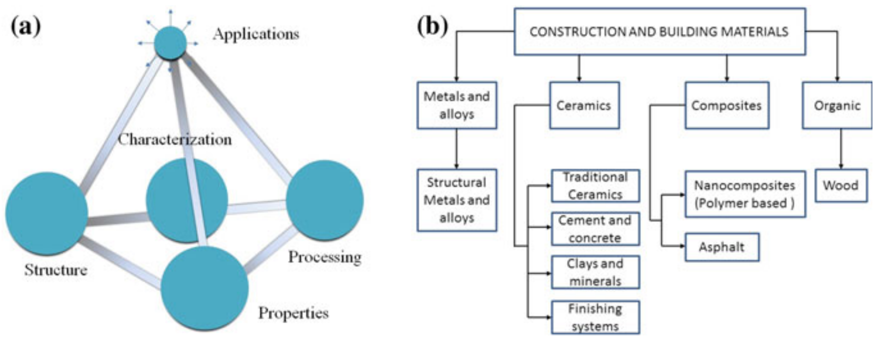

Fig. 1 **a** Diagram showing the applications growing area in nanomaterials; **b** construction and building materials from the present paper

nanocomposites and nanoadditives. In fact, aside with electronic and biomaterials are some of the engines that today drive materials science. As example, other fields such as wood have shown less progress in nanotechnology when compared to composites.

Therefore, in the last years, multiple and significant progress are changing the construction and building materials by a revolution in science and technology driven by nanotechnology. New trends and opportunities are emerging which must be taken into the account of young engineers, companies and researchers.

Materials and Methods

Metals and Metal Alloys in Building and Construction

Copper and steel are undoubtedly the most widely used metals in construction. Steel alloys are used in screws, bolts, as well as in beams and support structures and in particular as reinforcement within concrete concrete where either thick wires (rebars) or meshes are added in order to enhance the mechanical strength of concrete under tension and bending stress fields. The dimension of steel components for construction are typically in the centimeter to meter range and it is the advancement in the understanding of the effect of microstructure on the mechanical properties and corrosion resistance that has enabled the use of nanotechnology to achieve substantial improvements in the performance of metals and its alloys. For example, recent work by Lu et al. [1]. All text references should be consecutively numbered, using square brackets with the period after the reference; for example [1, 2] has shown that in low carbon steels microalloying with 0.1 wt% of niobium, titanium or vanadium results in hardening due to the controlled precipitation of carbides. The size of these carbides ranges between a few nanometers and one micrometer depending on processing conditions. It is important to note that when the size of the precipitates is below 10 nm there is an increase of approximately 200 MPa in the yield strength, which represents roughly a 25% improvement in the mechanical performance. While this is in itself an impressive enhancement, it is perhaps most important to recognize that it well known hardening techniques, like precipitation hardening, have seen a rebirth an expansion as a result of nanotechnology. Being able to characterize the microstructure of alloys and their precipitates in the nanometer scale has open the door for a whole new series of alloys for which the above is but one example.

In the case of copper, it is primarily used for electrical wiring and in piping where the use of polymers is not a desired or viable option. In addition, copper alloys such as brass are used in the weather protection of roofs, doors, siding, and facades due to its high corrosion resistance. Precisely in the field of corrosion Mao et al. [2] has demonstrated that through a process of nanocrystallization of a copper-nickel alloy (70 Cu–30 Ni) yields increased hardness and enhanced corrosion resistance. For reader interested in reading more about mechanical property enhancement in copper alloys using nanotechnology a number of sources including the work by Hoppel et al. [3] is available in the open literature.

Clays and Minerals

One of the most important aspects of working with clay is the determination of particle size. This is given by the genesis of the minerals that make up its internal composition. Kaolinitic clays, for example, are mainly composed of kaolinite (in Fig. 2a a nanoparticle of kaolinite is shown), halloysite, dickite and other minerals produced by the degradation of metamorphic rocks by effects of weathering. Formation processes allow the clay minerals, in some cases, to have particle sizes in the nanometer range, that is, which do not exceed 100 nm in average size. These sizes are critical in determining the application to these clays. Nanotechnology has now come to stay when using fine-grained clays is about. The interaction at the nanometer scale between particles had found important applications for this type of minerals and rocks.

Working with nanoparticles has allowed to change existing paradigms regarding the surface behavior of clays and thus achieve processing that until recently were not conceived; it is the case of mineral processing, classification processes [4] and concentration of minerals, such as flotation [5, 6]. For the classification and separation of minerals it was reached using banks of hydrocyclones for separating particles of nanometer size from those of micron size and thereby control key parameters in their use, such as chemical surface, which is key in controlling the rheology of slurries and suspensions, critical in the ceramic industry, paint, food, etc. With regard to the concentration of minerals, nanotechnology has advanced

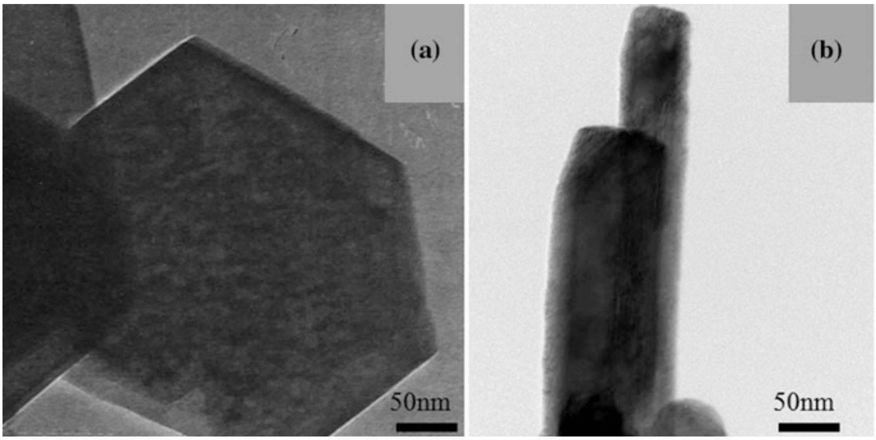

Fig. 2 Transmission electron microscopy (TEM) for **a** Kaolinite, **b** goethite nanocrystals

significantly in processes such as flotation of ultrafine particles; it is the case of feldspar contaminated by quartz or talc mixed with some iron oxide powders, which changed its color which made them suitable for the cosmetics industry. Today this is possible and has been given a major boost to some sites that until very recently were not considered.

Recent Works [7] have let to explain that, when the clay minerals have small size of particle, they could change the color of the clay, thus bleaching processes can be performed successfully performing effective separation of different sizes comprising mineral samples.

With respect to mineral transformation process, nanotechnology has enabled processes on an industrial scale for obtaining nano-sized crystalline structures in order to achieve special applications. Such is the case of the pigment industry [8, 9], coatings industry [10] and decorating industry [11], among others, which, by controlled particle size growth processes, have succeeded in designing products for specific colors, resistance to temperature, weathering, and extreme working conditions, such as acidity or alkalinity. All this thanks to the understanding of the processes of nucleation and growth and control of the technological aspects that allow handling. Figure 2b is a photo taken of goethite nanocrystals (FeO (OH)), used since ancient times as a pigment.

Ceramics

In general ceramic compounds are the materials most widely utilized in construction as described before, however engineering ceramics as those shown in Fig. 3, constitute an important area in modern applications in áreas such as electronic materials or high temperature ceramics. This is not surprising given the fact that clays and minerals used in bricks, stone, marble, granite, sand, as well as cement, and concrete are all ceramics. Since several of these are described in detail elsewhere, in this section only glasses are discussed.

Since its discovery, glass has been used broadly in construction as part of decoration but also as an integral part of the architecture as light management and exterior walls. Of the extensive number of recent advances in glass for building and construction as a result of nanotechnology, it is particularly worth mentioning tempered glass as a result of ionic exchange (also used in smartphones) which exhibit high fracture toughness enabling its use in buildings requiring adequate hurricane and wind damage protection.

Likewise, recent advancements in thin film coatings (i.e. coatings of submicron thickness) have enabled novel applications in the field of smart windows such as thermochromic windows and self-cleaning windows. An example of thermochromic windows (i.e. windows that change color or transparency with temperature changes) is achieved with thin film coatings of vanadium oxide (VO_2). For

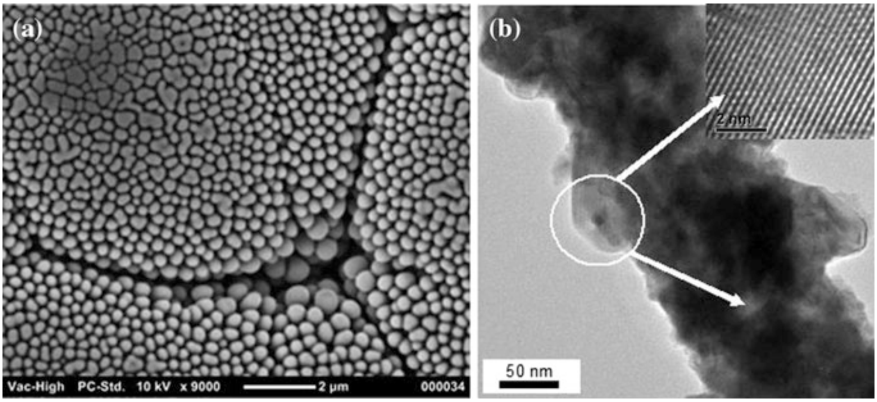

Fig. 3 **a** SEM micrograph revealing the surface morphology of an electrodeposited ceramic coating revealing the nanometer nodular structure; **b** TEM of a $BaTiO_3$ nanofiber synthesized by electrospinning. The inset shows the lattice fringes indicating the crystallinity of the polycrystalline nanofiber. Both images were collected by the Nino Research Group at University of Florida

example, Zhang et al. [12] have shown that a VO_2 coating of 56 nm maintains the transmittance in the visible spectrum combined with a 50% efficiency in blocking the infrared spectrum, which is the highest heating contributor. The development of this type of smart windows and related applications has enabled a leap change in building energy management practices and standards. The recent review by Kamalisarvestani et al. [13] is an excellent source of information in this particular topic.

As mentioned before, another area of recent interest and impact is that of self-cleaning windows. In this type of windows, coatings typically of titanium dioxide [14] or sílica [15] with thicknesses in the 120–150 nm range induce photocatalytic reactions when in contact with dust and other environmental contaminants and the product of these reactions is washed away by the rain thus leaving behind a clean window. It is important to note that there are already a number of commercially available smart window products and its broad use and expanded market share is anticipated. Jelle et al. [16] presents a list of applications for smart windows, discusses state of the art research areas in the field as well as future trends.

Cement and Concrete

Concrete, and cement as its main component, are the most widespread man made materials. These materials are very successful not only for their performance in buildings and infrastructure, but also for the low cost and raw materials availability.

Lastly, cement has been significantly progressing with nanotechnology, mostly because cement is a multiphase material strongly influenced by its components, such as hydrates, at the nanoscale.

On the other hand, since the hydration process is such a complex one that involves a lot of mechanisms and species reacting chemically in different time scales, from seconds to years, some fundamental aspects, at nano and even micro scales, are still unknown. Because of this aspect, nanotechnology will continue driving areas like cementitious materials specifically in the materials characterization and nano-additives.

For instance, the understanding of the main cement phase, the hydrated calcium silicate C–S–H which corresponds to nearly 60% of all hydrates in cement, was a significant progress due to nanotechnology [17]. In addition, researchers reported that C–S–H and other cement phases could be modified with nanotechnology through organic molecules [18] in order to tailor different properties. Moreover, since some cement structures do not have a long order range, identification by traditional methods such as X-ray diffraction (XRD) is very complex and not possible in some cases. However, other techniques such as transmission electron microscopy (TEM) and nuclear magnetic resonance (NMR) enabled us to build a clear atomic structure of C–S–H nano-crystals in the last 25 years [19–22].

Another significant achievement was the development of the third generation of super-plasticizers additives, such as PCE (polycarboxylate ether), used to improve the particle dispersion and to reduce the amount of water in cement (which is known as strength improver).

The accelerated development of nano-additives for concrete enabled the development of a wide varied amount of modified mixtures (see Fig. 4) with high mechanical performance and durability, for applications such as pre-fabricated parts, such as tubes, walls, and beams [23, 24]. Figures 2b, c show portlandite, one of the cement clinker phases. Finally, nanotechnology is also a way to decrease the negative environmental impact and costs in concrete, which is given a new generation of construction and building materials.

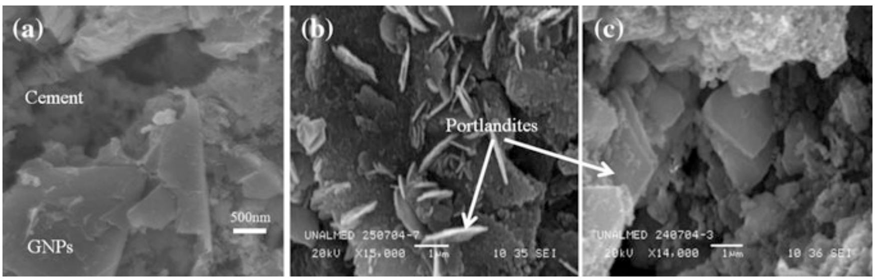

Fig. 4 Images taken with transmission electron microscopy (TEM)) for **a** reinforced concrete with graphite nanoplateles (GNPs), **b** and **c** the nanostructure Portland cement phase portlandite

Asphalt

Besides asphalt pavement is used at large scale in roads of big cities, its macroscopic behavior depends from its properties at micro and nanoscale. Therefore, research showed improvements in durability, fatigue life and routing for asphalt and its admixtures with nanotechnology. This was mainly obtained with nanoadditives (such as nanoclay, carbon nanotubes, and other nanostructures from silica, alumina, magnesium, calcium and titanium dioxide) [25].

As one example of many significant advances in this field, it has been found that nanoclay non-modified (NNM) increases slightly the asphalt viscosity, whereas the same nanoclay modified with a polymer (NMP) slightly decreases the asphalt viscosity. On the other hand, the addition of NNM improved the high temperature stability, whereas the addition of NMP do not produce significant changes, but increases the asphalt recovering. In summary, the addition of NNM in general increases the asphalt recovering [26].

Another good example is the addition of silica nanoparticles to improve fatigue, dynamic modulus, routing strength, and anti-aging behavior [27]. Similarly, a great result found was that adding only 1% of rubber nanopowder obtained by the sulfurization of latex nanoparticles in a dry process, asphalt has a higher cracking and routing strength at low temperatures. Moreover, by adding up to 3% of this powder the softening point can increase from 48.3 to 55.3 °C [28].

The examples shown above shows the great potential that nanotechnology has in the future of asphalt and other related materials.

Wood

Being one of the oldest and most widely used construction materials, it would seem rather incredible that nanotechnology would have enabled key advances even in wood. Nonetheless, same as with almost all materials, the ability to investigate the structure of wood in the nanometer range has yielded a better understanding of the origin of the observed properties and thus has enabled the tailoring and development of new properties and response to external stimuli like environmental conditions and in particular the relative humidity. Humidity control in wood is essential to ensure property homogeneity and in particular to control shape and limit deformations. In general, wood is hydrophilic, that is, it has an affinity for water and it can readily absorb it. Therefore, any modification to the wood characteristics that can make it repel water (hydrophobicity) is of great interest. It is precisely here where nanotechnology has demonstrated promising results. To highlight just one of the numerous works in this area, according to Artus et al. [29] deposition of silicon filaments, between 20 and 50 nm in diameter and 1 μm in length, on the surface of wood results in “superhydrophobicity”, a term used to highlight the extreme repulsion of water with contact angles above 150°, where 0° is indicative of a hydrophilic surface and 180° indicative of a perfectly hydrophobic surface. This is an impressive and transformative result as it represents a new paradigm in the interaction of water and wood. For additional reading about this and other processes that can be used to modify the properties of wood that are relevant for construction the reader is referred to the review by Wang and Piao [30].

Composite Materials

Nanocomposites are multiphase materials where at least one of its phases has one, two or three dimensions of less than 100 nm. Therefore, many topics of this paper could classify as nanocomposites. Therefore, in this section we will only consider those with polymeric matrix. As one of the many great applications, polymeric nanocomposites are used to repair and rehabilitate damaged construction and structures, such as tubes and bridges [31]. Nanocomposite coatings are required where a fast set material is needed, such as in metallic tubes repair with defects induced by corrosion, in such a way that no flow stopping is needed while tube is repaired, as shown in Fig. 5.

Known nanocomposites also act as fillers, and these can have a very diverse chemical composition (such as nanosilica SiO_2, nanoalumina Al_2O_3, or titanium dioxide TiO_2); nanoclays (such as montmorillonite $(Na,Ca)_{0.3}(Al,Mg)_2(Si_4O_{10})(OH)_2\ nH_2O$); or CNTs and carbón nanofibers [32, 33]. These nanoadditives change the resin rheology, increase the stiffness one gets set, and reduce the difference in the coefficient of thermal expansion between the filler nanocomposite and the substrate (such as in a metallic tube).

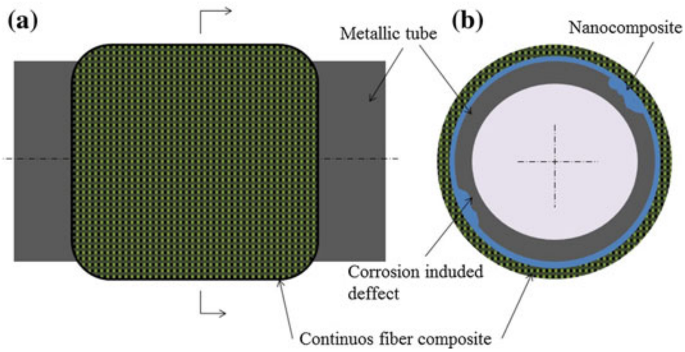

Fig. 5 **a** Typical repaired tube by polymeric nanocomposite resin with continuous fibers; **b** cross sectional detail

Finishing Systems

The application of nanotechnology has allowed the construction industry forward significantly in subjects which until a few years ago were considered finished and completed. This applies to finishing systems and decor. In recent years there has been significant progress in the development of new designs and technologies, which were considered impossible to achieve. Particularly in the ceramic industry it has opened a major way in the design of complex modern formats and techniques used as decorating inkjet [34], application of laser and plasma decoration, and special deposition techniques (PVD, CVD) [35]. New technologies allow very sophisticated decor finishes and the key to all these techniques is precisely the use of nanotechnology, as it has led to the use of products with distinct sizes and tailored particle distributions which has been possible to implement of appropriate technologies. The same has been achieved in the application of cement and concrete finishes, paints, wood and other natural elements, which change significantly their surface appearance, presenting sizes of very fine and controlled in terms of particle distribution.

As for the surface finish of construction products such as cement, concrete, ceramic, wood and other natural products, the use of some nanoparticles, used as additives, has great potential in technological development because these particles applied in small significant portions help to significantly improve the final properties of the paints and varnishes used on them so. Adding ZnO nanoparticles improves significantly the performance against UV radiation of the coating, while the addition of alumina (Al_2O_3) and silica (SiO_2) improves quality of the stripes. Paintings with self-cleaning properties and anti-graffiti eco solvent which dried in about three seconds and turn out to be much cheaper than conventional paints [36].

Installation and Lightweight Construction Systems

On the use of installation systems of building products, as well as light weight construction, nanotechnology also has an important application field that has been growing over the course of the years. The use of nanoparticles of iron oxide thermally activated adhesive materials allows remote start of the drying process by applying an electromagnetic field in the microwave-range radio frequency (1–10 GHz). Also, on completion of the drying process of the adhesive on scales smaller time than conventional processes, the undesirable heating of surrounding areas is reduced [37].

The applications of this kind of technology could be in all those in which it is desired to bond two pieces reducing unwanted heating of adjacent areas, by heating locally the glue. It is also used when it is desired to decrease the drying time of an adhesive, whereupon processes needed to complete valuably reduce welding parts. Furthermore nanoparticles absorb radiation and heat drying glue matrix [38].

Polycarboxylate based additives allow the tailoring of the different functional parts of the molecule to each of the functions needed in the installation materials. Polycarboxylates have a molecular structure composed by a main supported chain structure with free functional groups as side chains, which allow the interaction with the cement for diverse applications, and can be adapted using nanotechnology to the desired functionality [39].

Characterization Techniques

As it has been emphasized throughout, being able to observe and investigate the surface and microstructure of materials in the nanometer scale is perhaps the most important development that has allowed for the vast impact of nanotechnology. In general, any advanced characterization technique, provided the needed resolution, can be used to investigate nanotechnology either directly or indirectly. Nonetheless, without presenting extensive technical working details of the techniques, it is still worth highlighting some microscopy and spectroscopy examples.

(a) Scanning electron microscope (SEM) uses the interaction of a beam of electrons with the material to form an image and it therefore allows for the visualization of the material surface in the nanometer scale (which is smaller than the wavelength of the visible light). The current state of the art SEM have a typical resolution around 2 nm.
(b) Transmission electron microscope (TEM) is similar to SEM but with the difference that the samples utilized are ultrathin (nanometer thickness) and therefore allow the transmission of the electron beam and the image is then formed from the transmitted electrons. State of the art TEM with aberration correction can resolve sample features in the order or 0.1 nm.
(c) Atomic force microscope (AFM) is a scanning instrument that combines laser optics and piezoelectric conduction to detect forces in the order of nanoNewtons through a cantilever probe. The motion of the cantilever can itself be registered with nanometric spatial resolution. This combined force-space precision allows the formation of surface and topographical images of the samples with resolution around 1 nm. Given the versatility of the type of probe that can be used and different the modes of operations (contact or dynamic) AFM is perhaps one of the most widely techniques used in nanotechnology.
(d) X-ray photoelectron spectroscopy (XPS) is a technique that enables the estimation of the stoichiometry of the sample surface with typical resolution around 5 at.%. The unique advantage of XPS relies on the fact that it enables the separate characterization of the first 10 nm of material below the surface. Moreover, with techniques like ion ablation it is possible to remove the atoms between 1 and 8 nm below the surface and thus a detailed analysis of the composition as a function of distance from the surface in the nanometer scale is possible.

For additional information on this and other characterization techniques it is worth consulting volume 10 of the ASM Handbook.

Health Concrete and Environmental Risk for Using Nanomaterials

Nanoparticles and nanomaterials in general as we know have always existed in nature, however, it is just in this time when humans have been creating a lot of them by engineering, and therefore there are questions regarding their effect on the environment and human health. Due to the nanomaterials high surface to volume ratio, they have a highly reactive materials. This enables them as reactive oxygen species (ROS) and free radicals, important mechanisms of nanomaterials, which has an emerging science, the nanotoxicology [40]. ROS have been related with CNTs, carbon fullerenes and metal oxides nanoparticles, resulting in health issues such as inflammations, and protein, DNA and membranes damage [41]. Human body is more exposed in skin, respiratory and gastrointestinal tract due to the semi-open condition of these parts. Hristozov and Malsch [42] have drawn very important conclusions after investigation on the nanoparticles effect on human health. Figure 6 summarizes some of the information presented above. The main routes of exposures for mammals have been classified as dermal, ingestion, inhalation, and ocular. These correspond to the more vulnerable body parts typically more exposed to environment. Also, the main contamination sources are grouped in Fig. 6: combustion, medicine and cosmetics, mining and construction industry, energy, laundry and automobile industries. Particularly in case of construction and building materials industry there are additional issues regarding the final product presentation. Many of the supplied materials are powders that workers and people use at home, nanoparticles have to be stabilized in many ways if companies want to put it on a cement powder mix at store. Major advances are needed until this can be safe for all.

The first conclusion is that with the state of knowledge we have of the topic it is almost impossible to know any collective judgment about the potential risks for exposure to nanomaterials, although most of research show that nanomaterials have different types of hazardous effects on life. This is due to the limited number of studies of effects of nanomaterials in human and environment. Thus, engineering nanoparticles influence on life is even less known [42].

Lee et al. [43] have reported a good review on environmental health and safety considerations of nanoparticles in the construction industry. Research in several nanoparticles show their negative effects, for instance, carbon nanotubes (CNTs) cause pulmonary toxicity and inflammation in mammals [44, 45] associated with cell wall damage. C_{60} fullerenes show antimicrobial activity, which is toxicity to bacteria by an oxidation to cells mechanism [46, 47]. TiO_2 irradiated with UV cause inflammation, cytotoxicity, and DNA damage in mammalian cells [48]. SiO_2

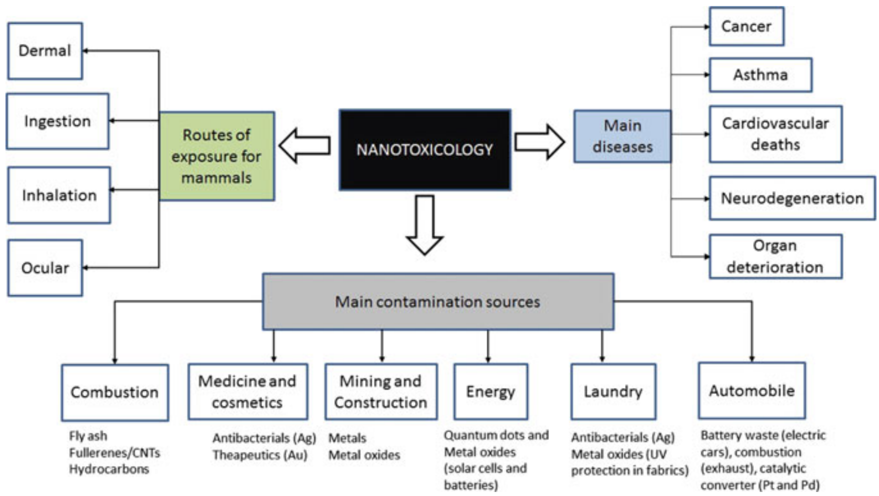

Fig. 6 Nanoparticle health concerns and environmental risks

nanoparticles have been related as carcinogenic [49–50] by causing problems such as membrane damage and tumor necrosis genes in rats. Quantum dots are toxic for both mammalian cells and bacteria due mainly to their hazardous heavy metals content such as cadmium and lead [51]. Copper and copper oxide can cause DNA damage in bacteria, algae, yeasts, mice, and human cells [52]. Figure 6 summarizes many of this examples in the main diseases: cancers, asthma, cardiovascular deaths, neurodegeneration, and multiple organ deterioration.

The second important conclusion relays on the fact that there are many actions and activities that need to be done in order to decrease the negative effects of nanoparticles. Moreover, the degree of their environmental mobility and bioavailability of nanoparticles need to be established.

Summary

Some of the most significant advances in nanotechnology of construction and building materials has been presented in this paper. As shown above, nanotechnology has gone into all different kind of materials and applications, solving old problems and some new challenges that are just emerging. Examples from metals and alloys, clay and minerals, ceramics, cement and concrete, asphalt, wood and composites, to finishing systems and some of the most used characterization techniques are discussed.

Therefore, it is clear to see that this area will be a great tool for construction materials understanding and improving, carrying out the industry to find the limits of materials such as tallest buildings and extreme durability of infrastructure.

Besides the progress, nanotechnology is still an emerging area with many challenges and opportunities, problems unsolved and business opportunities. Some open areas from the materials and processing are: particle agglomeration, scaling up, property repeatability, and interface enhancement.

Finally, nanomaterials effects on health and environment has still not much information to know all its effects. However, most research reveals its negative effects on life. Urgent actions must be taking into the account in order to avoid a public health worldwide problem. The industry of construction and building materials have extra challenges due not only to its large scale but also to the current manufacturing procedures which probably need to be fully redesigned when nanoparticles are used. This is not only an issue, it is a motivating challenge to engineers and scientist to work in new technologies of materials and manufacturing.

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