Review Paper

Application of nanotechnology in concrete and supplementary cementitious materials: a review for sustainable construction

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Abstract

The increasing research endeavors on nanotechnology encompasses a number of disciplines including the aspects of sustainable construction in civil and environmental engineering. Tremendous achievements have been reported on nanotechnology adoption on sustainable construction, but there are so much more to explore than has been achieved. Some of the advancements on the adoption of nanotechnology on sustainable construction, includes the enhancement of the rheology, strength and durability properties of concrete; which has been proved to be hinged on the nanoscopic characteristics of its constituent. Any modification at the nanoscopic level of concrete and its constituent influences its behavior, including its strength and durability characteristics. Hence, it is projected that the performance of concrete and sustainable construction materials in the future would be greatly enhanced by the application of nanotechnology to manipulate the atoms and molecules of these materials and their constituents at the nanoscale.

Keywords Nanotechnology · Cement · Concrete · Supplementary cementitious materials · Sustainable construction materials · Microstructure

1 Introduction

Nanotechnology is not exactly a new technology, it can be defined as the science and engineering of examining, monitoring, and modifying the behaviour and performance of materials at the nanoscale, which is between 1 and 100 nanometres. It is the process of creating a material or device with building blocks at the atomic and molecular scale [1]. Nanotechnology is an area of research and technology development aimed at both understanding and controlling matter at the molecular level and thereby affecting the bulk properties of the material [2]. Hence, it may be inferred to be the development of a high-performance, durable, novel material from the modification of the molecular structure of existing materials; thus, achieving greater benefits of the combination of the bulk properties of the parent material(s) for sustainable development. Additionally, Sanchez and Sobolev [3] asserted that nanotechnology is the understanding, control, and restructuring of matter on the order of nanometers (that is, less than 100 nm) to create materials with fundamentally new properties and functions. Nanotechnology encompasses two main approaches: (i) the "top-down" approach, in which larger structures are reduced in size to the nanoscale while maintaining their original properties without atomic-level control (e.g., miniaturization in the domain of electronics) or deconstructed from larger structures into their smaller, composite parts and (ii) the "bottom-up" approach, also called "molecular nanotechnology" or "molecular manufacturing," introduced by [4], in which materials are engineered from atoms or molecular components through a process of assembly or self-assembly

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as presented in Fig. 1. While most contemporary technologies rely on the "top-down" approach, molecular nanotechnology holds great promise for breakthroughs in materials and manufacturing, electronics, medicine and healthcare, energy, biotechnology, information technology, and national security [5].

2 Global index on nanotechnology

There exists a varying degree of national priorities placed on the importance of nanotechnology around the world. The global trend in the research of nanotechnology ranks China, Unites States of America, India, Korea, Germany, and Japan with the top sheer volume of nanotechnology-related papers. Although, the BRICS (Brazil, Russia, India, China and South Africa) are all striving to become nanotechnology hubs, Nigeria and South Africa ranks below the top 25 countries in the research and adoption of nanotechnology. The contributions of BRICS to this field nevertheless remains relatively modest, compared to China accounting for about 25 articles per million populations, Russia 23, Brazil and South Africa 9 and India 6. Their academic outputs in nanotechnology is growing, related patents and products are not always progressing at the same pace. In 2015, the ratio of nanotechnology patents to articles on nanotechnology was 2.47 per 100 articles for South Africa, 2.28 for China, 1.67 for Brazil, 1.61 for India and 0.72 for Russia. In comparison, Italy recorded 4.46, the UK 8.39 and Canada 10.08 [6]. Similarly, according to [7], a key indicator for national priorities on nanoscience; which is the ratios of the share of Nano-articles of a country of total global nano-articles to share of articles of the country to total global articles within the last 5-year period are compared for Nigeria, South Africa and the top six global leaders in nanotechnology research as presented in Fig. 2. Although, both Nigeria and South Africa recorded 0.57 nano-article ratio index, Nigeria seem to have recorded

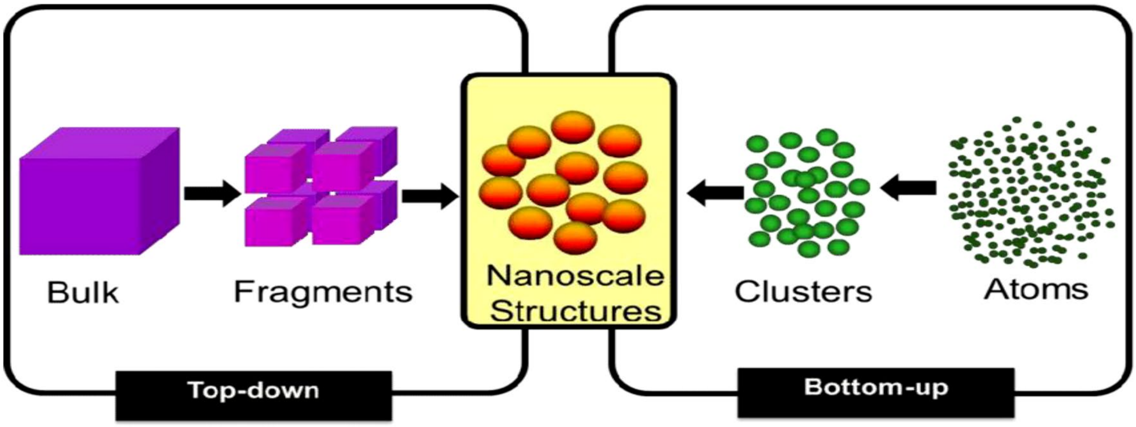

Fig. 1 Illustration of the "top-down" and "bottom-up" approaches in nanotechnology [5]

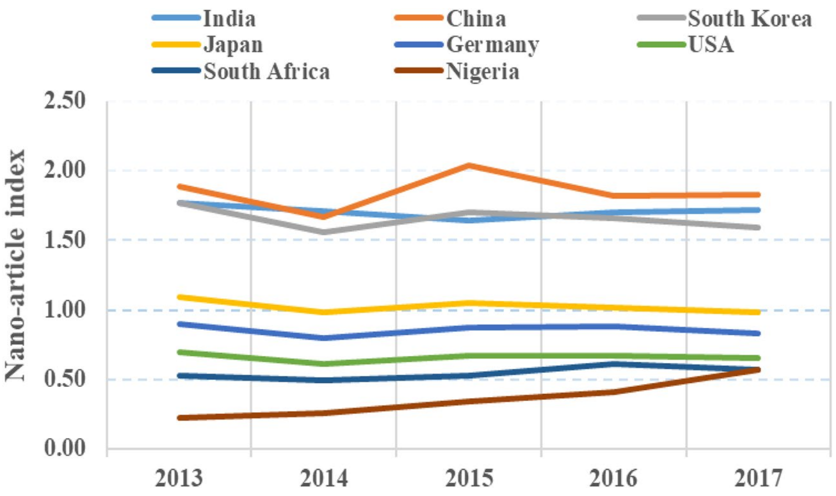

Fig. 2 Index for national priorities for Nanoscience [7]

61.4% increase between 2013 and 2017, while South Africa increased by only 7% within the same period. Figure 3 presents the top 25 countries with the highest volume of nanotechnology-related papers in 2014.

3 Nanomaterials

Further to the advent of nanotechnology, the novel materials being developed due to the modifications and restructuring of the bulk materials to the order of nanometers; are referred to as nanomaterials. Nanomaterials have recorded tremendous breakthroughs in the field of construction; and has continued to gain research and development interests mostly in the areas of concrete technology, due to its evident improvements in enhancing performance and durability of concrete. Some of these nanomaterials, according to [8] includes.

3.1 Nano silica

Nano silica is produced from micro based silica, and has been reported to enhance ultra-high-performance concretes (UHPC); in terms of strength and durability. It has also been reported to improve workability at the minimum dosage of superplasticizers. Although, its disadvantage of cost and scarcity in some parts of the world, is unconnected to its demand; as some countries have to import Nano silica to be used in concrete industry [9].

3.2 Nano alumina

Nano alumina is a product of alumina itself. Although, limited studies are available on the use of Nano alumina in concrete; its addition in concrete especially UHPC influences setting time. The function of Nano alumina in cement is to speed up the initial setting time for UHPC, thus reducing segregation and flocculation in concretes.

3.3 Nano kaolin

Nano kaolin is a by-product of kaolin. Kaolin, also known as kaolinite; is a clay mineral, part of the industrial minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral [10, 11]. Rocks that are rich in kaolinite are known as kaolin or china clay [12]. Kaolinite contains white mineral that is also known as dioctahedral phyllosilicate clay. It is formed from clay which is produced by chemical weathering of aluminum silicate minerals such as feldspar.

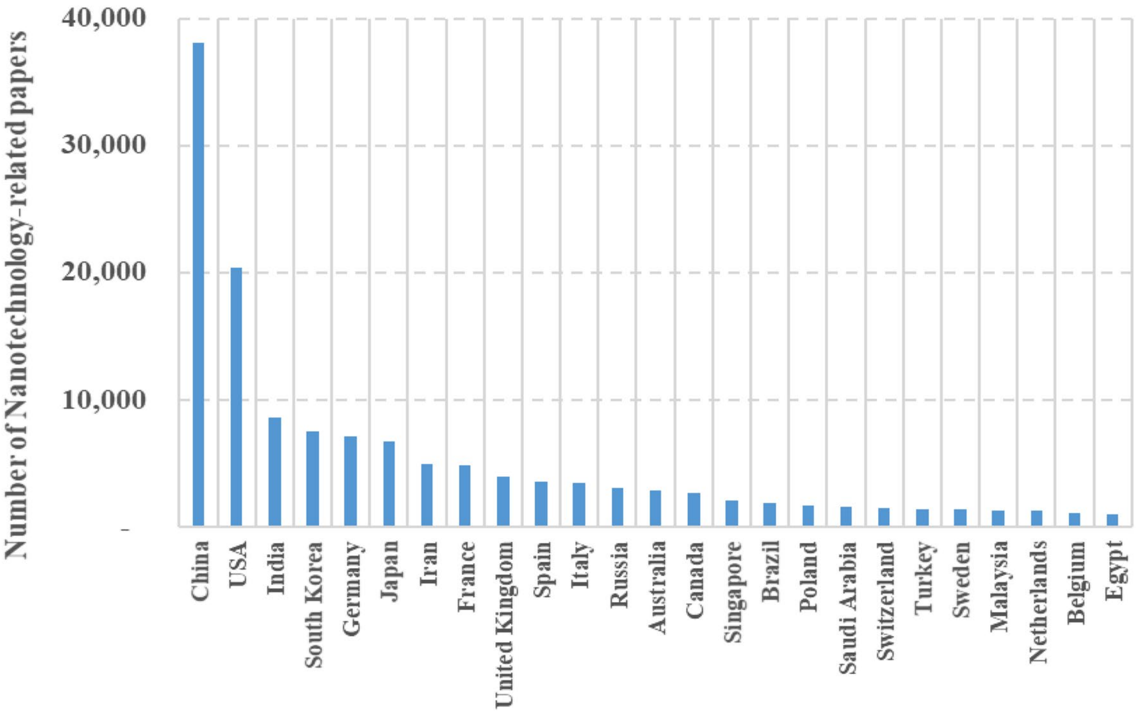

Fig. 3 Top 25 countries with the highest volume of Nanotechnology-related papers in 2014 [7]

3.4 Nano clay

Nano clay is nanoparticles of layered mineral silicates. Depending on the chemical composition and nanoparticle morphology, Nano clays are organized into several classes such as montmorillonite, bentonite, kaolinite, hectorite, and halloysite. Nano clay is one of the most affordable materials that have shown promising results in polymers. Nano clay is made of montmorillonite mineral deposits known to have "platelet" structure with average dimension of 1 nm thick and 70–150 nm wide. The unique structure of montmorillonite clay is it possesses several qualities that make it an excellent base for manipulation through nanotechnology. These qualities include stability, an interlayer space, high hydration and swelling capacity and a high chemical reactivity.

4 Nano-concrete

Nanotechnology offers the possibility of great advances in construction, particularly in concrete (a nanostructured, multi-phase composite material); which is the most heterogeneous construction material. The properties of concrete are governed by the varying characteristics of its constituents; which gives it a great advantage to enjoy the benefits of nanotechnology for the modification of the atomic and molecular matters of its various constituents in order to develop an enhanced concrete. Scholarly research reports on the adoption of nanotechnology in concrete and building constructions, have focused on the nanostructure, the modification of the atomic structure of concrete and cement-based materials and their fracture mechanism [3, 13–21]. Nanotechnology improves the bulk property of concrete, helps to obtain thinner final products, faster setting time and lowered levels of environmental attack. Some of the novel advancement on nanotechnology is its ability to use marginal and recycled materials. It is believed that nanotechnology will be able to provide systems to coat or modify problem systems so that they become usable [17]. If processes could be developed that would modify the adverse properties of marginal aggregates, many sources currently not allowed for some concrete uses could become acceptable making concrete construction more economical [22]. Nanotechnology has also proved to be beneficial in the prevention of cracks and reduction of shrinkage in concrete. It is likely that nanotechnology will be able to offer tools to modify the shrinkage of hydrated cement systems [23], reduce or even eliminate the number of joints required, minimize curling by reducing concrete's change in volume from temperature changes, minimize warping by reducing the change in volume from loss of moisture [2]. Nanotechnology could greatly increase the life of concrete pavements or structures, if a method could be developed to make concrete approach the point of being impermeable [2]. The use of nanotechnology-based tools and nanomaterials to monitor and modify the permeability of a given concrete system will immediately lead to longer-lasting concrete structures [23]. Scholarly reports have shown that nanotechnology could help increase compressive strength through by improving the aggregate paste bond, and the durability properties of (hardened) concrete [2, 3, 14, 15, 18].

The application of nanotechnology, sometimes referred to as the nano-modification of concrete deals with the nanoscience; which is the measurement and characterization of the nano and microscale structure of cement-based materials to better understand how this structure affects macroscale properties and performance through the use of advanced characterization techniques and atomistic or molecular level modeling. In fact, nano-engineering encompasses the techniques of manipulation of the structure at the nanometer scale to develop a new generation of tailored, multifunctional, cementitious composites with superior mechanical performance and durability potentially having a range of novel properties such as: low electrical resistivity, self-sensing capabilities, self-cleaning, self-healing, high ductility, and self-control of cracks [3, 24–26].

However, for a greater achievement in nano-concrete, a great knowledge and understanding of the calcium–silicate–hydrate gel (C–S–H) is important. The chemical reactions between cement, water and resulting products that are produced create a material that is highly complex; and the dominant component, C–S–H gel, has a local structure of a precipitate with nanoscale features that are difficult to model and understand. It is the crucial component liable for strength and other properties in cementitious systems; which lies in the few nanometer ranges. The structure of C–S–H is akin to clay, with thin layers of solids separated by gel pores filled with interlayer and adsorbed water. Although, scholarly reports from experiments and studies have concluded that two types of this nano-sized material, C–S–H gel exist; one with low density and other with high density. But it is still not clear how these two types of C–S–H gel structure affect the mechanical properties of concrete material [3, 23, 27–29], the low-density C–S–H seems to be more important than the high-density C–S–H, because of its tendency to grow outward into the porosity; which is the most important characteristics of C–S–H gel as presented in Fig. 4.

Additionally, Constantinides and Ulm [31] opined that, high density C–S–H gel has a higher stiffness and hardness values than low density C–S–H gel. The proportion of high- and low-density C–S–H in cement paste depends on the mix design of cement paste. The research further

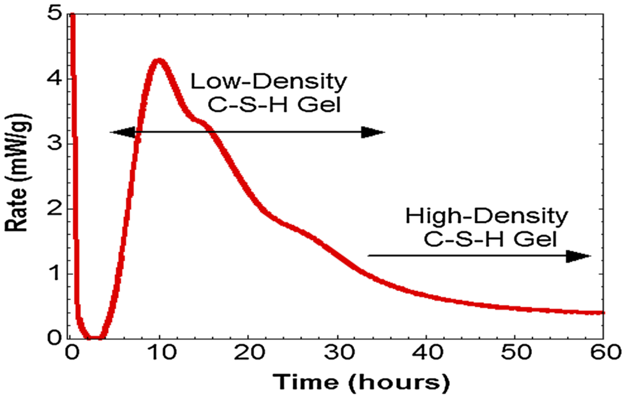

Fig. 4 Rate of hydration versus time, showing when the low-density and high-density morphologies form [30]

concluded that, the stiffness and hardness of low density and high-density C–S–H do not change from one cement paste to another. The stiffness and hardness values are intrinsic properties of the C–S–H gel. Meanwhile, Taylor [32] reported that C–S–H has no fixed stoichiometry, its chemical composition changes from point to point within cement paste and hence, it is often defined by its Calcium–Silica (Ca:Si) ratio. Experimental techniques such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) found that Ca/Si ratio within C–S–H gel ranges from 0.6 to 2.0. The reports of [33, 34] revealed that the C–S–H gel is the predominant solid volume in the microstructure of hardened concrete paste, which is composed of a highly heterogeneous system of several kinds of solids and pores of various shapes and sizes. The C–S–H gel occupies approximately 50% of the hardened concrete, while the other half of its composition include; another hydration product, $CaOH_2$, some unhydrated cement particles, depending on the degree of hydration or water/cement ratio and some minor components such as AFm and Aft phases (Ettringite and monosulphate), which are generally crystalline and vary considerably in morphology and size.

However, the nano-engineering of C–S–H; which requires detailed information about its structure and properties, would greatly impact on the strength and durability performances of concretes.

5 Nanotechnology for supplementary cementitious materials (SCM) in concrete

Issues concerning the use of waste materials to influence the strength, durability, cost of construction and maintenance of concrete and concrete structures are becoming increasingly popular in the research of concrete and environmental engineering. The use of waste materials as supplementary materials such as corncob ash (CCA), rice husk ash (RHA), silica fume (SF), ground granulated blast-furnace slag (GGBS), etcetera; in concrete have enhanced the rheological characteristic of concretes, the durability performance of concrete structures and the reduction of waste in the environment [35–40]. Moreover, concrete production has substantially endangered the earth through the emission of carbon dioxide, CO_2 during the manufacture of Portland cement (PC). Five percent of CO_2 global emission occurs in concrete production with the manufacture of cement being the major contributing factor [41]. The influence of Portland Cement (PC) as the dominant binding material in concrete while the other constituent materials are fillers and enhancers [42, 43], translates to high demand on PC while the other materials occur naturally in abundance and are used in their natural states with little or no processing. This translates to the increasing rate of Portland cement and concrete production due to increasing infrastructural development, as concrete is the impetus of infrastructural development of any nation; despite the high cost of Portland cement in concrete production which translates to an increase in the cost of housing and infrastructural developments. Thus, an enhancement in the production of concrete through nanotechnology is a necessity to checkmate the environmental issues arising from cement production.

Although, some of the advancements on the use of SCM at the nanoscale as presented in Table 1, indicated a scant literature on the application of nanotechnology in some SCM like corncob ash (CCA), groundnut husk ash (GHA), ground-granulated blast furnace slag (GGBS), coconut shell ash (CSA); which has shown great pozzolanic potentials for use in concrete. The challenges of the use of these waste materials as supplementary materials in concrete at the nanoscale level are perhaps the lack of vision to identify those aspects that could be adopted through its use, lack of skilled personnel and perhaps the high cost of carrying out the research and its implementation. But, use of waste materials as supplementary materials in concrete at the nanoscale level would greatly improve the properties of concrete.

6 Conclusion

Nanotechnology has been evident in the development of novel materials through the modification of the atoms and molecules of a particular material or a combination of other materials; with concentrations on the desired characteristics in the parent material to developing an entirely new novel material for an intended purpose. Thus, if the novel accomplishments of research outcomes on the use

Table 1 Some advancements on nanotechnology adoption for SCM in concrete and mortar

S/N	Authors	Concrete/mortar	SCM used	Additive/replacement	Properties explored
1.	[38]	Concrete	Rice husk ash	Replacement	Compressive strength, splitting tensile strength, SEM, x-ray diffractometer (XRD) analysis
2.	[44]	Concrete	Silica fume, fly Ash, slag	Replacement	Bond and flexural properties
3.	[45]	Mortar	Fly ash	Replacement	Compressive strength, SEM, x-ray diffractometer (XRD) analysis
4.	[46]	Concrete	Silica fume	Replacement	Chloride penetration, water absorption, electrical resistivity
5.	[47]	Mortar	Fly ash	Replacement	Compressive strength
6.	[48]	Concrete	Silica fume	Replacement	Compressive strength, rate of heat of hydration, porosity
7.	[49]	Concrete	Fly ash, slag and silica fume	Replacement	Compressive strength, rate of heat of hydration, setting time
8.	[50]	Mortar	Fly ash	Additive	Compressive strength, rate of heat of hydration
9.	[51]	Mortar	Silica fume	Additive	Rheological, compressive strength, water absorption
10.	[52]	Paste	Silica fume	Additive	Compressive strength, bond strength, setting time
11.	[53]	Mortar	Silica fume	Additive	Compressive strength, SEM, rate of heat of hydration
12.	[54]	Concrete	Fly ash	Replacement	Water permeability
13.	[55]	Concrete	Fly ash	Replacement	Heat of hydration, pore size

of wastes as supplementary construction materials were to be considered vis-a-vis the positive and negative influences on the bulk properties of concrete, it is expected that novel materials could be developed by leveraging on the nanoscopic properties of the molecules that positively influence the bulk properties of concrete; perhaps from a combination of selected waste materials and eliminating any other possible molecules that negatively influences the bulk properties of the concrete using nanotechnology.

Thus, research endeavors on the use of nanotechnology for other SCM such as CCA, CHA, GGBS, GHA should be explored for greater sustainable construction, as the benefits of nanotechnology adoption in concrete and SCM would among other benefits:

1. Develop a new generation of high-performance concrete material with respect to their mechanical and durability properties for sustainable construction.
2. Reduction in the construction cost and energy consumption, improved bulk property of concrete and lean construction.
3. Evolve novel concrete materials through nanotechnology-based innovative processing of cement and cement paste.
4. Promotion of fundamental multiscale model(s) for concrete through advanced characterization and modeling of concrete at the nano-, micro-, meso-, and macro scales.
5. The adoption of the use of waste or recycled materials and other supplementary cementitious materials to corroborate sustainable environment, development and socio-economic impact, as evident in countries that prioritize the importance of nanotechnology.

However, a better understanding of the engineering properties and the complexity of cement-based concrete and supplementary cementitious materials at the nanoscale, is a multidisciplinary and multidirective approach consisting of civil engineering, material science, physics and other related disciplines; to modify or influence the important processes related to the production and use of concrete and construction materials, including their strengths, durability and tailored properties.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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