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Nanotechnology in Eco-efficient **Construction Materials, Processes** and Applications

Second Edition

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Introduction to nanotechnology Introduction to nanotechnology
in eco-efficient construction

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1.1 Recent nanotechnology advancements and limitations

In the past decades, nanotechnology which is not considered a sector by itself but a highly dispersed multidisciplinary area has been on a rise not only in terms of papers and patents but also in terms of applications. A review on paper and patent production for the period $2000-16$ shows that United States is the dominant player both in publications in top journals and also in patents although China has shown a relevant growth (Zhu et al., 2017). A recent survey has tracked the patent production in the field of nanotechnology (Ozcan and Islam, 2017), using the patent provider Thomson Innovation. The study shows that there are around 50,000 patent inventions, of which around 30,000 are owned by corporations, around 14,000 by inventors, around 11,000 by academia, and almost 2,000 by government. The shared patents explain the difference in the total. Of course, as Fig. 1 in the paper of Ozcan and Islam (2017) shows, different countries show different proportion of owners in the patent production. Inventors are the majority of the owners in United States. With regard to corporates, the United States and Japan have similar levels of patent ownership. France, for instance, has a higher proportion of government ownership, while in China its academia has the largest proportion. Of course it is important to take into account the method used for patent retrieval because the authors point out that there are some patents on the nanotechnology class that are not related to this field. Sabatier and Chollet (2017) using bibliometric data and a survey of French nanotechnology scientists showed that promoting ground-breaking, innovative research provides an important advantage for future scientific production. However, it is important not to overemphasize the importance of patents because van Raan (2017) showed that only a small amount of patents represent important, "radical," technological breakthroughs. Also in an important essay, Archibugi (2017) mentioned that intellectual property rights may delay the diffusion of knowledge and that disruption by itself does not necessarily lead to progress or to greater economic efficiency, and if it is not properly managed it can lead not only to company losses, but to societal damages as well. In fact, Shapira and Youtie (2015) mentioned that many nanotech sales forecasts were adjusted downwards because some of the promised scale benefits are unlikely to be realized. On one hand complex nanomaterials may not be very environmental friendly and life cycle assessment (LCA) may require further

investigations. Up to this date the recyclability of nanomaterials is not being adequately tackled, as well as their environmental impacts in the end-of-life stage (Pacheco-Blandino et al., 2012). On the other hand the toxicity of various nanomaterials for human health and for the environment is still under debate (Kim et al., 2016). Safety management of nanoparticles and nanomaterials is also a critical issue (Spitzmiller et al., 2013). Still the potentially revolutionary technologies may have limited impact upon macroeconomic performance, if they do not give rise to a new wave in terms of capital accumulation and public investment in infrastructure (Lundvall (2017). According to this author, countries and organizations promoting "experience based" knowledge and combining it with science-based knowledge are more innovative than those that only give attention to codified knowledge. He also states that learning from experience may feed wisdom and that learning societies where men and women are expected to contribute to the production and use of knowledge are to be preferred to societies where only small intellectual elites produce knowledge. An interesting case in this regard is that of Russia, a country that shows a declining share of nano papers in spite of an increase in research funding (Terekhov, 2017) and a rigid academic structure that does not allow newcomers nor does engage in collaborations with the private sector (Karaulova et al., 2017). Also important in the field of nanotechnology is the performance of Asian countries that Ludvall (2017) deems crucial for the world economic growth. China being the new world scientific powerhouse (Tollefson, 2018) also identified nanotechnology as a priority area in its national agenda of science and technology development $(2006-20)$, and has increased R&D investment in the field. In fact, China has consequently emerged as one of the key global players in nanotechnology, producing the second largest number of nanotechnology papers after United States (Wang and Guan, 2010). China has made significant advances and currently has the fastest growing nanotechnology publications. However it still lags behind in publication in leading nanotechnology journals. An analysis of papers published in nano-related journals with an impact factor above 20 shows that USA published 1068 papers, Germany (221), UK (193), France (149), Japan (121), and China only produced 76 papers (Dong et al., 2016). Of course, this may change in the coming future because China's one-thousand-talents plan (www.1000plan.org) to attract its overseas researchers has already recruited more than 2000 researchers, most of them trained in the USA (Gao et al., 2016). Still in China, the pathways from laboratory research to successful commercialization remain problematic. The Chinese nanotech industry is relatively weak in commercializing basic research and in its production of nanotechnology devices (Shapira and Wang, 2009; Zhang et al., 2017). As to India, the other Asian giant, although and according to the World Bank is now growing more than China and will be fifth largest world economy in 2018, the fact is that concerning nanotechnology India is still lagging behind several other countries (Momaya and Lalwani, 2017). It is a relevant fact that these authors are aware of the fact that technological innovations can have negative externalities thus confirming the position of Archibugi (2017) previously mentioned.

1.2 Nanotech-based materials for eco-efficient construction

Since 2013 when the first edition of this book was published, the number of publications in the field of nanotech-based eco-efficient construction materials saw a huge rise. Back then, a search on the Scopus database showed only a few publications. Now the same search returns several hundred. Of course let us not forget that in practical terms there are several and confusing definitions of what constitutes a nanomaterial and about the requirements to identify nano-enabled products. Some products are advertised as having nanoenabled features, something that is simply not true, while others fail to disclose the fact that they have nanoparticles or were obtained by nanomanipulation (Jones, 2016). Also, in the introduction chapter of the first edition it was argued that too little nanotech efforts were put in important construction materials like concrete, the material most consumed by the construction industry. Scopus now shows that nanotech concrete—related publications have risen around 500%. Of course, some publications have exaggerated the promises of nanotechnology in the field of construction industry, failing to produce evidence that support such claims. Hanus and Harris (2013) wrote that "Nanotechnology has the potential to reduce the environmental impact and energy intensity of structures, as well as improve safety and decrease costs associated with civil infrastructure," but no reference is given to back this statement. Also no cost data is given concerning the use of nanoparticles in concrete and in Section 2.2 the authors wrote that "The cost of CNTs is currently prohibitively high to allow for the use of CNT/cement composites" thus contradicting their initial claim. They also mention that the future implementation of advanced structural health monitoring systems will increase as the technology matures and associated costs decrease. However, this is just an expectation, which is very far from the cost decrease of current infrastructure mentioned in the introduction. Also they confirm that high cost is reported to be a main drawback for the use of carbon nanotubes (CNT) sensors in concrete. They also mention that self-cleaning hydrophobic paints are potentially valuable in the construction industry for the reduction of costs associated with maintaining building walls and façades, but again no data is given concerning any possible life cycle cost comparison. Instead, the authors prefer to "focus on up-front build costs over long-term cost, performance, sustainability and safety." However, instead of blaming the construction industry because of the so-called "focus on up-front build costs over long-term cost, performance, sustainability and safety," it would make more sense to highlight the fact that so far nanotechnology research has given very little importance to the factors that are important for the construction industry and that show a gap between what researchers consider important and what the construction industry needs. Taalbi (2017) showed that solving real-life problems was a source of innovation for several industries, meaning that it is not understandable that those engaged in nanotech for the construction industry have given so little attention to cost, because on the five criteria that identify the emerging technologies of great impact (Archibugi, 2017) the first one is precisely "drastic reduction in costs." The contribution of nanotechnology for sustainability and the 2030 agenda for sustainable development that are related to

the construction industry are also very important. Infrastructure resilience is the ninth goal of 2030 United Nations Agenda for Sustainable Development. It is also one of the 14 Grand Challenges of Engineering. Overpopulation will not only require new infrastructure, but it will put increased pressure on the existent infrastructures. That is why almost 50% of the chapters of this book concern infrastructure materials including health monitoring-related materials. Concrete infrastructure encompasses bridges, piers, pipelines, dams, pavements, or buildings that are crucial to services and economic activities of modern civilization. European design codes now require a service lifetime of more than 75 years for concrete structures in large public works. But, experience has shown that infrastructures begin to deteriorate after only 20 or 30 years. Concrete deteriorates due to several causes including, for instance, mechanical deterioration like impact or excessive loading or deterioration due to physical causes like erosion or shrinkage, but also due to chemical detrimental reactions when it is exposed to environmental conditions containing chlorides from seawater or from deicing salts, atmospheric carbon dioxide, or other aggressive media (Glasser et al., 2008). In United States alone, costs related to wasted fuel and time loss due to traffic congestion is estimated to be between 50 and 100 billion dollars (Schlangen and Sangadji, 2013). Only in the city of Hong Kong, more than 580,000 vehicles cross its 900 highway bridges on a daily basis (Pei et al., 2015). This traffic volume is expected to duplicate in the next decades and as a consequence by 2035 it is expected that there will be 2000 million vehicles on the road (Pacheco-Torgal, 2017). This means that concrete highways bridges will be subject to increased use and will reach the end of its service life sooner than expected, and repair and rehabilitation costs will increase even further. The acting decision however is related to the assessment of the infrastructure performance, but monitoring activities are also costly and not all countries can afford it; in the United States bridges are inspected every 2 years (Rehman et al., 2016). The lack of regular inspections worsens the problem and contributes to premature infrastructure deterioration, thus leading to possible bridge failure with the inevitable loss of human lives. This shows the importance of the development of materials with self-healing ability. The development of materials that can provide real-time monitoring is extremely important in this context. Energy efficiency is also a very important issue under the 2030 United Nations Agenda for Sustainable Development. That is why seven chapters of this book are related to this theme as a way to minimize climate change impacts (goal 13) because energy production is the main aspect that is responsible for global greenhouse-gas (GHG) emissions. As the source of two-thirds of global GHG emissions, the energy sector is therefore pivotal in determining whether or not climate change goals are achieved. Photocatalytic water treatment is also covered in this book because it is a very important issue. For instance, Bhati and Rai (2017) show a worrying water scarcity scenario in India in the next decades. Also limited freshwater availability is identified as one of nine planetary boundaries and 4 billion people face severe water stress during at least 1 month per year, and 1.8 billion at least 6 months per year (Vanham et al., 2018). And that is why availability and sustainable management of water is also a goal of the UN agenda for sustainable development. This book's structure gives an added value because other books concerning nanotechnologies for the construction sector have preferred to focus on technologic advancements and much less on societal challenges.

1.3 Outline of the Book

This book provides an updated state-of-the-art review on nanotechnologies for ecoefficient construction materials. Part I encompasses mortars and concrete-related applications (Chapters $2-7$).

Chapter 2 concerns the influence of nanoparticles on the mechanical strength of ultra-high performance concrete (UHPC). The influence of various supplementary cementitious materials such as metakaolin and fine ground fly ash and curing regimes (in water, steam, and autoclave curing) on the properties of UHPC are analyzed. The influence of the nanosilica as the most frequently applied nanomaterial and the curing regimes on the strength of UHPC are studied. Nanomaterial dispersion and distribution have significant influence on the properties of cement-based materials. Techniques for better homogenization of nanoparticles are listed.

Chapter 3 discusses the effect of nanoparticles on the self-healing capacity of high performance concrete. Additionally, modifications promoted in certain properties by self-healing systems not based on nanoparticles in HPC are also given.

Chapter 4 overviews the findings of inclusion of graphene oxide (GO) in the cementitious materials. This chapter describes in one way the improvements in the performance of the cementitious composites and in the other way the new properties that can be shaped.

Chapter 5 deals with applications of nanomaterials in alkali-activated binders. The advantages and disadvantages of applying nanomaterials are assessed, and the healthrelated issues on applying nanomaterials are discussed. The effects of different types of nanomaterials, including nanosilica, nano-TiO₂, nanoclay, and nanocarbon tube on the performance of alkali-activated materials and their optimal dosage are summarized.

Chapter 6 covers the case of geopolymer composites reinforced with nanofibers. The effects of reinforcements on fracture toughness of geopolymers are addressed. A comparative analysis between the nanofibers with low and high interfacial bonding with geopolymer is presented.

Chapter 7 provides a review of the use of nanoindentation for evaluation of properties of cement hydration products. The effect of fly ash addition on the mechanical properties of hydration products is also discussed based on the results of experimental nanoindentation studies.

Applications for pavements and other infrastructure materials are the subject of Part II (Chapters $8-17$).

Chapter 8 reviews the performance of asphalt mixture with nanoparticles. It includes the types of nanoparticles, laboratory techniques of preparation of nanoparticles modified by asphalt mixture; properties like resilient modulus, dynamic creep, rutting distress, moisture susceptibility, and aging.

Chapter 9 summarizes the current research and findings on performance enhancement of the nanomodification on asphalt mixture. It reviews the main nanomaterials applied for the modification, and it also addresses the dispersion protocol for these nanomaterials into the asphalt binder.

Chapter 10 addresses the case of graphene oxide-GO-modified asphalt. The performance of this material is assessed through Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), gas chromatography-mass spectrometer (GC-MS), and thermogravimetric (TG) analysis.

Chapter 11 reviews the recent progress of classification, fabrication and signal measurement, sensing mechanism, and application of nanocomposites for structural health monitoring.

Chapter 12 presents a case study chapter on concrete with nanomaterials and fibers for self-monitoring of strain and cracking subjected to flexure. The effect of nanocarbon black (NCB) and conductive fibers on the workability of fresh concrete is analyzed, the relationships between the FCR and the strain of initial geometrical neutral axis (IGNA) are established, and the self-sensing ability to the loaddeflection process and cracking behavior of triphasic conductive concrete beam subjected to bending are investigated.

Chapter 13 is related to icephobic nanocoatings for infrastructure protection. This review focuses on organic, inorganic, and hybrid nanocoatings, especially from the past decade, that have shown promise for future infrastructure applications. The chemical components of different coatings along with the application technique, anti/deicing tests and results have been summarized.

Chapter 14 presents a review on nanocoatings for protection against corrosion. A range of coating materials, including polymers, metals, and ceramics, is described. The focus is on self-repairing nanocoatings. Various self-healing mechanisms and attitudes for achieving self-healing anti-corrosion coatings are examined. Developments and trends in coating technology are also discussed. The final section emphasizes particularly on functional nanocoatings in commercial applications.

Taking into account the toxicity of the conventional coatings based on heavy metals, Chapter 15 covers the protection against corrosion by using nanofiller-based coatings. Various aspects of nanocoating performance against steel corrosion are focused in this chapter including the nanofiller type, their incorporation into varying corrosion coatings, and efficiency towards corrosion protection of steel substrate.

Chapter 16 concerns fire retardant nanocoating for wood protection. The prospects and multifunctionality of nanocoatings for wood were demonstrated using as example the influence of layered aluminosilicates, nanooxides, nanosilica sol, and nanostructured carbon materials on the fire resistance of polymers, as well as on the flame retardant effectiveness of intumescent coatings and impregnations.

Part III encompasses applications for building energy efficiency (Chapters 18-23).

Chapter 17 reviews the current state-of-the-art of the aerogel-enhanced opaque systems. First cement-based products are reviewed. Then, the chapter describes aerogel-enhanced renders and plasters, proposed by different companies worldwide or developed by the author. Later, the focus moves on to aerogel-enhanced blankets. Finally, future research challenges for making aerogel-enhanced products more common in buildings are presented.

Chapter 18 presents an overview of advanced glazing technologies, various aspects of aerogel windows and glazing units including: application in buildings, research progress, commercial status, case studies, and challenges ahead.

Chapter 19 reports a review of current research trends aiming at the design of multifunctional architectural glazings. Challenges, opportunities, and technological evolutions are reported, with special reference to highly performing materials, like perovskites.

Chapter 20 introduces the basics of electrochromic technology with a view towards its nanotechnology aspects, presents a case study on electrochromic foil for glass lamination, and ventures into some forward-looking aspects. Special consideration is given to the energy savings and other assets that are possible with electrochromic glazing.

Chapter 21 addresses the case of $VO₂$ -based thermochromic materials (flexible foils and coated glass) for energy building efficiency. Future issues about the direction of these materials are discussed.

Part IV is concerned with photocatalytic applications (Chapters $24-29$).

Chapter 22 provides a short overview of these mechanisms, focusing then on construction materials modified through the addition of titanium dioxide nanoparticles. Examples will be given of laboratory experiments carried out in the recent years, and of current applications in the built environment; attention will also be paid to the International standards that have been, and are still being, developed for this technology.

Chapter 23 addresses the formulation of new photocatalysts with wider range of radiation harvesting by doping with metals or nonmetals, composites, or mixtures to increase interaction with substrate, and promoting pollutant adsorption has been discussed. Different techniques for coating application; main characterization methodologies to determine properties of substrate, photocatalyst, and coated thin film; and demonstration of photodegradation activity are examined.

Chapter 24 presents an overview about the self-cleaning efficiency of nanoparticles applied on façade bricks. It covers the degradation of building façade s by natural and artificial agents. It also includes a short description of superhydrophobic additives. Photocatalytic and superhydrophilic additives are also discussed. The methods for façade preparation, the determination of self-cleaning properties, and the assessment of durability are also covered.

Chapter 25 covers nanotreatments to inhibit microalgal fouling on building stone surfaces. Ananalysis of the biocidal ability of photocatalytic $TiO₂$ -based nanocompounds (in combination with Ag and Cu nanoparticles) sprayed on travertine surfaces to limit or inhibit algal colonization (using accelerated test in laboratory conditions) is presented.

Chapter 26 describes the features of self-cleaning coating system. The chapter includes case studies concerning cooling load reduction for sites in Japan, Malaysia, and Thailand.

Chapter 27 addresses the case of photocatalytic water treatment. Oxidation processes and photocatalysis are reviewed. Synthesis and characterization of titanium dioxide thin films are addressesd. The chapter also covers the degradation of different contaminants.

Finally, Part V concerns toxicity, safety handling, and environmental impacts (Chapter 31; Chapters $28-31$).

Chapter 28 reviews nanoparticle toxicity and their adverse health effects. The following aspects are covered: nanoparticle size, shape and aggregation, and composition. Inhalation and ingestion of nanoparticles are addressed.

Chapter 29 is concerned with managing risks related to the use of nanomaterials in the construction industry, including management of emission and exposure scenarios.

Chapter 30 covers measurement techniques of exposure to nanomaterials in workplaces. Definitions as well as techniques and parameters for exposure measurements are reviewed. Devices and measurement techniques for workplaces are analyzed.

Chapter 31 closes Part V with a chapter on the life cycle of engineered nanoparticles.

In this chapter, we analyze potential releases across the life cycle of engineered nanomaterials (ENMs), and then focus on the application of the methodology of LCA to quantify the environmental impacts of ENMs throughout their life cycle. We use a review of available studies to highlight the benefits of applying LCA to ENMs, and describe data and methodological gaps that still require increased research efforts.

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