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REVIEW ARTICLE

Modern developments related to nanotechnology and nanoengineering of concrete

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ABSTRACT This paper reports on modern developments related to nanotechnology of cement and concrete. Recent advances in instrumentation and design of advanced nano-composite materials is discussed. New technological directions and historical milestones in nanoengineering and nanomodification of cement-based materials are presented. It is concluded that there is a strong potential of nanotechnology to improve the performance of cement-based materials.

KEYWORDS nanotechnology, cement, concrete, nanoparticle, nano-composite, nanomodification, carbon nanotubes, C-S-H gel, photocatalyst

1 Introduction

Characterizing, understanding and manipulating of materials at nano-level, the dimension compared to distance between the atoms, or 10^{-9} meter, have led to unprecedented possibilities to develop new materials with novel and enhanced properties [1–4]. Recent work in nanotechnology and nanoscience promises exciting opportunities for the field of construction materials [5]. While the science related to nanotechnology is new, nanosized devices and objects have existed since ancient times when humans began to use nanosized materials in glass [1], to modern times where “classic” photography employed silver nanoparticles sensitive to light. It has been proven that the exceptional mechanical performance of biomaterials such as bones or mollusk shells is due to the presence of nanocrystals of calcium compound [2,3]. The nanocomposite material of the abalone shell consists of nanosized particles of calcium carbonate bound together by a glue composed of a carbohydrate protein mix [3]. This type of nanostructure leads to very high strength and toughness of the shell due to interlocking of nano-blocks of calcium carbonate is responsible for the crack arrest and dissipation of energy. Better understanding and mimicking the processes of “bottom-up” construction used by nature is one of the most promising directions in nanotechnology [1,3].

The elementary building unit in nanotechnology is a quantum dot or nanoparticle; which can be represented as a cluster of tens to thousands of atoms of 1–100 nm in diameter. When nanoparticles are created by the “bottom-up” approach, the size and shape of a particle can be controlled by production conditions. These particles can also be considered as nanocrystals because the atoms within the particle are perfectly ordered. When the dimensions of a material are reduced from macro- to nano-size, significant changes occur in electronic conductivity, optical absorption, chemical reactivity, and mechanical properties. In reducing the size, more atoms are located on the surface of particle, and, in addition to a remarkable surface area of nanopowders (Fig. 1), this imparts a considerable change on surface energies and surface morphologies. All these factors alter the basic properties and the chemical reactivity of nanomaterials [1,2,4]. The shift in properties helps to develop the improved catalytic ability and to design better pigments and paints with self-cleaning and self-healing features [1–5]. Nanosized particles have been used to enhance the mechanical performance of plastics and rubbers [1–3], as they help to make cutting tools harder and ceramic materials ductile. For example, new nano-ceramic materials based on metal and oxides of silicon and germanium demonstrate superplastic behavior, undergoing elongations up to 1000% before failure [6].

The most promising contemporary developments

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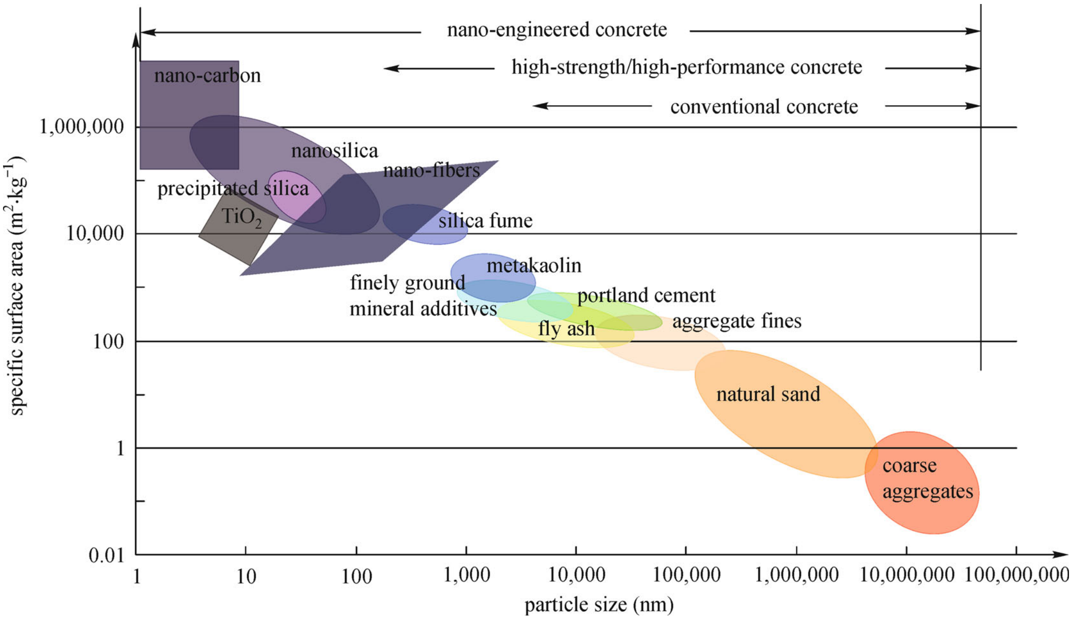


Fig. 1 The particle size and specific surface area scale related to concrete materials, after [7]

include the synthesis of the new forms of carbon: fullerene (C_{60}), carbon nanotubes (e.g., single-wall nanotubes, SWCNT) and graphene. The synthesis of SWCNTs is achieved under precisely controlled conditions in the presence of a catalyst; in case of the deviation from the production route, multi-wall carbon nanotubes (MWCNTs) are formed [1]. The application areas of nanotubes vary widely from the nanoelectronic devices and tips for scanning-probe microscopes to bio and chemical sensors, catalyst support, gas storage and separation, drug delivery, self-healing technologies, and finally, enhancement of composite materials strength. For example, exceptionally high tensile strength of nanotubes (which is calculated to be 20 times higher than steel, at the level of 45 GPa) makes these materials an ideal reinforcing component of modern fibers and films with possible applications in the cables supporting long-span or high-rise structures [7].

The combination of carbon nanotubes and conventional polymer based fibers and films is another challenge. For example, the incorporation of 10% SWCNTs into the strongest man-made fiber Zylon, resulted in the new material with up to 50% strength enhancement [8,9]. It is expected that better exfoliation along with improved dispersing and alignment of the individual nanotubes can boost the performance of composite fibers or, alternatively, reduce the volume of the nanotubes used [1,5]. Dalton et al. [9] introduced a significant breakthrough related to SWCNT-reinforced fibers which achieved the strength of 1.8 + GPa. These fibers match the energy-absorbing capacity of spider silk up to the breaking point of silk at 30% (165 J/g) and continue absorbing energy until reaching the toughness of 570 J/g, compared with 50 J/g and 33 J/g for Spectra and Kevlar fibers, respectively [9]. The application of these new fibers in composite materials is very promising.

The nanoscience and nano-engineering (nanomodification) of cement based composites are terms which describe two main directions related to nanotechnology of construction materials [10,11]. *Nanoscience* deals with the measurement and characterization of nano- and micro-scale structure of materials used to understand how this structure affects the macroscale properties and performance through the use of advanced characterization techniques and atomistic or molecular level modeling. *Nano-engineering* encompasses the techniques of manipulation at the nanometer scale to develop a new generation of multifunctional composites with superior mechanical performance and durability potentially having a range of novel properties such as: low electrical resistivity, self-sensing capabilities, self-cleaning and self-healing [10]. Composite can be nano-engineered by the incorporation of nano-sized building blocks or objects (e.g., nanoparticles and nanofibers) to control material behavior and add novel properties, or by the grafting of molecules onto cement particles, aggregates, additives (including nano-sized additives) to provide surface functionality, which can be adjusted to promote specific interfacial interactions [9–11].

The majority of recent nano-research related to concrete materials has investigated the structure of cement-based materials and corresponding fracture mechanisms [3,5,7,9–11]. With new advanced equipment, it is possible to observe the structure at its atomic level and even measure the strength, hardness and other basic properties of the micro- and nanoscopic phases of materials [1–4]. The application of atomic force microscopy (AFM) for investigating the "amorphous" C-S-H gel discovered that at nanoscale this product has a highly ordered structure [12]. Considerable progress over recent years has been achieved by the employment of nano-scale characterization techniques to understand the nano-scale structure and processes such as:

- Nuclear magnetic resonance;
- Atomic force microscopy;
- Ultrasonic force microscopy;
- Focus-ion-beam (FIB) nanotomography;
- Micro-and nano-indentation;
- Neutron and X-ray scattering;
- X-ray absorption spectroscopy (XAS) and X-ray fluorescence nanoprobe.

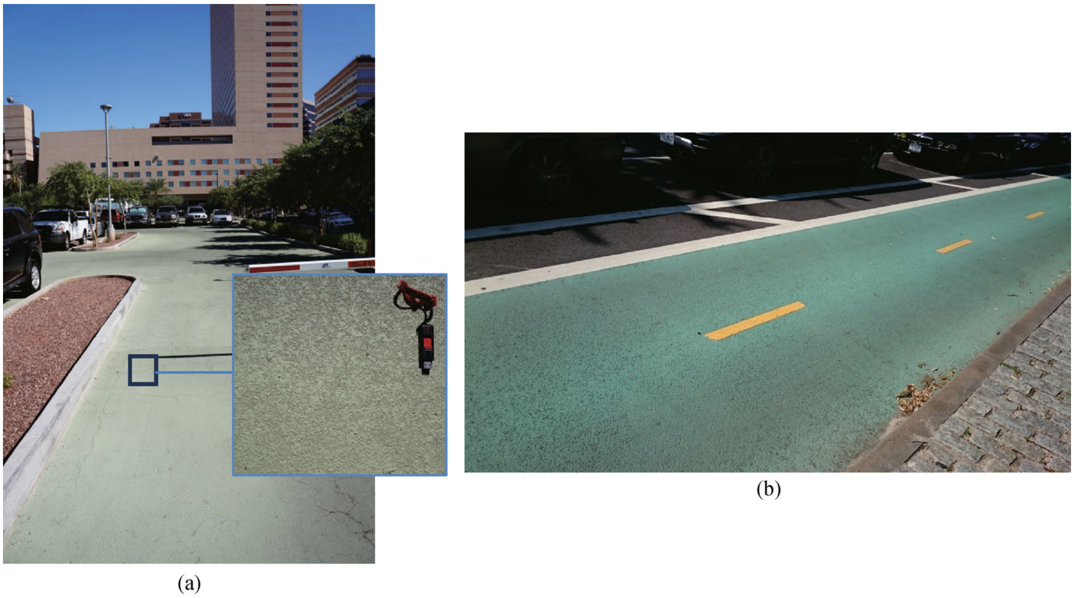
Better understanding the structure at nano-level helps to influence important processes related to the production and use of construction materials: strength, fracture, corrosion and even enable tailoring the desired properties. For instance, for façade and interior applications, the development of finishing materials with new self-cleaning properties, discoloration resistance, anti-graffiti protection, high-scratch and wear-resistance is extremely important. The self-cleaning concrete, mortars, and water-based paints were developed based on the photocatalyst technology [13]. The self-cleaning effect related to the decomposition of organic pollutants and gases is achieved when TiO_2 photocatalyst thin film is set on a surface and can emit active oxygen under UV light (Fig. 2). Another aspect of self-cleaning is provided by the hydrophilicity of the surface, which helps to rinse away dust and dirt. Photocatalytic properties can be also used to engineer cement based materials for energy harvesting applications [14]. Nano-SiO_2 and nano-Al_2O_3 have proved to be a very effective additives to polymers and cement-based composites to improve strength, flexibility, and durability [15,16].

2 Nanotechnology of concrete

Concrete, the most ubiquitous man-made material, is a nano-structured, multi-phase, composite material that ages over time [7,9–11]. The properties of concrete exist in, and the degradation mechanisms occur across multiple length scales (nano to micro to macro) where the properties of each scale derive from those of the next smaller scale (Fig. 3) [10,11]. The amorphous phase, calcium-silicate-hydrate (C–S–H) is the "glue" that holds concrete together and is itself a nanomaterial [12].

Nano-chemistry with its "bottom-up" possibilities offers new products that can be effectively applied in concrete technology. One example is related to the development of new admixtures for concrete, such as the polycarboxylic ether (PCE) superplasticizers designed for the extended slump retention of concrete mixtures [7]. Mechano-chemical activation of cement with PCE based grinding modifiers was found to be very effective method to tailor the behavior of cement-based materials in fresh and hardened state [15]. The reported improvement of performance (up to 115 MPa vs. the strength of reference cements of 72–89 MPa) was achieved due to the formation of organo-mineral nano-layers or nano-grids on the surface of cement as well as surface amorphization.

It was proposed that, when nanoparticles are incorporated into conventional building materials, such materials


(a)

(b)

Fig. 2 The application of photocatalytic cement-based coatings. (a) parking lot and close-up view of the surface after 3-year service (Phoenix, AZ, USA) and (b) bike lane (Brooklyn, NY, USA)

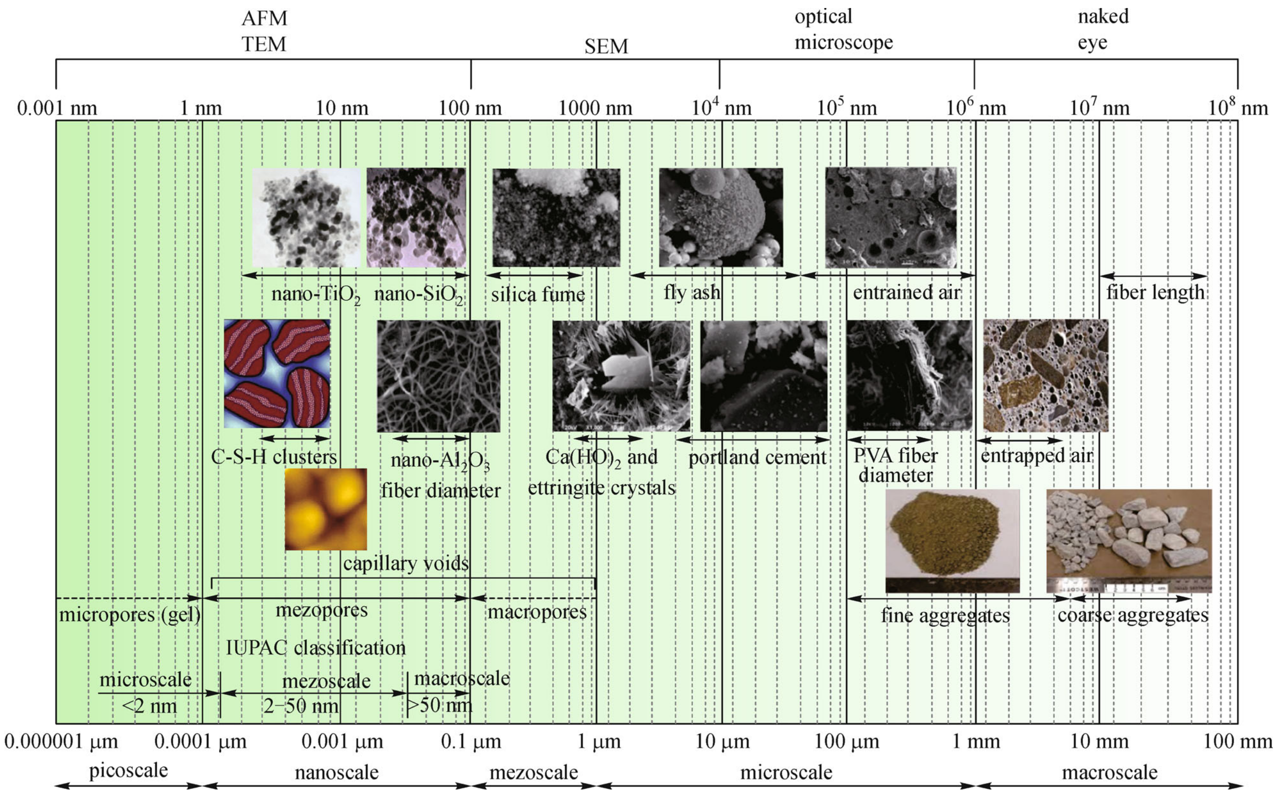
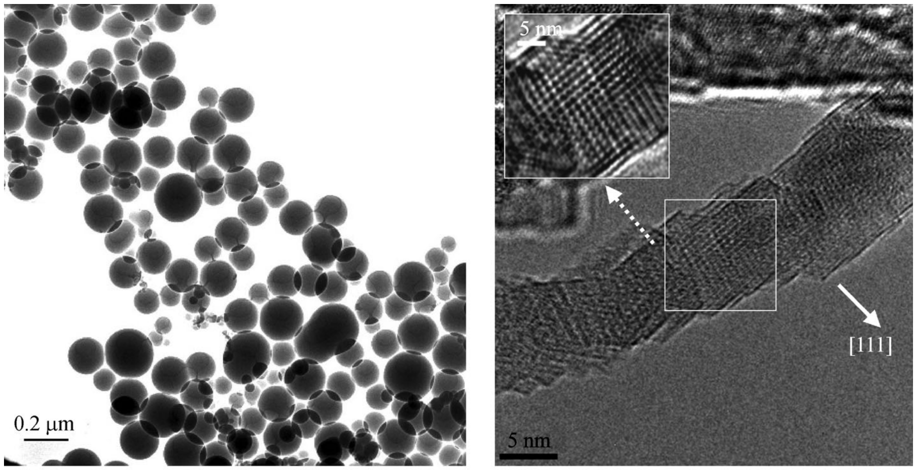


Fig. 3 The scale ranges related to concrete, after [16]



(a) (b)

Fig. 4 Nanocomponents under the TEM. (a) nanoparticles of SiO_2 [15] and (b) nanofibers of Al_2O_3 (courtesy of ANF)

can possess advanced properties required for the construction of high-rise, long-span or intelligent civil and infrastructure systems [5,7,9–11]. For example, SiO_2 nanoparticles (nanosilica, Figs. 1, 3, 4(a)) can be used as an additive for high-performance and self-compacting concrete, thereby improving workability and strength [5,7,10–24]. The particle size and specific surface area scale related to concrete materials reflect the general trend to use finer materials [7]. For decades, major developments in concrete performance were achieved with the application of super-fine particles such as silica fume, and now, with nanosilica. Nanofibers (such as nano-Al_2O_3, Fig. 4(b), right) are another promising component for application in concrete [11].

3 Concrete with nanocomponents

3.1 Nano-binders

Chemically precipitated C-S-H was suggested as an effective admixture to improve the performance of concrete [17]. It was proposed that nano-sized C-S-H particles with an average size of 5–10 nm act as a nucleation seeds for the hydration products of portland cement. The positive effect of C-S-H admixture is attributed to the significant reduction of porosity, the size of the pores, and consequently, the permeability of cement paste.

Nano-binder was proposed as a material designed with a nano-dispersed cement component to fill the gaps between the particles of mineral additives [7]. The nano-sized cementitious component can be obtained by the colloidal milling of portland cement (the top-down approach) or by the self-assembly using mechano-chemically induced topo-chemical reactions (the bottom-up approach) [15,25].

3.2 Nanoparticles

The most of the experimental work up to date was conducted using nano-SiO_2 particles [5,7,9–11,14–24]. The accelerating effect of nano-SiO_2 on the hydration of C_3S was reported by Björnström et al. [20]. The increased rates of C_3S phase dissolution, subsequent accelerated formation of C-S-H gel, and the removal of non-hydrogen bonded OH^- groups were revealed with DR FTIR spectroscopy and DSC for samples containing up to 5% of colloidal silica. The team of Collepardi et al. was among the first to study the performance of low-heat self-compacting concrete (SCC) produced with nano-SiO_2 [18]. Nanosilica (the size of 5–50 nm) was used in a form of slurry as a viscosity-modifying agent at a dosage of 1%–2% of cementitious materials. The design of SCC with a low-heat release was achieved by using blended cement (with 60% of blast furnace slag) and incorporating of limestone and fly ash powders. It was reported that the addition of nano-SiO_2 makes the concrete mixture more cohesive and reduces bleeding and segregation. The best performance was demonstrated by concrete with ground fly ash, 2% nanosilica, and 1.5% of superplasticizer. This concrete had the desired behavior in fresh state and the highest compressive strength [18]. Nano-SiO_2 was used as an effective viscosity modifying agent in high–density, high-strength cementitious grout [19].

Li performed a laboratory study of superplasticized high-strength concrete incorporating 4% of nano-SiO_2 and 50% type F fly ash [21]. It was demonstrated that the pozzolanic reaction of nano-SiO_2 is very quick, reaching 70% of its ultimate value within three days; and, in a two-week period, this reaction was completed by ~95%. The investigation of the hydration process confirmed the assumption that the pozzolanic activity of fly ash can be significantly improved by the application of nano-SiO_2. It was demonstrated that adding nano-SiO_2, even at small dosages (3%), reduces the amount of CH formed at the aggregate's interface and reduces the size of CH crystals, over-performing SF [22].

The addition of nano-SiO_2 was the most effective way to improve the compressive and the bond strength, especially, at the early stages of hardening [15,23,24]. Porro et al. [23], investigated the effect of different dosages and the size of SiO_2 nanoparticles on the performance of portland cement pastes. The compressive strength of the cement pastes increased with the reduction of the particle size of the nanoparticles. This improvement of strength and durability was attributed to the formation of larger silicate chains of the C-S-H gel in mixtures with nano-SiO_2.

The relatively small quantities, less than 1% (by weight of cement), of nano-sized materials are sufficient to improve the performance of nanocomposites [7,10]; yet, the commercial success of nanomaterials depends on the ability to manufacture these materials in large quantities and at a reasonable cost relative to the overall effect of the nanoadditives. Nanomaterial technologies, which could lead to the industrial outputs, involve plasma arcing, flame pyrolysis, chemical vapor deposition, electrodeposition, sol-gel synthesis, mechanical attrition, and the use of natural nanosystems [1,7]. Among chemical technologies, sol-gel synthesis is one of the widely used "bottom-up" production methods for nano-sized materials such as nano-silica. The process involves the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a liquid phase (gel). Usually, tetraethoxysilane (TEOS) is applied as a precursor for synthesizing nanosilica [4]. The details of the "bottom-up" sol-gel synthesis of nano-SiO_2 particles with the size range of 5–100 nm and the effect of this material on the performance of cement systems were reported [15,24]. According to the XRD results, the manufactured nano-SiO_2 is a highly amorphous material with predominant crystallite size of 1–2.5 nm. The obtained nano-SiO_2 particles are forming highly agglomerated xerogel clusters with the size of 0.5–10 μm. The particles within the clusters are of the size of 5–70 nm and the BET surface area of 116,000–500,000 m^2/kg. It was demonstrated that the performance of nano-SiO_2 in cement system depends on the conditions of synthesis (i.e., molar ratios of the reagents, type of the reaction media, pH and the duration of the reaction). The best nano-SiO_2 products with particle size ranging from 5–20 nm were synthesized at highest molar concentrations of water. The addition of developed nano-SiO_2 to port land cement mortars improved the compressive strength. The distribution of nano-SiO_2 particles within the cement paste is an important factor governing the performance; therefore, the disagglomeration of nanoparticles is essential for the design of composite materials. The application of superplasticizer, ultrasonification and high-speed mixing was effective approach to incorporate nano-SiO_2 [15,24].

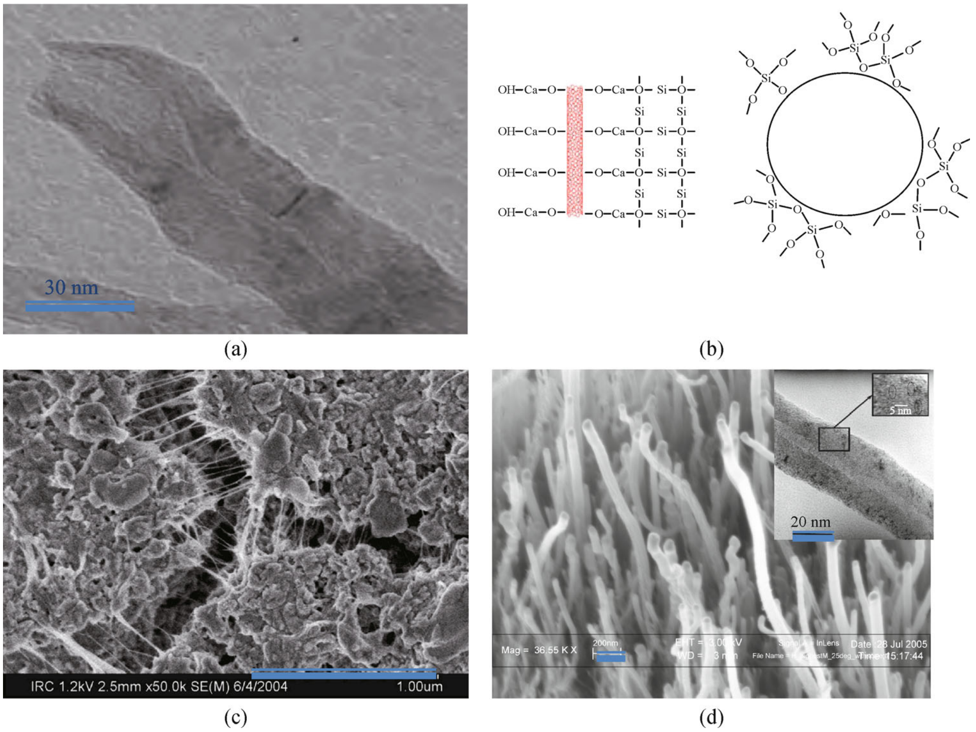
The beneficial contribution of the nanoparticles to the formation of "optimal" microstructure and overall performance of cement-based materials is due to the following factors [7,10]:

- Well-dispersed nano-particles increase the viscosity of the liquid phase, helping to suspend the cement grains and aggregates and improving the segregation resistance and workability of the system;
- Nano-particles fill the voids between cement grains, resulting in the immobilization of "free" water ("filler" effect);
- Well-dispersed nano-particles act as centers of crystallization of cement hydrates, thereby accelerating the hydration;
- Nano-particles favor the formation of small-sized crystals (such as $Ca(OH)_2$ and AF_m) and small-sized uniform clusters of C-S-H;
- Nano-SiO_2 participates in the pozzolanic reactions, resulting in the consumption of $Ca(OH)_2$ and formation of an "additional" C-S-H;
- Nano-particles improve the structure of the aggregates' contact zone, resulting in a better bond between aggregates and cement paste;
- Crack arrest and interlocking effects between the slip planes provided by nano-particles improve the toughness, shear, tensile,and flexural strength of cement based materials.

3.3 Carbon nanostructures

Carbon nanostructures (CNS) such as nanotubes (CNT), nanofibers (CNF) and graphene are potential candidates for nano-reinforcement of cement-based composites, Fig. 5 [26–35]. CNS exhibit extraordinary strength with moduli of elasticity on the order of TPa and tensile strength in the range of GPa, and these have unique electronic and chemical properties [1–4,7–11]. Compared to CNTs, vapor grown CNFs have a lower production cost and are suitable for mass production. While CNTs/CNFs have been extensively studied in polymeric composites, their use in cement composites has remained limited [5]. Most research efforts have focused on CNTs compared to CNFs and have been performed on cement pastes and mortars [7,10,26,27].

Incorporating CNTs/CNFs with unique mechanical properties into cement composites was found to be a complicated task [10]. However, good interaction between CNT and cement matrix has been demonstrated (Fig. 5), indicating the potential for crack bridging and enhanced stress transfer [28]. One of the main challenges is the proper dispersion of CNTs/CNFs into cement paste,



(a) (b)

(c) (d)

Fig. 5 The use of carbon nanostructures: (a) TEM image of functionalized CNTs with "open" tip and (b) mechanism of interaction of functionalized CNTs and cementitious matrix [30]; (c) crack-bridging effect of CNT [28]; (d) the structure of CNF investigated by SEM and TEM [35] partially due to their high hydrophobicity and partly due to their strong self-attraction [26,27]. A number of methods have been investigated to improve the dispersion and to activate the graphite surface in order to enhance the interfacial interaction through surface functionalization and coating, optimal physical blending, and the use of surfactants and superplasticizing admixtures [27–32].

The team of Makar et al. [28] was among the first to demonstrate that CNTs can affect the early-age hydration and that a strong bond is possible between the cement paste and the CNTs. The employed dispersion process consisted of CNT sonication in isopropanol followed by the addition of cement, evaporation, and grinding, which produced cement particles coated with CNTs. Both MWCNTs and SWCNTs, when added to cement paste as a pre-mix with Arabic gum (used as a dispersing agent), enabled to increase the Young's modulus and hardness as determined by nanoindentation measurements [28].

Further work utilizing the functionalization of CNT reported on improved dispersion, good workability, and improvement of flexural and compressive strength [30]. To improve the interaction between the CNT and cementitious matrix, the functionalization of CNT was carried out using one-to-five mix of concentrated HNO_3 and H_2SO_4. It was reported that the introduction of functionalized CNTs affects the composition of hydrated cementitious composites due to the creation of additional crystallization centers accelerating the hydration processes. Furthermore, the formation of oxygen-containing functional groups on the surface of functionalized CNTs leads to up to 60% increase in 1-day compressive strength compared with the reference mortar; this value was also higher than that for composite containing unmodified CNTs [30].

Shah et al. [27] found that, after dispersion in

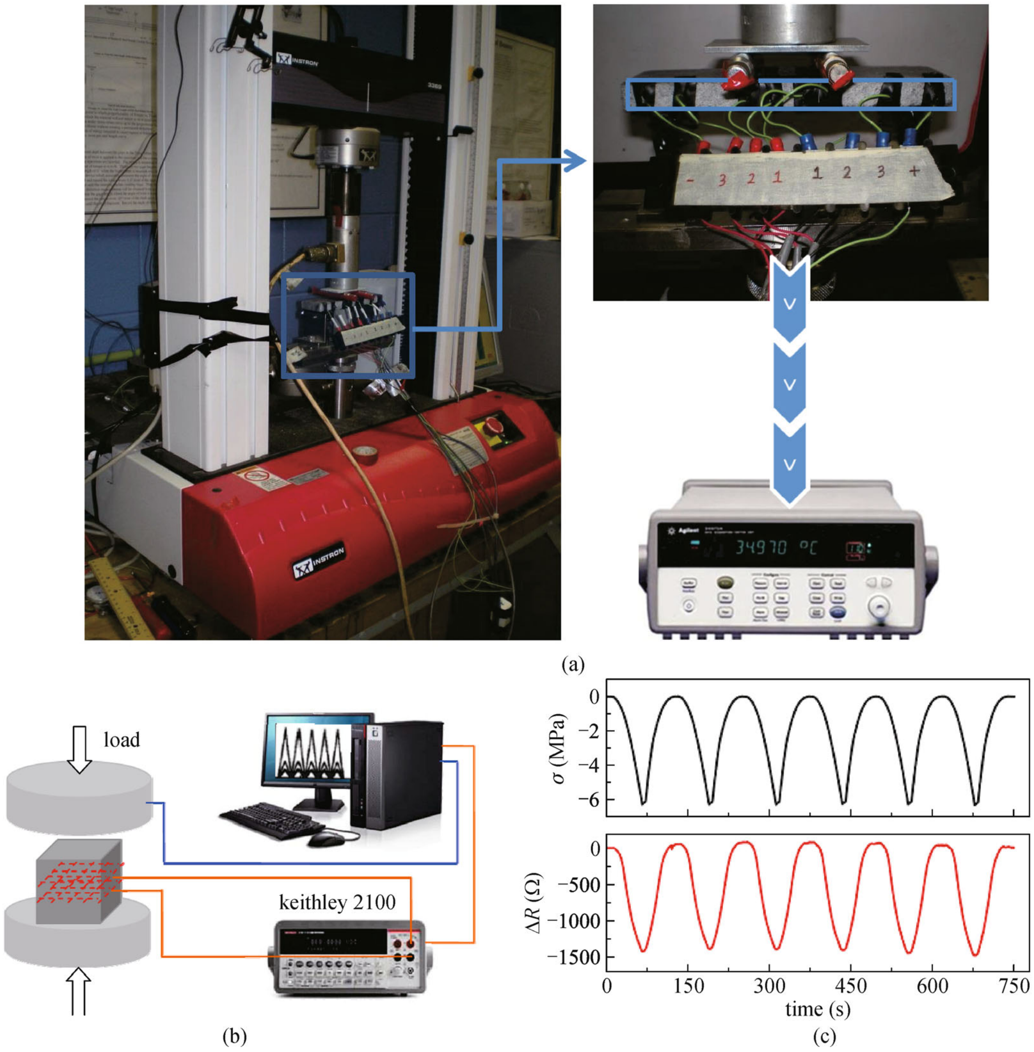


Fig. 6 The smart composites: (a) experimental setup used for testing of smart CNF-PVA fiber-reinforced composites, after [35]; (b) compressive test of CNT composite and response of the material to cyclic loads [37]

water using surfactant and ultrasonification, small amounts of CNTs (from 0.048 wt% to 0.08 wt%) produced a significant (50%) increase in the Young's modulus of cement pastes. Combination of silica fume and 0.002 wt%–2 wt% of CNF resulted in the improved interfacial interaction between the CNFs and the cement matrix [34].

Numerous studies on CNTs/CNFs emphasize that resolving the issues related to dispersion and understanding the complexity of the fundamental mechanisms within the matrix and the interactions at interfaces are the key to realize the potential benefits of CNTs/CNFs in cement composites.

4 Developing new functionalities

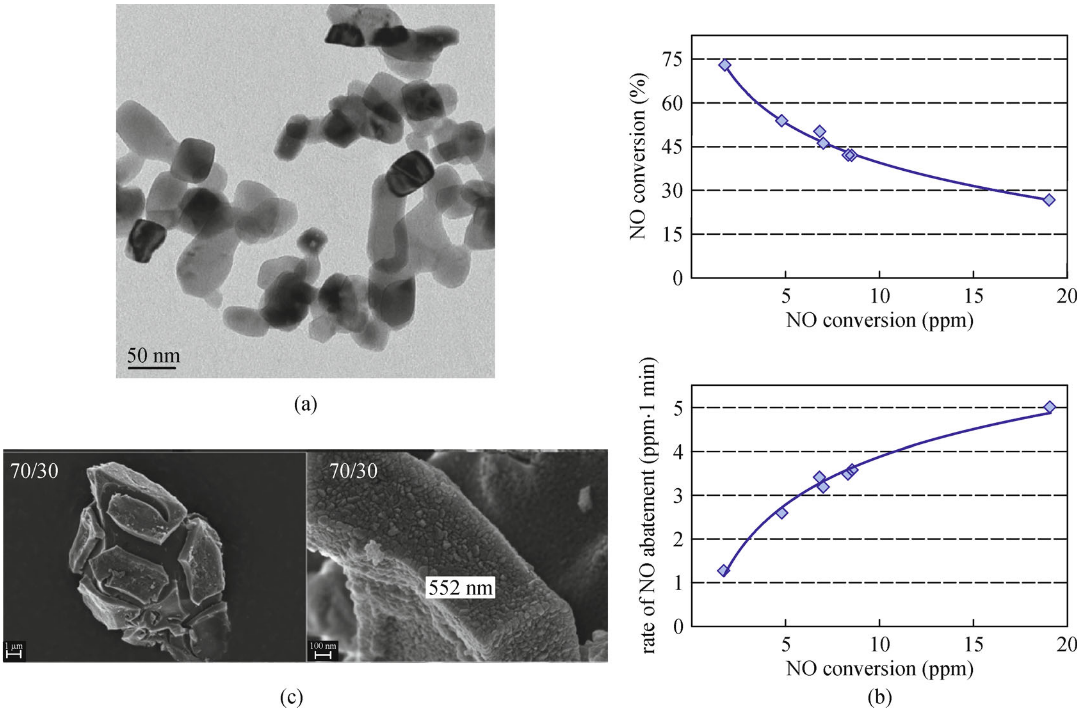
4.1 Smart stress-sensing composites

The composites reinforced with CNT/CNF can function as a piezoresistive strain sensor (Fig. 6). Due to the high conductivity the introduction of carbon nanostructures into composite decreases the electrical resistivity as required for smart applications [35–37]. Han et al. introduced a self-sensing material with multi-walled carbon nanotubes for traffic monitoring [37]. In addition to the strain-sensing ability, the addition of CNFs increases the tensile and flexural strength, tensile ductility and flexural toughness of PVA fiber-reinforced composites, which can make the self-sensing applications feasible [35].

4.2 Photocatalytic concrete

Architectural concrete needs to maintain the aesthetic characteristics such as color over the entire service life, even in highly polluted urban environments. Application of photocatalytic materials is a smart solution for oxidizing and destroying organic pollutants and, subsequently, removing inorganic matter from the surface of architectural concrete. It was reported that the photocatalytic cement matrix is very effective for NO_x abatement [38–40]. Under solar radiation, NO in the air is oxidized and converted to nitrate. A photocatalytic cement technology has been used for a number of construction projects including the "*Dives in Misericordia*" Church (architect Richard Meier) located in Rome, Italy [10]. A detailed review on the mechanisms of TiO_2-based photocatalys is in construction materials was presented by Chen and Poon [39].

One of the most popular photocatalytic materials used in cement is anatase polymorph of nano-sized TiO_2 (Fig. 7(a)). It was proved that cement-TiO_2 composite is a very effective photocatalytic couple (Fig. 7(c)). The photocatalytic TiO_2 was applied in white cement-based concrete with self-cleaning and air-purification features [7,38,40]. Accelerated 8-hour irradiation stimulating intensive solar light (corresponding to one month of



(a)

(c)

(b)

Fig. 7 The TiO_2 based materials: (a) TiO_2 nanoparticles [10]; (b) core-shell composite particles [41]; and (c) NO conversion by photocatalytic cement based coating (right), after [10] sunlight exposure) of phenanthroquinone colored TiO_2 cement based specimens resulted in restoration of an original white color [38,41]. Nano-TiO_2 containing concrete provides effective photocatalytic degradation of pollutants, such as NO_x, carbon monoxide, VOCs, chlorophenols, and aldehydes originated from vehicle and industrial emissions [38–41].

New developments in photocatalysts involve the use of doped TiO_2 materials and core–shell composites [41]. By adjusting the size of the seed and applying a thin layer of titania an effective core–shell composites can be created, Fig. 7(b) [41]. The silica–titania core–shell composites can be prepared by different methods, such as sol–gel method, flame processes or chemical vapor deposition. Kamaruddin and Stephan described the synthesis of core–shell composites based on milled quartz as the core, coated via hydrolysis and condensation of tetrapropylorthotitanate, TPOT [41]. The results indicated that the formation of TiO_2 shell thicknesses of 100–550 nm can be controlled by using different amounts of TPOT during the coating process. After calcination at 650 C the shells were composed of only the anatase phase. Due to high surface area samples 60/40 and 70/30 (with 40 and 30 wt% of TiO_2) had the highest photonic efficiencies exceeding the performance of reference photocatalyst P25 [41].

5 Conclusions

Portland cement, one of the largest commodities consumed by humankind, has significant, but not completely explored potential. Better understanding and precise engineering of an extremely complex structure of cement-based materials at the nanolevel will result in a new generation of concrete that is stronger and more durable, with desired stress-strain behavior and possibly possessing the range of newly introduced "smart" properties, such as electrical conductivity, temperature-, moisture-, and stress-sensing abilities. At the same time, this new concrete should be sustainable, cost and energy effective — in essence exhibiting the qualities modern society demands [7,9]. Among new nano-engineered polymers are highly efficient superplasticizers for concrete and high-strength fibers with exceptional energy-absorbing capacity. Nano-binders or nano-engineered cement-based materials with nano-sized cementitious component or other nano-sized particles are the next ground-breaking development. In this way, mechano-chemistry and nanocatalysts can change the face of modern cement industry by significantly reducing the clinkering temperature and even realizing the possibility of cold-sintering for clinker minerals in mechano-chemical reactors.

To improve the performance of composites, the principle of particle packing at the nanoscale can be used. This concept has led to recent developments and fine-tuning of nano-silica particles and nano-Al_2O_3 fibers with the aim of improving processing characteristics, strength and durability. Indeed, nanoparticles, such as silicon dioxide, were found to be a very effective additive to polymers and concrete, a development recently realized in high-performance and self-compacting concrete with improved workability and strength. Nano-fibers such as multi-wall carbon nano-tubes and nano-fibers alter the fracture properties of cement composites enabling to produce smart and ductile concrete composites. Incorporation of nano-sized TiO_2 particles introduces new characteristics such as self-cleaning, due to their photocatalytic properties [39,40].

With new advanced instruments, it is possible to observe the structure of composites at the atomic level and even to measure the mechanical response of different phases at a nanolevel. For example, the application of Atomic Force and Transmission Electron Microscopy reveals that the "amorphous" C-S-H gel at nanoscale has a distinct ordered structure. Advanced instruments such as Nano-indenters can observe and measure the mechanical properties at a nano-scale.

Nanotechnology has changed and will continue to change our vision, expectations, and abilities to control the material world. These developments will greatly affect modern construction and the field of cement-based materials. However, in spite these developments, the nanotechnology is still in its pre-exploration stage — it is just emerging from fundamental research onto the industrial floor; thus its full-scale applications — especially in concrete — are very limited. Yet, the tremendous potential of nanotechnology to improve the performance of cement-based materials and processes is most promising.

References

1. Bhushan B, ed. Handbook of Nanotechnology. Berlin: Springer, 2004
2. Poole C P, Owens F J. Introduction to Nanotechnology. New York: John Wiley & Sons, 2003
3. Gann D. A Review of Nanotechnology and its Potential Applications for Construction. Sussex: SPRU, 2002
4. Klabunde K J, ed. Nanoscale Materials in Chemistry. New York: Wiley, 2004, 304
5. Sobolev K, Sanchez F, Raki L, Betts J, Kovler K, Sonebi M, Ferrara L, McDonald D B, Taylor P C, Livingston R A, Shah S P, Basheer M P A, Kurtis K E, Wang K. Bibliography on Application of Nanotechnology and Nanomaterials in Concrete. Skokie: Portland Cement Association, 2008
6. Calderón-Moreno J M, Schehl M, Popa M. Superplastic behavior of zirconia-reinforced alumina nanocomposites from powder alcoxide mixtures. Acta Materialia, 2002, 50(16): 3973–3983
7. Sobolev K, Ferrada-Gutiérrez M. How Nanotechnology Can Change the Concrete World: Part 1. American Ceramic Society

Bulletin, 2005, 10: 14–17

8. Dalton A B, Collins S, Muñoz E, Razal J M, Ebron V H, Ferraris J P, Coleman J N, Kim B G, Baughman R H. Super-tough carbon-nanotube fibres. Nature, 2003, 423(6941): 703
9. Nanotechnology of Concrete: Recent Developments and Future Perspectives. Sobolev K, Shah S P, eds. Michigan: American Concrete Institute, 2008
10. Sanchez F, Sobolev K. Nanotechnology in concrete—A review. Construction & Building Materials, 2010, 24(11): 2060–2071
11. Sobolev K, Sanchez F. Nanoengineered Concrete. In: Encyclopedia of Nanotechnology. Bhushan B, ed. Berlin: Springer, 2015
12. Plassard C, Lesniewska E, Pochard I, Nonat A A. Investigation of the surface structure and elastic properties of calcium silicate hydrates at the nanoscaled. Ultramicroscopy, 2004, 100(3-4): 331–338
13. Watanabe T, Kojima E. US Patent, 6 294 247, 2001
14. Hosseini T, Flores-Vivian I, Sobolev K, Kouklin N. Concrete embedded dye-synthesized photovoltaic solar cell. Nature Scientific Reports, 2013, 3: 2727
15. Sobolev K, Flores I, Hermosillo R, Torres-Martínez L M. Application of nanomaterials in high-performance cement composites. In: The Proceedings of ACI Session on Nanotechnology of Concrete: Recent Developments and Future Perspectives. Sobolev K, Shah S P, eds. Michigan: American Concrete Institute, 2008, 93–120
16. Flores-Vivian I, Pradoto R G K, Moini M, Kozhukhova M, Potapov V, Sobolev K. The Effect of SiO_2 Nanoparticles Derived from Hydrothermal Solutions on the Performance of Portland cement Based Materials. Materials & Design, 2016
17. Thomas J J, Jennings H M, Chen J J. Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement. Journal of Physical Chemistry C, 2009, 113(11): 4327–4334
18. Collepardi M, Ogoumah-Olagot J J, Skarp U, Troli R. Influence of Amorphous Colloidal Silica on the Properties of Self-Compacting Concretes Proceedings of the International Conference. In: Proceedings of the International Conference in Concrete Constructions. Dundee: University of Dundee, 2002, 473–483
19. Green B H. Development of a High-Density Cementitious Rock-Matching Grout Using Nano-Particles. In: Sobolev K, Shah S P, eds. The Proceedings of ACI Session on Nanotechnology of Concrete: Recent Developments and Future Perspectives. Denver: American Concrete institute, 2008, 121–131
20. Björnström J, Martinelli A, Matic A, Borjesson L, Panas I. Accelerating effects of colloidal nano-silica for beneficial calcium-silicate-hydrate formation in cement. Chemical Physics Letters, 2004, 392(1-3): 242–248
21. Li G. Properties of high-volume fly ash concrete incorporating nano-SiO_2. Cement and Concrete Research, 2004, 34(6): 1043–1049
22. Qing Y, Zenan Z, Deyu K, Rongshen C. Influence of nano-SiO_2 addition on properties of hardened cement paste as compared with silica fume. Construction & Building Materials, 2007, 21(3): 539–545
23. Porro A, Dolado J S, Campillo I, Erkizia E, de Miguel Y, Sáez de Ibarra Y, Ayuela A. Effects of nanosilica additions on cement pastes. In: Applications of nanotechnology in concrete design; London: Thomas Telford, 2005
24. Flores I, Sobolev K, Torres L M, Valdez P L, Zarazua E, Cuellar E L. Performance of Cement Systems with Nano-SiO_2 Particles Produced Using Sol-gel Method. In: Proceedings of the TRB 1st International Conference on Nanotechnology in Cement and Concrete, Irvine, California, USA, May 5–7, 2010
25. Sobolev K. High performance cement: A solution for next millennium. Materials Technology, 1999, 14(4): 191–193
26. Sanchez F, Zhang L, Ince C. Multi-scale performance and durability of carbon nanofiber/cement composites. In: Bittnar Z, Bartos P J M, Nemecek J, Smilauer V, Zeman J, eds. Nanotechnology in Construction: Proceedings of the NICOM-3, Prague, Czech Republic, 2009, 345–350
27. Shah S P, Konsta-Gdoutos M S, Metaxa Z S, Mondal P. Nanoscale modification of cementitious materials. In: Bittnar Z, Bartos P J M , Nemecek J, Smilauer V, Zeman J, eds. Nanotechnology in Construction: Proceedings of the NICOM-3, Prague, Czech Republic, 2009, 125–130
28. Makar J M, Margeson J, Luh J. Carbon nanotube/cement composites—early results and potential applications. In: Proceedings of 3rd International Conference on Construction Materials: Performance, Innovations and Structural Implications. Vancouver, August 22–24, 2005; 1–10.
29. Sbia L A, Peyvandi A, Soroushian P, Balachandra A M, Sobolev K. Evaluation of modified-graphite nanomaterials in concrete nanocomposite based on packing density principles. Construction & Building Materials, 2015, 76: 413–422
30. Petrunin S, Vaganov V, Sobolev K. Cement Composites Reinforced with Functionalized Carbon Nanotubes. In: Proceedings of XXII International Materials Research Congress. Materials Research Society: Cancun, 2013, vol. 1611
31. Peyvandi A, Sbia L A, Soroushian P, Sobolev K. Effect of the cementitious paste density on the performance efficiency of carbon nanofiber in concrete nanocomposite. Construction & Building Materials, 2013, 48: 265–269
32. Konsta-Gdoutos M S, Metaxa Z S, Shah S P. Multi-scale mechanical and fracturecharacteristics and early-age strain capacity of high performance carbonnanotube/cement nanocomposites. Cement and Concrete Composites, 2010, 32(2): 110–115
33. Metaxa Z S, Konsta-Gdoutos M S, Shah S P. Carbon nanofiber cementitious composites: Effect of debulking procedure on dispersion and reinforcing efficiency. Cement and Concrete Composites, 2013, 36: 25–32
34. Sanchez F, Ince C. Microstructure and macroscopic properties of hybridcarbon nanofiber/silica fume cement composites. Composites Science and Technology, 2009, 69(7-8): 1310–1318
35. Hoheneder J, Flores-Vivian I, Lin Z, Zilberman P, Sobolev K. The performance of stress-sensing smart fiber reinforced composites in moist and sodium chloride environments. Composites. Part B, Engineering, 2015, 73: 89–95
36. Konsta-Gdoutos M S, Aza C A. Self sensing carbon nanotube (CNT) and nanofiber (CNF) cementitious composites for real time damage assessment in smart structures. Cement and Concrete Composites, 2014, 53: 162–169
37. Han B, Yu X, Kwon E. A self-sensing carbon nanotube/cement composite for traffic monitoring. Nanotechnology, 2009, 20(44):

445501

38. Cassar L, Pepe C, Tognon G, Guerrini G L, Amadelli R. White Cement For Architectural Concrete Possessing Photocatalytic Properties. In: Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC), Durban, South Africa, 2003
39. Chen J, Poon C. Photocatalytic construction and building materials: fromfundamentals to applications. Building and Environment, 2009, 44(9): 1899–1906
40. Faraldos M, Kropp R, Anderson M A, Sobolev K. Photocatalytic hydrophobic concrete coatings to combat air pollution. Catalysis Today, 2016, 259: 228–236
41. Kamaruddin S, Stephan D. Quartz–titania composites for the photocatalytical modification of construction materials. Cement and Concrete Composites, 2013, 36: 109–115