Book : Recent Advances in Nano-tailored Multifunctional Cementitious Composites

Chapter : Overview of tailoring cementitious composites with various nano materials

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Abstract

Incorporating nano materials brings great changes in tailoring the nano-micro-macroscale structures of bulk cement paste phase and interfacial transition zone in the cementitious composites through the nano-core effect, thus achieving stronger, more durable, and smart/multifunctional cementitious composites. Due to the nano modification to cement paste in combination with the supplement of nano scale continuity for multi-scale raw materials of cementitious composites, nano materials gradually show the potential to become the indispensable seventh component of cementitious composites besides cement, water, fine aggregates, coarse aggregates, chemical additives and mineral additives. Therefore, tailoring cementitious composites with nano materials provides a promising approach to develop the new generation of cementitious composites (e.g., ultra-high performance, smart/multifunctional and resilient) and sustainable infrastructures.

This chapter aims to provide a systematic overview of tailoring cementitious composites with various types of nano materials. It initially covers the principle of tailoring cementitious composites with nano materials and dispersion of nano materials in cementitious composites. The chapter, then, presents the properties of cementitious composites with 0D, 1D and 2D nano materials, namely hydration, rheology, workability, durability, functional and mechanical properties. It also highlights various applications of cementitious composites with nano materials, including structural health monitoring, traffic detection and pollutant purifying. The paper concludes by presenting the future prospects of cementitious composites with nano materials.

Contents

1. Introduction

Cementitious composites are acknowledged as the most commonly used construction and building materials due to their excellent mechanical properties, durability, accessibility, easily shaping, and low cost. It can be expected that cementitious composites will continue to serve as the primary materials in constructions in the next few decades. However, there is a significant potential for improved cementitious composites properties, including brittleness, low tensile strength, poor deformation performance, and high cracking tendency. In addition, traditional cementitious composites only serve as load-bearing materials without functional properties.

Nano materials have the potential to modify the structure of cementitious composites by following a bottom-up approach at four elementary scale levels, as shown in Fig. 1.1 [1], namely (1) Level I (10^{-8}~10^{-6} m): different types of calcium silicate hydrate (C-S-H); (2) Level II (10^{-5}~10^{-4} m): C-S-H gels together with calcium hydroxide (CH) crystals, unhydrated binder particles, and micrometer pores; (3) Level III (10^{-3}~10^{-2} m): cement paste phase, aggregate phase, and interfacial transition zone (ITZ) and (4) Lever IV (>10^{-1} m): structural element/structures/infrastructures. Usually, performance of each level is influenced and predicted by the next smaller scale. Small changes at nanoscale are likely to exert big impacts on the four levels of cementitious composites, owning to the excellent mechanical, thermal, acoustic, optical, magnetic, and electrical performances of nano materials. Therefore, using nano materials provides a promising approach to develop cementitious composites with superior mechanical properties, durability, and smart/multifunctional properties (e.g., ultra-high performance, smart/multifunctional and resilient).

Since the beginning of this century, nano materials as the smallest gradation composition bring significant changes to cementitious composites through the nano-core effect, including modifying C-S-H structures at level I, reducing calcium hydroxide (CH) crystal size and filling pores at level II, modifying bulk cement paste phase and ITZ at level III, and realizing superior mechanical properties, durability, and smart/multifunctional properties at level IV. Tailoring cementitious composites with nano materials can improve the integrity and uniformity of cementitious composites, such as matrix compactness and water-retaining ability. Therefore, as shown in Fig. 1.2, nano materials gradually show the potential to become the indispensable seventh component of cementitious composites, besides cement, water, fine aggregates, coarse aggregates, chemical additives and mineral additives.

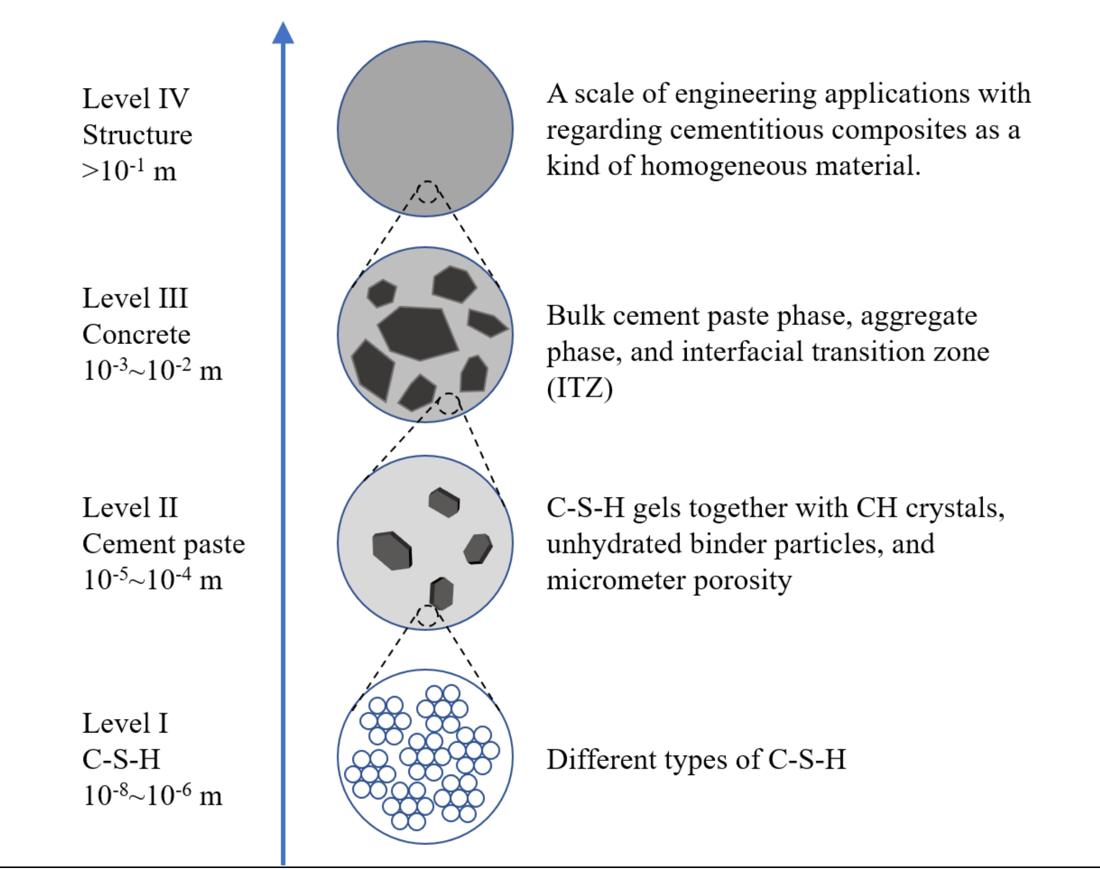


Fig. 1.1 The illustration of four elementary scale levels of the structure in cementitious composites [1]

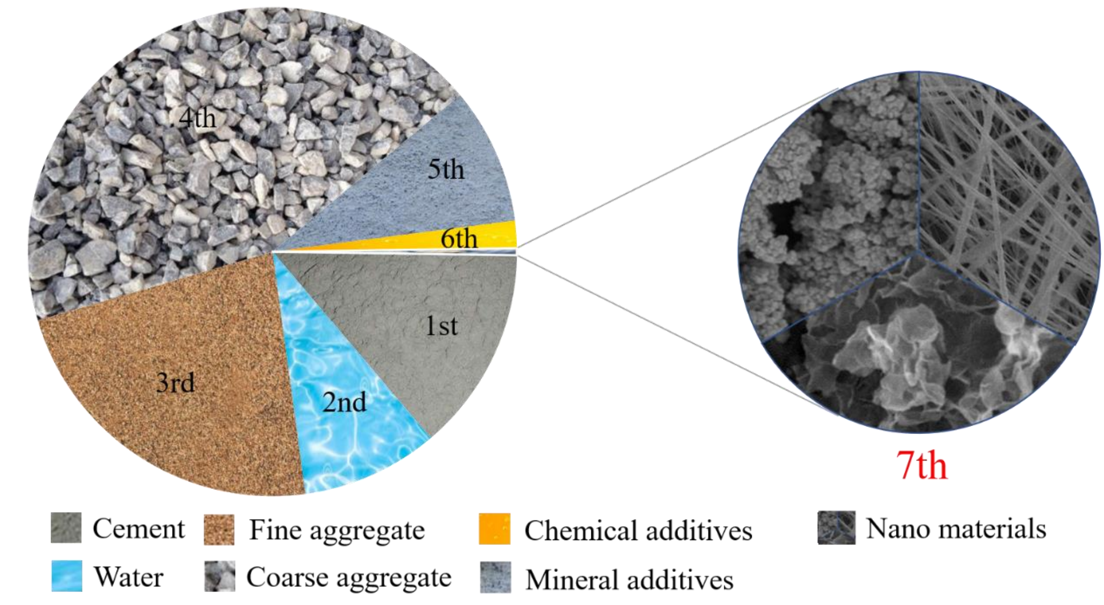


Fig. 1.2 Seven components of cementitious composites with nano materials

The study of cementitious composites with various nano materials started in 1989 by utilizing nano ZrO_2 to enhance strength and fracture toughness [2]. The past two decades have witnessed a dramatic growth of research interest in the use of various nano materials to tailor properties and functionality of cementitious composites as summarized in Table 1.1 Besides, some hybrid nano materials, such as self-assembled carbon nanotubes (CNTs)/nano carbon black (NCB) [3], are used to tailoring cementitious composites. Much attentions have been paid to some representative materials for tailoring cementitious composites, such as nano SiO_2, nano TiO_2, CNTs, and graphene. Fig. 1.3 shows the approximate appearance of cementitious composites with these typical nano materials [2, 4-8]. Nano SiO_2 can consume CH crystals because of their pozzolanic activity. Cementitious composites with nano SiO_2 show improvement of 45.6% in compressive strength, and 16.0% in flexural strength [9]. Tailoring ultrahigh performance concrete (UHPC) with nano SiO_2 shows a superior self-healing behavior with the enhancement of 39.4% in compressive strength, and 33.7% in flexural strength after a 28-day recovery [10]. Nano TiO_2 is a representative of nano materials to endow cementitious composites with purifying ability. He et al. [11] reported incorporating iron coating nano TiO_2 particles is efficient for degrading vehicle exhausts. Nano carbon materials such as NCB, CNTs, carbon nanofibers (CNFs) and graphene, are featured by high modulus, strength, toughness, and excellent electrical conductivity, thermal conductivity, electromagnetic wave absorbing and shielding properties. CNTs can improve dynamic impact toughness by 100.8%, and dissipation energy of UHPC by 93.8% [12]. Tailoring cementitious composites with CNTs is efficient to detect stain, stress, and damage of structures [13], and is conductive to shield electromagnetic wave radiation [14]. Cementitious composites with nano materials have gained significant achievements on applications of structural health monitoring, traffic detection, pollutant purifying, and energy saving.

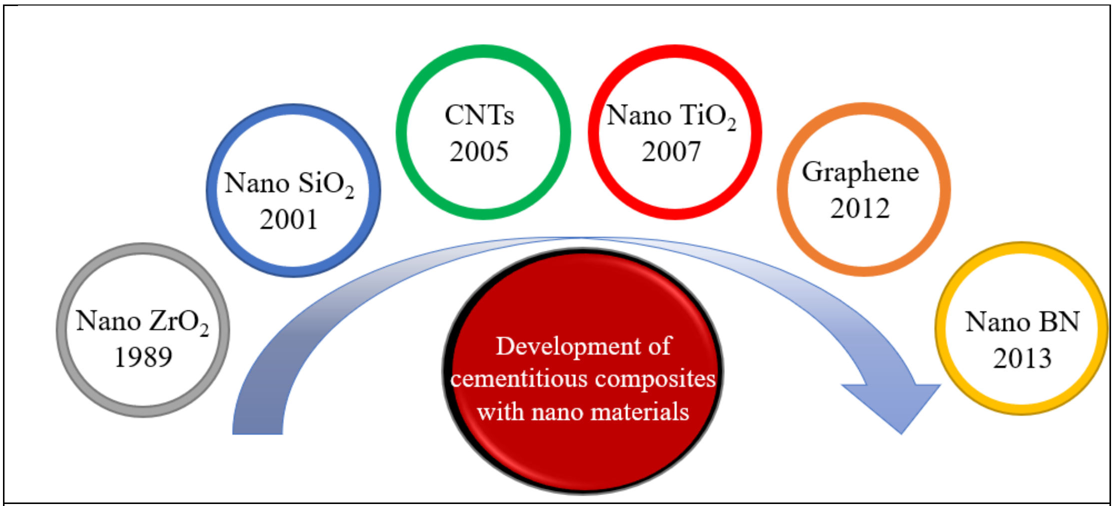


Fig. 1.3 The development of cementitious composites with various nano materials [2, 4-8]

Table 1.1 Classification of various nano materials applied in cementitious composites [15]

Classification of nano materials			Dimensions
Nano binders	Nano cement		0D
	Nano silica fume		
	Nano fly ash		
Nano materials added in cementitious composites	Nano oxide	Nano SiO_2	
		Nano TiO_2	
		Nano ZrO_2	
		Nano Al_2O_3	
		Nano MgO	
		Nano ZnO	
		Nano Zn_2O	
		Nano CuO	
		Nano Fe_2O_3	
		Nano Fe_3O_4	
		Nano Cr_2O_3	
	Nano salt	Nano $CaCO_3$	
		Nano $BaSO_4$	
	Nano carbon materials	Nano carbon black	
	Nano C-S-H seed		
	Nano clay		
	Nano perovskite		
	Nanocellulose		1D
	Nano carbonized bagasse fibers		
	Al_2SiO_5 nano tubes		
	Nano SiC		
	Nano carbon materials	Carbon nano tubes	
		Carbon nanofibers	
		Graphene	2D
		Oxidized graphene	
	Nano BN		
	Nano Ti_3C_2		
Note: 0D,1D, and 2D denote nano materials with nano size in three dimensions, 2 dimensions and 1 dimension, respectively.			

This chapter presents a systematic review of tailoring cementitious composites with various nano materials. It firstly introduces basic principles of tailoring cementitious composites with various nano materials, i.e. the nano-core effect. Then, dispersion of nano materials in cementitious composites, which is the key technique for tailoring cementitious composites with nano materials, is introduced. It also provides basic properties and performances of typical cementitious composites with nano materials including hydration, rheology, workability, mechanical properties, durability and functional properties, and concludes the evolution of the applications of cementitious composites with nano materials. Prospects of cementitious composites with nano materials is presented in the last section.

2. Basic principles of tailoring cementitious composites with nano materials

2.1 Brief introduction of nano materials

Nano materials are characterized by their tiny sizes of 1-100 nm in at least one dimension, amounting to the scale of 10-100 atoms closely arranged together. According to the morphology, nano materials are usually classified by 0D nano particles with nanometer size at three dimensions, 1D nanometer tube with nanometer size at two dimension, and 2D nano plate with nanometer size at one dimension. Due to the tiny size, nano materials have large specific surface area, surface energy, and large fraction of surface atoms. The appearance of large fraction of surface atoms makes nano materials easily form physical adsorption or chemical reaction with other particles, providing kinetic feasibility for tailoring cementitious composites. Besides, the sharply tiny size renders nano materials having significantly different properties from micro/macro materials in various aspects of mechanics, thermology, acoustics, optics, magnetics and electrics.

2.2 Nano-core effect in bulk cement paste phase

The nano-core effect is the combination of the nano effect and core effect of nano materials in cementitious composites. The small size makes nano materials at a low content extensively distributed in the cementitious composites. Due to the ultra-high specific surface area and surface energy, the wide distributed nano materials can adsorb ions and hydration products, thus forming numerous nano-core-shell structures. The brief description of the nano-core effect is illustrated in Fig. 2.1.

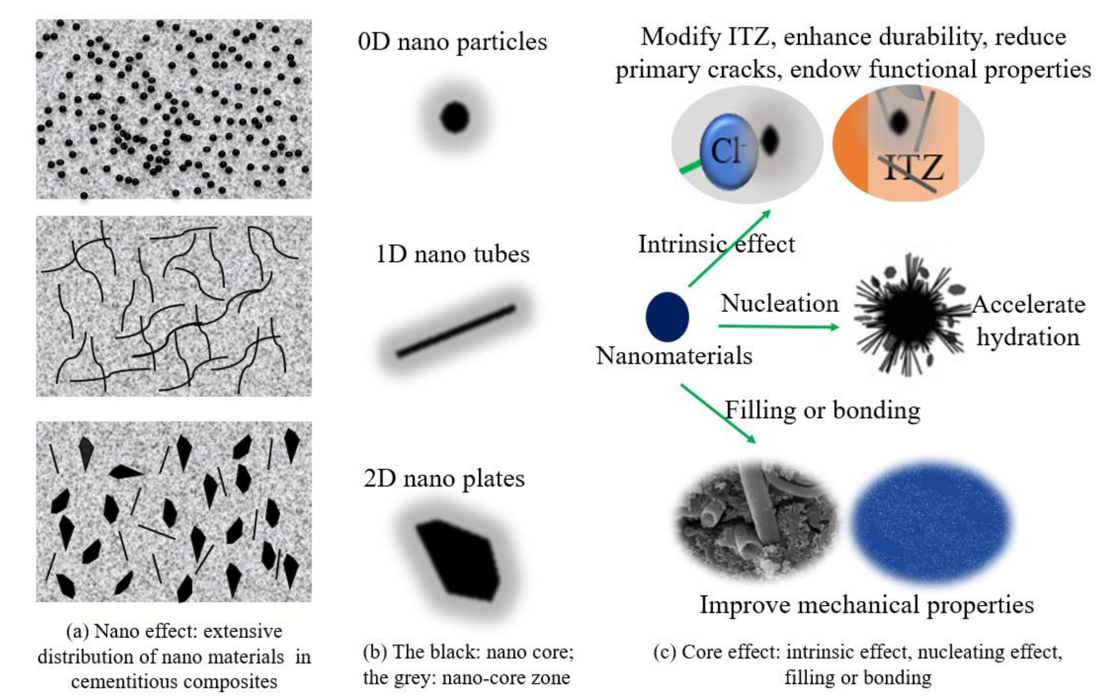


Fig. 2.1 The brief description of nano-core effect (a) nano effect (b) nano core and nano-core zone (c) core effect in cementitious composites

2.2.1 Nano effect

The nano effect of nano materials in cementitious composites includes small size and high surface area.

(1) Small size

The number of typical nano materials at the content of 0.1 vol.% in 1 cm^3 cementitious composites along with their size is illustrated in Fig. 2.2. It can be seen that the particle number ranges from 3.2×10^8 to 8.0×10^{16}, demonstrating that numerous nano materials at a low content can extensively distribute in cementitious composites, achieving big impacts on cementitious composites. In addition, the small size endows nano materials with unique physical and chemical properties. For example, nano SiO_2 has higher pozzolanic activity than micro SiO_2 [16].

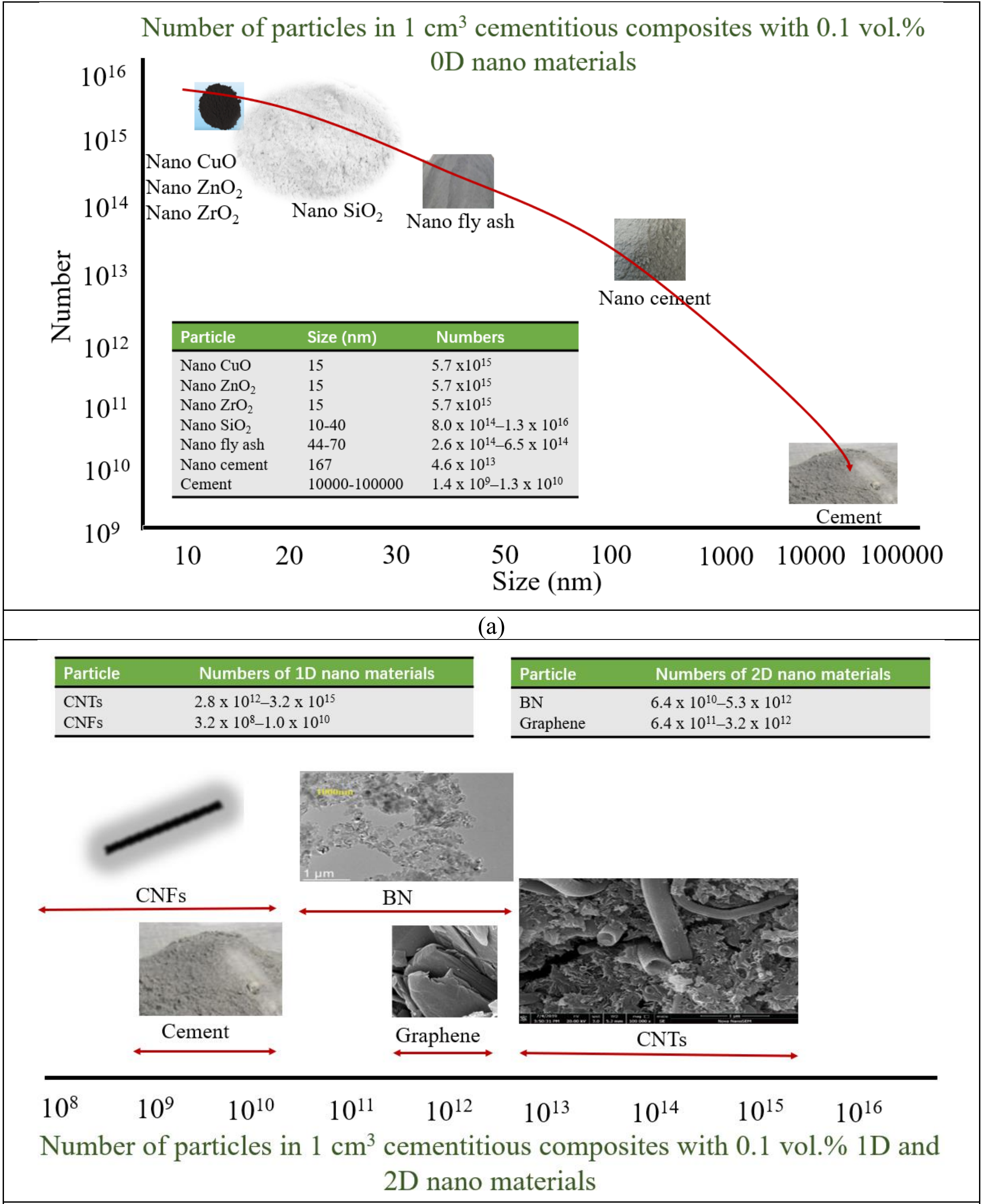


Fig. 2.2 Approximate estimate about numbers of particles in 1 cm^3 of cementitious composites with (a) 0.1 vol.% 0D nano materials; (b) 0.1 vol.% 1D and 2D nano materials (assuming that nano materials are in ideal geometrical shape and exist in single particle) [17]

(2) Large surface area

The specific surface area of typical nano materials and raw materials of cementitious composites are shown in Fig. 2.3.

It can be seen that the surface area of nano materials is about 35-3571 times of that of cement particles. Large surface of nano materials provides areas for nano materials to interact and synergize with other components in cementitious composites, usually with the disappearance, formation, and transformation of hydration products in cementitious composites matrix (such as CH crystals, C-S-H gel and ettringite). Therefore, the large surface area is the important fundamental for the whole hydration process.

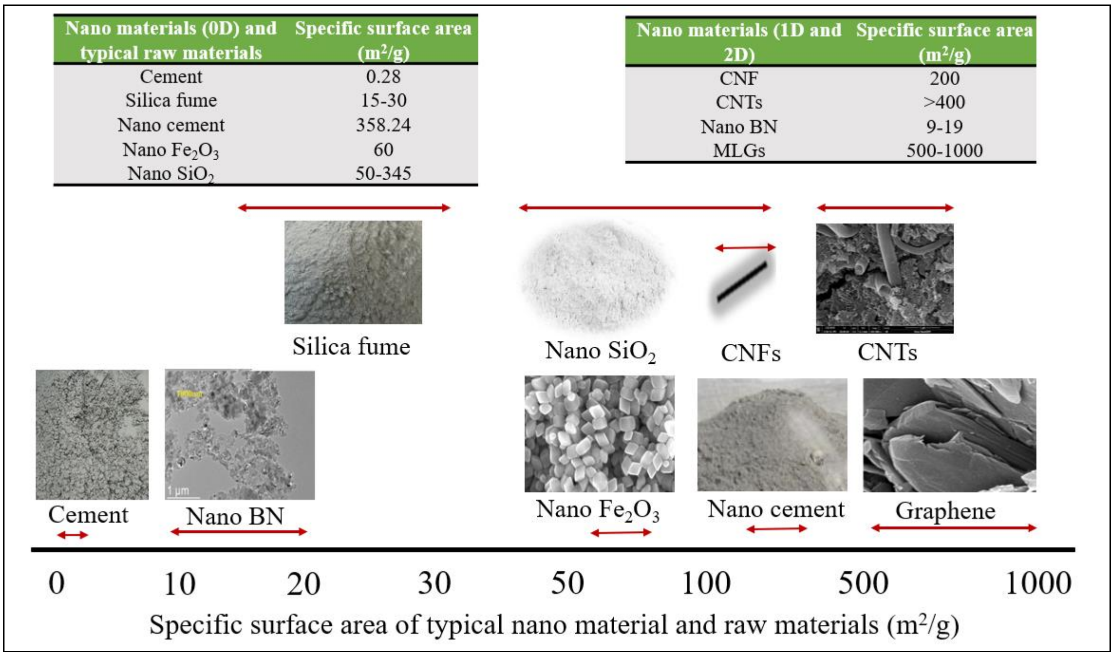


Fig. 2.3 Specific surface area of typical nano materials and raw materials [17]

2.2.2 Core effect

Nano materials exist in cementitious composites as a core surrounded by hydration products (core shell), as depicted in Fig. 2.1 (b). Thanks to the extremely tiny size, nano materials perform great mechanical properties. The core effect includes the intrinsic, nucleating, filling or bonding, and pining effects as explained below.

(1) Intrinsic effect

Table 2.1 shows the classification of intrinsic characteristic of nano materials and their benefits to cementitious composites, that can be classified into the following four aspects.

(a) Adsorption of ions, water and hydration products: Adsorption of ions can significantly cut down the transportation of ion, resulting in less corrosion. On the other hand, adsorption of water at early stage decreases the water to binder (w/b) ratio of matrix around nanomaterials, thereby enhancing the early-strength and adsorption of hydration products produces a more compact matrix. Furthermore, adsorption of water at early stage and release of further hydration products are beneficial for self-curing;

(b) Reducing inherent defects as some nanomaterials can transfer heat of hydration, and reduce thermal stresses accordingly;

(c) Modification of hydration process: The active or pozzolanic nanomaterials can participate in hydration reaction or secondary hydration, thus consuming CH crystal and transferring C–S–H gel to the needle-like or the columnar, decreasing the orientation of CH crystals, and reducing CH crystal size;

(d) Functional effects: Electrical, thermal, electromagnetic, sensing, and photocatalytic behaviors will endow cementitious composites the corresponding functional properties.

Table 2.1 Classification of intrinsic characteristics of nano materials and their benefits to cementitious composites [17]

Classification of intrinsic characteristics of nano materials			Benefits
Physical properties	Morphology	Dimension	Strengthen bond of nanomaterial with matrix; Enhance nucleating effect
		Size	
		Roughness	
	Density		Reduce dosage of nano materials

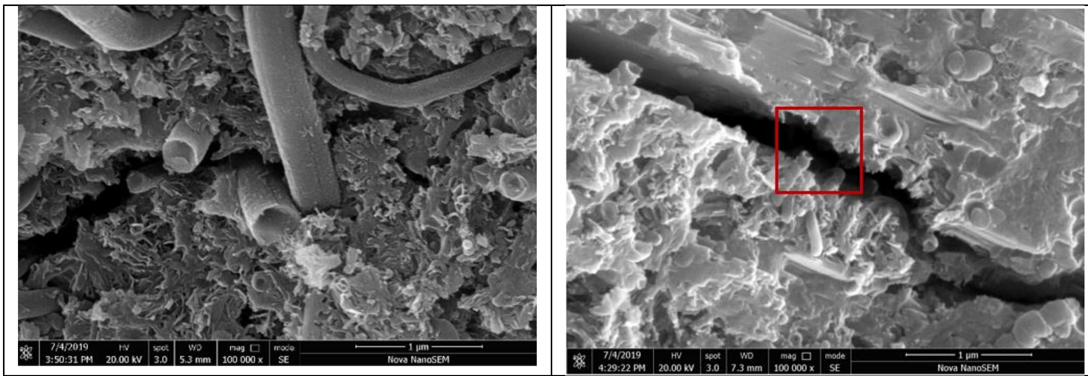
			with low density
	Surface features	Hydrophilic/hydrophobic	Beneficial to dispersion of nano materials
		With functional group	Strengthen bond of nanomaterial with matrix; Beneficial to the dispersion of nano materials
		Charged or absorbable	
Mechanical properties	Strength		Improve mechanical properties of cementitious composites with nano materials
	Modulus		
	Hardness		
	Toughness		
	Damping		
	Wear resistance		
Hydration activity	Active		Accelerate hydration and participate in secondary hydration
	Pozzolanic		
Multifunctional properties	Electrical properties	Electrically conductive	Improve electrical conductivity of cementitious composites
		Electromechanical	Endow self-sensing property with cementitious composites
		Electrothermal	Endow self-heating property with cementitious composites
	Thermal conductivity		Increase thermal conductivity and create
	Electromagnetic shielding and absorbing		Endow cementitious composites with electromagnetic shielding and absorbing properties
	Photocatalytic properties		Endow cementitious composites with photocatalytic capability

(2) Nucleating effect

Addition of nano materials accelerates the hydration process due to nucleation and growth of hydration products on nano materials with large surface area and high surface energy. Nano materials as the "nucleus" wrapped by hydration products act as nano core in matrix, allowing the hydration products uniformly distribute throughout the cementitious composites.

(3) Filling or bonding effect

Nano materials with tiny size are the smallest raw materials to fill pores in cementitious composites, thus decreasing the porosity and increasing the compactness. Along with the filling effect in cementitious composites, nano materials tightly bond with matrix, allowing stress transfer due to bridge-effect and pull-out effect, as shown in Fig. 2.4.



(a) Bridge-effect | (b) Pull-out effect

Fig. 2.4 SEM images of nano materials in cementitious composites [14]

(4) Pinning effect

Hard inactive nano materials (such as TiO_2 and ZrO_2) form nano-core-shell structures by adhering hydration products during the hydration process. The nano-core-shell structures with hard core can inhibit crack growth at the initial stage and deflect cracks when the crack tip reaches the hard core, improving the fracture toughness of cementitious composites. In addition, ZrO_2 with tetragonal structure would transform to ZrO_2 with monoclinic structure due to stresses. The transformation will consume the energy of damage, and inhibit the extension of cracks.

2.3 Nano-core effect in ITZ

Cementitious composites can be considered as a three-phase material, composed of aggregate phase, bulk cement paste phase, and ITZ between them. The ITZ has the characteristics of low strength, high porosity, high CH content, ettringite content, high metal cation content, and low molar ratio of CaO to SiO_2 (Ca/Si ratio), acting as 'the weakest link in the chain'. Nano materials can tailor microstructures in ITZ, which is not only governed by the nano-core effect but also dependent on the nano material enrichment effect in ITZ.

Few studies demonstrated that the presence of different types of nano materials can modify ITZ between aggregate and bulk cement paste, enhancing interfacial bond strength, reducing ITZ thickness by optimizing intrinsic compositions and microstructures of ITZ between aggregate and bulk cement paste [18-21].

The modification of nano materials on ITZ through nano-core effect is attributed to a nanofiller enrichment layer formed near the aggregate surface due to the wall effect and nanomaterial migration [22]. Firstly, the smaller particles in fresh cementitious composites migrate to the surface of aggregate due to the wall effect, leading to the increase of local content of nano materials in ITZ. Then, nano materials move with water in the voids among binder particles because water is absorbed by hydrophilic aggregate. Therefore, a nanomaterial enrichment layer forms in ITZ between aggregate and bulk cement paste. The formation process of nanomaterial enrichment layer in ITZ is illustrated in Fig. 2.5.

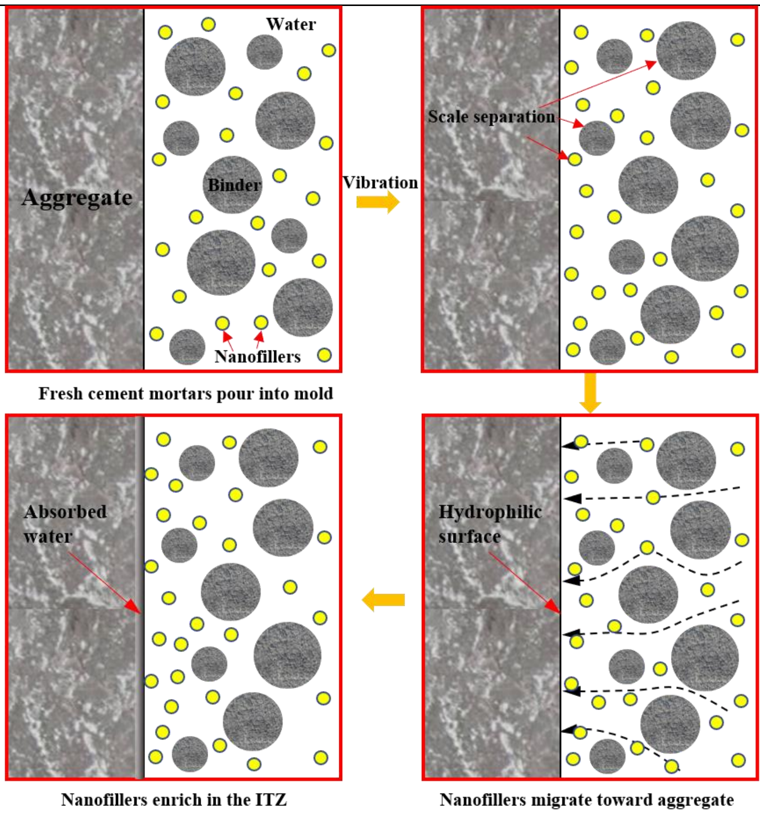


Fig. 2.5 The formation process of nanomaterial enrichment layer in ITZ [22]

The presence of nanomaterial enrichment layer in ITZ provides numerous nucleation sites for hydration products. Nano materials can adsorb metal cations (such as Ca^{2+} and Al^{3+}) at the early hydration stage, thus reducing the enrichment of metal cations in ITZ. The adsorbed Ca^{2+} cannot form CH crystals due to the coordination number limitation, the size and content of CH crystals in ITZ. Meanwhile, the adsorbed Al^{3+} is beneficial to modify ITZ in cementitious composites with nanomaterials. It will inhibit the formation of calcium aluminate hydrate (C-A-H), thereby reducing the content of ettringite (reaction product of C-A-H and sulfate). Also, low aluminum doping in C-S-H gels is propitious to increase the ordered degree of C-S-H and decrease the distance between C-S-H layers.

In addition, the modifying mechanism of nano materials on ITZ is the same as that on bulk cement paste. The enriched nano materials in ITZ form numerous nano-shell-core structures, thereby densifying interfacial microstructures, restricting cracks due to pinning effect, and deflecting cracks due to bridge effect. The effect of nano materials on ITZ between aggregate and bulk cement paste is shown in Fig. 2.6.

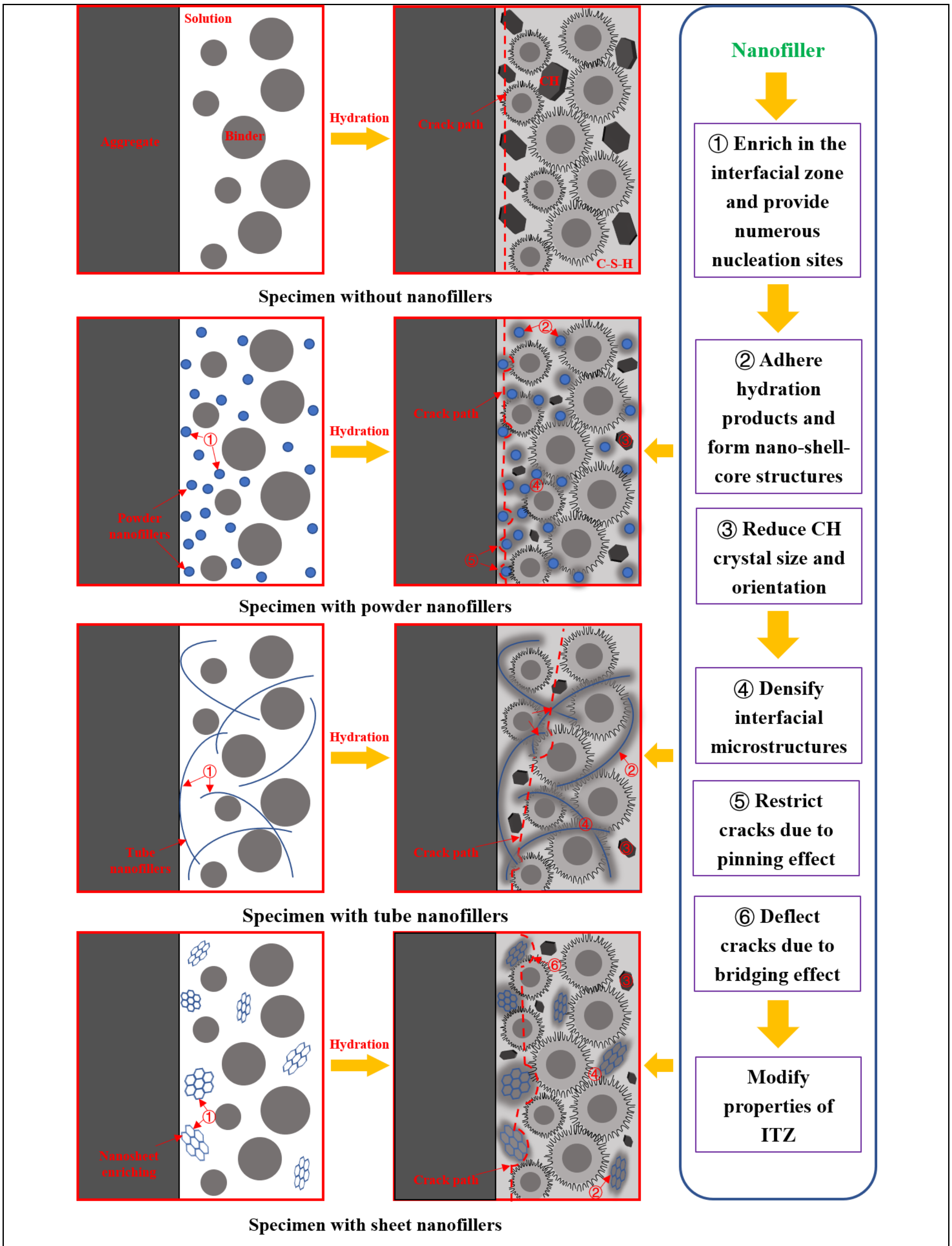


Fig. 2.6 Effect of nano materials on ITZ between aggregate and bulk cement paste [18]

2.4 Nano-core effect zone

Nano core are extremely tiny, with the result that intrinsic and nucleating effects only influence on hydration products in short range. The hydration products adsorbed by nano materials act as the shell of nano core. The formation of a nano-core-shell element can represent nano-core effect zone (as shown in Fig. 2.1). Nano-core effect zone is a transition zone that differs from cementitious composites in long range. Cementitious composites with nano materials depend on properties, distribution, and numbers of nano-core-shell element to some extent. The properties and performances of nano-core-shell element depend on the nano-core effect.

2.5 Factors affecting nano-core effect

Nano-core effect is dominated by intrinsic properties of nano materials, dispersion of nano materials and composition of cementitious composites.

Intrinsic properties of nano materials are the primary factors governing the nano-core effect. Uniform dispersion of nano materials can effectively enhance the properties of cementitious composites. Because aggregation of nano materials will reduce numbers of nano-core-shell elements and weaken nano-core effect, or even damage cementitious composites due to the appearance of weak areas in matrix. The composition of cementitious composites affects the nano-core effect as well. The w/b ratio determines the dispersion of nano materials to a certain extent. Different physical properties and chemical compositions of various cement, silica fume and fly ash can also affect the nucleating effect by influencing hydration.

3. Dispersion of nano materials

Nano materials are liable to aggregate in cementitious composites or reunite during the hydration process due to their large specific surface area and high surface energy. The aggregation will weaken the nano-core effect, which consequently makes reinforcing mechanism failure, or even damages strength of cementitious composites by producing weak areas in matrix. Therefore, uniform dispersion is the key for tailoring cementitious composites with nano materials. Different strategies about the dispersion of nano materials have been proposed for seeking out a technology with simplicity, economy and efficiency. Fig. 3.1 shows typical measures to disperse nano materials and the typical dispersion methods for each nano material used in cementitious composites are summarized in Table 3.1.

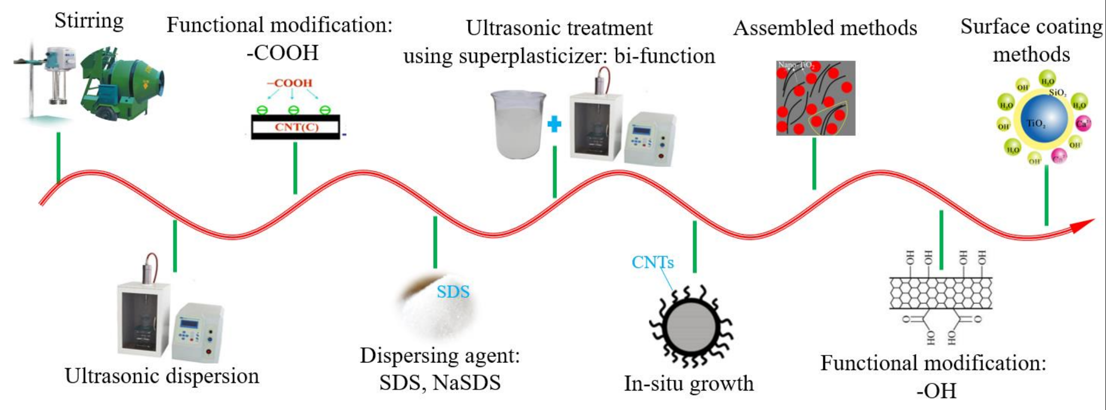


Fig. 3.1 Diagrammatic sketch of typical measures for dispersing nano materials [23]

Table 3.1 The typical dispersing method for nano materials used in the cementitious composites

Dimension	Nano materials	Dispersing methods		References
0D	Nano ZrO_2	Shear mixing		[24]
				[25]
	Nano TiO_2	Shear mixing		[26]
				[27]
		Ultrasonic treatment		[28]
				[29]
		Assembled methods	CNT/micro TiO_2	[30]
		Surface coating method	SiO_2 coating nano TiO_2	[31]
			Al_2O_3 coating nano TiO_2	[32]
		Ultrasonic treatment + SP		[33]
	Nano SiO_2	Shear mixing		[34]

				[35]
				[36]
				[37]
		Dispersing agent	SRA	[38]
		Ultrasonic treatment		[39]
				[40]
		Shear mixing + SP		[41]
1D	CNT	Ultrasonic treatment + SP		[22]
		In-situ growing on cement, clicker, and sand		[42]
				[43]
		Assembled methods	CNT/micro TiO_2,	[30]
			CNT/NCB	[3]
		Functional modification	-COOH, -OH	[44]
		Dispersing agent	SDS, SDBS	[45]
			SDC	[46]
			PAC	[47]
	CNFs	Shear mixing		[48]
		Ultrasonic treatment + SP		[49]
2D	Graphene	Shear mixing		[50]
		Ultrasonic treatment + shear mixing		[51]
	Nano BN	Ball milling		[6]
		Stirring		[52]
				[22]
Note: SP, SDS, SDBS, SDC, SRA, and PAC denote superplasticizer, sodium dodecyl sulfonate, sodium dodecylbenzene sulfonate, sodium deoxycholate, shrinkage reducing admixture and polyacrylic acid polymers, respectively.				

3.1 Traditional methods

Traditional methods are the basic measures to disperse nano materials in cementitious composites, including mechanical methods and physical surface modification utilizing dispersing agents. The specific classification and their advantages and disadvantages are generalized in Table 3.2.

Table 3.2 Specific classification of traditional dispersing methods and their advantages and disadvantages [23]

Traditional methods	Classification		Advantages	Disadvantages
Mechanical method	Shear mixing		Beneficial to manufacture	Large energy consumption Complicated operation
	Stirring		Beneficial to manufacture	Lake of efficiency
	Ultrasonic dispersion		Realization of well dispersion	Inconvenience for manufacture
				Large energy consumption
Dispersing agent	Surfactants	ionic	Easy control	Possibly restrain hydration, setting and hardening Possibly exert negatively impact on mechanical and durability performance
		non-ionic	Low energy consumption	
	Polymers		Strengthen bond between nano materials and hydration products	

Mechanical methods include ordinary stirring, shear mixing with high speed and ultrasonic dispersion [53]. Ordinary stirring and shear mixing with high speed are suitable for manufacture. But the two methods will consume large energy and lack efficiency. Owing to the apparent effectiveness and simplicity of processing, and low cost, ultrasonic dispersion has been widely applied to get a solution where well-dispersed nano materials suspend. Ultrasonic energy is proposed to accurately describe the dispersing effect and decide the ultrasonic time under a certain treatment power [54]. Dispersing agents (including surfactants and polymers) for physical surface modification work by wrapping nano materials tightly to form core shell particles, and making them repel from each other due to the van der Waals interactions between nano material particles. Dispersing agents is a pure physical process that will not alter structural features of nano materials, nor affect their properties. Much works have been done on dispersing agents, such as sodium dodecyl sulfonate (SDS) [45], sodium dodecylbenzene sulfonate (SDBS) [46], sodium deoxycholate (SDC) [47], polyacrylic acid polymers [47], superplasticizer (SP) [55, 56], and shrinkage reducing admixture [38]. These dispersing agents are effective indeed, but the application of some of them alone in cementitious composites may affect strength and durability. Among these agents, SP is the most popular as a bi-functional agent without damaging properties of cementitious composites. Because, it can not only disperse nano materials but also increase the workability of cementitious composites as water reducing admixture. The utilization of SP to disperse nano materials such as nano SiO_2 [55, 56], nano TiO_2 [57], nano ZrO_2 [58], nano carbon materials [44, 59] has been certified valid.

The combination of dispensing agents and traditional methods are more effective than their application alone, especially the combination of SP and ultrasonic dispersion. The utilization of dispersion agent such as SP is more complex and time-consuming, because they should be deposited on nano materials before fabrication of cementitious composites which will last for a long time [60]. Therefore, to seek out a technology with simplicity, economy and efficiency, SP and nanomaterial are directly added in the water for ultrasonic treatment, instead of ultrasonic treatment after pre-treatment of nano materials by dispersing agent.

3.2 Functional modification

Functional modification aims to alter surface structures of nano materials, thereby increasing their wettability and solubility. Measures of oxidizing nano materials and adding functional group have been certified effective by the utilization of strong acids [61], ozone [62], strong oxidant, and plasma excitation [63]. Functional modification has the ability to alter the structure and properties of nano materials, therefore it is usually applied on inert material, such as carbon-based nano materials (such as CNTs and graphene). Much researches have been conducted on cementitious composites with nano materials through the treatment of functional modification, such as hydroxyl functionalized CNTs (CNTs-OH) [44], carboxyl functionalized CNTs (CNTs-COOH) [44, 64, 65] and oxidized graphene [66, 67].

3.3 In-situ growing method

In-situ growing method refers to the act of making nano materials grow on raw materials to form the combined particles with larger size. The dispersion of nano materials is improved because nano materials can extensively distribute in cementitious composites with raw material particles. Nano carbon materials are the most commonly utilized to grow on surface of raw materials, such as CNTs or CNFs on mineral admixtures (silica fume and fly ash) [42], cement or clinker [42, 68], sand [43] and aggregates [69]. CNTs or CNFs also can grow on the surface of reinforced fibers such as carbon fiber [70]. In-situ growing method also can strengthen bond of nano materials with hydration products. But the growth is inefficient and complicated.

3.4 Assembled methods

Assembled methods includes electrostatic self-assembly and chemically graft.
Electrostatic self-assembly is a novel technology to disperse nano materials utilizing the electrostatic adsorption between nano materials and macro, micro or nano particles with opposite electrical charges. For example, CNTs and CNB has been self-assembled to disperse each other [3, 71]. TiO_2 with size of 450 nm has been utilized to disperse CNTs through electrostatic self-assembled method to form CNTs/micro TiO_2 composite fillers [30]. It is reported self-assembled materials may be more liable to disperse because size of self-assembled unit is larger [30] (as shown in Fig. 3.2). With the incorporation of larger size of micro TiO_2, the effective content of CNTs to form the conductive network in cementitious composites largely increases [72]. Zhang et al. [30] generalized it as the excluded volume effect, and proposed two formulas to calculate the effective CNT content in cementitious composites. The results showed the effective CNT content increases by 4.85% after adding CNT/micro TiO_2 at the content of 5.78%. Electrostatic self-assembly method is characterized by its stability and simple process without chemical reaction and pollution. Properties of materials formed by electrostatic self-assembled method integrates properties of each component of composite fillers, which is beneficial to multifunctional properties.

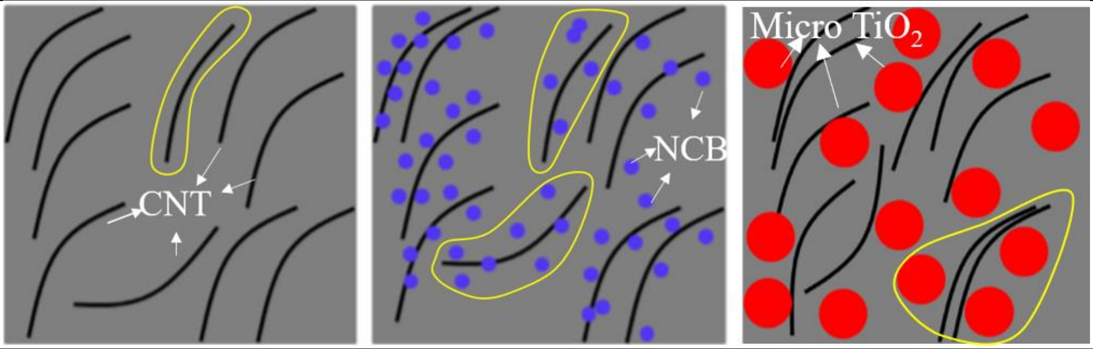


Fig. 3.2 Diagrammatic sketch of CNT, electrostatic self-assembled unit of CNT/NCB and CNT/micro-TiO_2. Zone wrapped by yellow color represents size of electrostatic self-assembled unit [30].

Chemical graft aims to attach nano materials to micro/macro materials through chemical reactions. Lots of attention of researchers are paid on fibers grafted by nano materials, because attaching nano materials to fibers will increase roughness of surface of fibers, which will strengthen bond between fibers/nano composite and cementitious matrix. The typical representatives are hydrophobic polymer grafted by nano SiO_2 [73], carbon fibers by nano SiO_2 [74] and CNTs [75], polyvinyl alcohol (PVA) fibers by nano SiO_2 [75], and polyethylene fibers grafted by CNFs [76]. There are also binders grafted by nano materials existed, such as silica fume grafted by nano SiO_2 [77]. Nano materials are extensively distributed in matrix along with fibers, thus realizing the dispersion of nano materials. This method also benefits multifunctional properties but it may cause pollution during chemical reaction process.

3.5 Surface coating method

Surface coating method refers to wrapping nano materials utilizing another type of materials. The method is found not only beneficial to multifunctional properties but also effective for dispersion of nano materials. The typical representative is SiO_2 coating nano TiO_2, where lots of Ti-O-Si bonds are observed in the coated interface. The appearance of Ti-O-Si bonds makes nano TiO_2 more negative charged, and easier dispersed in water due to the existence of more electrostatic repulsion between nano

TiO_2 particles [78]. But this method has disadvantages of operational complexity and high cost.

4. Tailoring cementitious composites with 0D nano materials

4.1 Nano SiO_2

Nano SiO_2 is a kind of 0D nano particles with pozzolanic activity. In addition to filling pores in cementitious composites, it can participate in the secondary hydration reaction, thus making cementitious composites more compact. Tailoring cementitious composites with nano SiO_2 has effects on hydration, rheology, workability, mechanical properties, functional properties of cementitious composites.

4.1.1 Hydration

Usually, nano SiO_2 accelerates hydration process and improves hydration degree of cementitious composites, because nano SiO_2 with pozzolanic activity can participate in hydration and secondary hydration process. Senff et al. [36] observed the time reaching maximum temperature is shifted earlier by 51% when nano SiO_2 at the content of 2% is added in cement mortar. The hydration heat of cement paste also increases by 6.2% in 72 hours [35]. References [79-81] reported initial and final setting time is shortened after incorporating nano SiO_2 into cementitious composites, and the reduction is more obvious as the nano SiO_2 content increases.

4.1.2 Rheology

Factors such as SP content and w/b ratio will affect cementitious composites with nano SiO_2. Jiang et al. [82] reported plastic viscosity of cement paste decreases as the nano SiO_2 increases. Moreover, the saturated point of SP content in cement paste with nano SiO_2 is 0.75%, and above this value, the rheology parameters change slowly. Ouyang et al. [41] build up a viscosity prediction model of cement paste with nano SiO_2, with the assumption that cement paste with nano SiO_2 is a suspension. The model can accurately predict the viscosity of cementitious composites from viscosity of nano SiO_2 suspension and relative viscosity of pure cement paste when nano SiO_2 is less than 5.5%. The model can also calculate the absorbed water layer of thickness around nano SiO_2 particles.

4.1.3 Workability

Up to date, there are two points existed in workability of cementitious composites with nano SiO_2. The first view believes nano SiO_2 brings obstacle to workability due to the deterioration of flowability. References [16, 83-85] are the strong support for this view. The other point is that nano SiO_2 can improve the workability by increasing integrity and uniformity of fresh cementitious composites, which is consequently beneficial to mechanical behaviors. Collepardi et al. [86] reported nano SiO_2 at the content of 1% can decrease the bleeding water content of self-compacting concrete by 50%, while the deterioration of flowability is only 9.7%. This is to say, the positive effect of nano SiO_2 on water retainment far exceeds its deterioration on flowability in self-compacting concrete.

4.1.4 Mechanical properties

(1) Static mechanical properties

Researches [87-92] investigated the effect of nano SiO_2 on strength performances of cementitious composites. It can be concluded that there is an optimal content of nano SiO_2 to make cementitious composites reach the highest strengths. The observed best modifications includes 168.8% in compressive strength [35], 31.8% in flexural strength [90], and 83.3% in tensile strength [90]. Besides, Hasan and Milad [93] suggested nano SiO_2 at content of 6% can significantly enhance the fatigue life of concrete.

Szymanowski and Sadowski [19] reported incorporating amorphous nano SiO_2 into cement mortar will approximately improve the bond strength between the cement mortar overlay and the concrete substrate up to 20%. The results reflect the modification of nano SiO_2 to ITZ between two type of cementitious composites, which is the evidence behind the improved strength.

(2) Dynamic mechanical properties

The main benefit of tailoring cementitious composites with nano SiO_2 is to increase dynamic strength behaviors, especially the ability to absorb dynamic energy. Wang et al. [94] incorporated nano SiO_2 into UHPC, and reported the dynamic compressive strength, impact toughness and specific energy absorption are improved by 25.0%, 13.6% and 211.2%, respectively. Li et al. [95] reported that average peak stress and peak strain of UHPC are improved by 21.7% and 31.1% due to the presence of nano SiO_2.

4.1.5 Durability

The modification of nano SiO_2 on transportation of cementitious composites consists of two main parts: ion and water adsorption, and pore filling. Results in Table 4.1 demonstrate the reduction of transportation firstly rises with nano SiO_2 increasing, and then decreases when nano SiO_2 exceeds the optimal limitation. This is to say, pore filling effect play a more important role than ion adsorption in terms of transportation of cementitious composites. Apart from improvement for chloride anti-corrosion, nano SiO_2 can reduce the occurrence of alkali-silica reaction, consequently decreasing the expansion of cement mortar consequently.

Incorporating nano SiO_2 can reduce mass loss, strength loss, water absorption and increase dynamic elastic modulus of specimen after freeze-thaw circles [96-98]. Tailoring concrete [4] and UHPC [99] have better abrasion performance due to the presence of nano SiO_2. Moreover, the limewater curing is more preferable than the water curing [100, 101]. Additionally, Ibrahim et al. [102] indicated cement mortar with nano SiO_2 exhibits better anti-fire ability under the temperature of 26°C, 400°C and 700°C.

Table 4.1 Transportation performance of cementitious composites with nano SiO_2 at 28 days

Matrix	Nano SiO_2 content	Decrease/increase (relative values)			References
		Chloride penetration	Water absorption	Gas permeability	
UHPC	1%/	-60.0%	-	10.04%	[99]
	3%	-78.6%	-	10.49%	
	1%	-	-	7. 5%	[92]
	2%	-	-	24.2%	
	3%	-	-	31.9%	
	4%	-	-	25.7%	
Ordinary cementitious composites	1%	-18.04%/	-	-	[4]
	3%	-10.49%	-	-	
	3%	-48.88%	-	-	[103]
	6%	-84.0%	-	-	
	3%	-	-19.93%	-	[97]
	5%	-	-28.27%	-	
	7%	-	-20.01%	-	
	1%	-	-54.8%	-	[104]
	2/%	-	-60.4%	-	
	3%	-	-67.1%	-	
	4%	-	-72.7%	-	
	5%	-	-69.6%	-	
	0.5%	-	-11.1%	-	[105]
	1%		-14.7%	-	
	1%	-61.7%	-	-	[106]

4.1.6 Functional properties

(1) Self-sensing properties

Nano SiO_2 allows cementitious composites self-sensing by modifying the electrical properties of cementitious composites. Table 4.2 shows research results on the electrical resistivity of cementitious composites with nano SiO_2. In most cases, nano SiO_2 increases the electrical resistivity. But from Table 4.2, the effect of nano SiO_2 on the electrical properties of cementitious composites is still controversial.

Cementitious composites with nano SiO_2 can sense damage, strain, and stress. Öztürk et al. [107] reported increase of electrical resistance in damaged UHPC containing nano SiO_2 is 18.5% higher than the control group. Vipulanandan and Mohammed [108] showed that the sensitivity of cement paste consisting SiO_2 is over 500 times higher than the referenced group. Meanwhile, they indicated the sensitivity largely depends on the curing ages and nano SiO_2 content. The sensing ability of cementitious composites with nano SiO_2 is in the state of immature development.

(2) Self-healing properties

The presence of nano SiO_2 can provide more nucleation sites at cracks surface, which consequently accelerates the self-healing efficiency of cementitious composites. Wang et al. [10] investigated the self-healing of UHPC with nano SiO_2, and found that, compared to the control group, the compressive strength increases by 39.4% after a recovery of 28 days, and flexural strength increases by 33.7%. Öztürk et al. [107] reported, compared to the control group, the increase of 12.8% in electrical resistance of ECC with nano SiO_2 after recovering for 7 days and 21.2% after 90 days. Moreover, initial individual microcracks close to or less than 100 μm are completely healed at the surface of with nano SiO_2.

(3) Thermal properties

The incorporation of nano SiO_2 has shown to enhance the thermal conductivity of cementitious composites [109, 110]. Zaidi et al. [109] reported thermal conductivity of cement mortar with nano SiO_2 (1%-3%) is located in the range from 0.762 to 1.051 W/(m·K). Abd et al. [110] showed that incorporation of nano SiO_2 is beneficial to reduce thermal stress inside cement paste by observing the micro change of specimen length and calculating thermal expansion coefficient under the high temperature.

Table 4.2 The effect of nano SiO_2 on resistivity of cementitious composites

Matrix type	Nano content	Increase/decrease of resistivity (relative values)				References
		3 days	7 days	28 days	90 days	
Ordinary cementitious composites	0.5%	6.7%	-	11.9%	-	[9]
	1.0%	15.9%	-	21.1%	-	
	1.5%	17.5%	-	33.0%	-	
	2.0%	19.4%	-	47.0%	-	
UHPC	2.0% (C40/45/50)	-	0%/8.2%/42.6%	77.8%/82.0%/134.7%	270.9%/252.5%/231.9%	[111]
	3.0%	-	-45.3%	-	-61.0%	[107]

4.2 Nano TiO_2

Nano TiO_2 has various types with different crystal structures including rutile, anatase, brookite, and rutile and anatase hybrid phases. Besides, surface coating nano TiO_2, such as SiO_2/Al_2O_3 coating and SiO_2 coating, has been attempted to tailor cementitious composites. The presence of nano TiO_2 will cause an effect on hydration, rheology, workability, durability, mechanical and functional properties of cementitious composites. More importantly, nano TiO_2 inherent with photocatalytic properties can release free radicals to react with some harmful gases (NO_X and SO_2) under UV radiation, thereby endowing cementitious composites with pollutant purifying ability.

4.2.1 Hydration

Due to the large surface area of nano TiO_2, much water is absorbed by nano TiO_2 during the fabrication process, consequently, causing an effect on hydration rate and degree. However, there is no consistent conclusion temporarily.

The common views believe that nano TiO_2 can accelerate hydration rates and improve hydration degree [112-115]. Zhang et al. reported the initial/final setting time is shortened by 37.9%/15.7%, 63.4%/37.4%, and 6.5%/46.2% with incorporation of nano TiO_2 at the content of 1%, 3%, and 5%, respectively [115]. Besides, the small particle size (15−25 nm) of nano TiO_2 is more effective than the large nanoparticle size (20−30 nm) [116]. However, Folli et al. [117] believed that nano TiO_2 is inert and will not improve cement hydration degree.

4.2.2 Rheology

Jiang et al. [82] and Li et al. [118] provided a comprehensive assessment of rheology behaviors of cementitious composites, based on various parameters of nano TiO_2, including content, crystal phase, diameter, and nanomaterial modification type. The shear stress increases with nano TiO_2 content at any shear rate [82]. The nano TiO_2 with a smaller diameter of 20 nm has the largest yield stress and minimum viscosity [118]. Moreover, the cement paste with the rutile nano TiO_2 exhibits the largest yield stress and minimum viscosity among three crystal types. The cement paste with SiO_2/Al_2O_3 coating nano TiO_2 shows larger yield stress and smaller minimum viscosity than the SiO_2 coating form, because the electro-static repulsion between SiO_2/Al_2O_3 coating nano TiO_2 particles is smaller [118].

4.2.3 Workability

Similar with nano SiO_2, there are also two arguments about the effects of nano TiO_2 on flowability of cementitious composites. From Table 4.3, it can be concluded that the fluidity of cement paste and cement mortar presents a decreasing trend with the increase of nano TiO_2 content. However, in self-compacting cement mortar, nano TiO_2 at the content of 1% and 3% can improve the flowability [119]. The possible reason is that nano TiO_2 wrapped by water reducing agent can act as rollers to lubricate cement particles. It can be further inferred that addition of nano TiO_2 also can enhance the water retainment and cohesion of fresh self-compacting concrete due to the adsorption of water.

Table 4.3 Flowability of cementitious composites with nano TiO_2

Matrix type	Nano TiO_2 content	Increase/decrease (relative values)			References
		Fluidity	Slump flow diameter	V-tunnel flow time	
Ordinary cementitious composites	1%	-2.8%	-	-	[115]
	3%	-19.8%	-	-	
	5%	-20.8%	-	-	
	5%(with/without SP)	-32.6%/-40%	-	-	[120]

	10%(with/without SP)	-48.9%/-57.1%	-	-	
UHPC	1%/	-	-	-5.5%	[119]
	3%/	-	3.3%/	-12.7%	
	5%	-	4.9%	-25.5%	
	1%/	-	-1.3%	4.0%	[121]
	2%/	-	-2.5%	10.0%	
	3%/	-	-5.0%/	16.0%	
	4%/	-	-7.5%	20.0%	
	5%	-	-8.8%	24.0%	

4.2.4 Mechanical properties

(1) Static mechanical properties

The presence of nano TiO_2 can improve the static strength behaviors of cementitious composites. Table 4.4 shows the static strength performance of cementitious composites with nano TiO_2 at 28 days, showing that the improvement of strength is largely content-dependent on nano TiO_2. Szymanowski and Sadowski [20] incorporated tetragonal crystal TiO_2 into cement mortar as the overlayer placing on ordinary concrete substrate. The highest value of pull-off bond strength between the overlayer and the concrete substrate is obtained when nano TiO_2 at the content of 0.5% is incorporated into the overlayer. This can be considered as a province for the modified ITZ between two cementitious composites.

(2) Dynamic mechanical properties

The most benefit of tailoring cementitious composites with nano TiO_2 is to increase the ability of absorbing dynamic energy. Wang et al. [22] found that the incorporation of nano TiO_2 improves dynamic compressive strength, impact toughness, and specific energy absorption of UHPC up to 59.7%, 39.9% and 246.9%, respectively.

Table 4.4 Static strength performances of cementitious composites with nano TiO_2 at 28 days

Matrix type	Nano TiO_2 content	Increase/decrease (relative values)			References
		Flexural strength	Compressive strength	Tensile strength	
Ordinary cementitious composites	0.1%	-	13.2%	-	[33]
	0.5%	-	20.8%	-	
	0.9%	-	14.15%	-	
	1%	-	10.9%	-	
	0.25%/	9.4%	10.5%	-	[28]
	0.75%	15.1%	19.3%	-	
	1.25%	13.2%	15.1%	-	
	1.75%	7.6%	4.3%	-	
	0.5%	-	6.7%	-	[122]
	1%	-	10.2%	-	
	1.5%	-	19.1%	-	
	1%	5.56%	14.2%%	9.5%	[123]
	2%	14.81%	/26.5%	23.8%	
	3%	27.78%	/36.4%	33.3%	
	4%	16.67%	/26.4%	23.8%	
	0.5%	-	-	44.4%	[124]
	1%	-	-	66.7%	
	1.2%	-	-	50.0%	
	2%	-	-	5.6%	
UHPC	0.78%	17.3%	8.2%	-	[125]
	2.32%	47.1%	18.5%	-	
	3.88%	20.8%	16.23%	-	

	2%	22%/	14.8%	21.3%	[126]
	3%	34.1%	25%	30%	
	4%	40.2%	29%	34.1%	
	5%	34.1%	24.4%	25.9%	
	6%	31.1%	17%	21.9%	

4.2.5 Durability

Table 4.5 summarizes the main outcome of research investigations on transportation performances of cementitious composites with nano TiO_2. It can be observed that, nano TiO_2 can significantly decrease the transportation of cementitious composites, and the transportation performances are also related to the curing method.

Incorporating nano TiO_2 can improve the corrosion resistance of cementitious composites. From parameters such as electrical resistivity, charge pass and ultrasonic pulse velocity, references [113, 119, 126] indicated cementitious composites with nano TiO_2 exhibit a superior anti-chloride corrosion ability to the composites without nano TiO_2. Besides, nano TiO_2 also can help cementitious composites resisting the sulfate attack [27].

Additionally, Szymanowski and Sadowski [20] and Wang et al. [99] reported the addition of nano TiO_2 can increase abrasion resistance of cementitious composites. The resistance ability also slightly depends on the curing methods [99].

Table 4.5 Transportation performance of cementitious composites with nano TiO_2 at 28 days

Matrix	Nano TiO_2 content	Decrease (relative values)		References
		Water absorption coefficient	Chloride diffusion coefficient	
Ordinary cementitious composites	0.5% (water/ limewater curing)	22.0%/15.4%		[114]
	1% (water/ limewater curing)	35.3%/12.9%		
	1.5% (water/ limewater curing)	46.5%/3.3%		
	2% (water/ limewater curing)	55.9%//4.7%		
UHPC	1% (7.5/17.5/25mm) (90d)	-	5.8%/15.6%/13.0%	[121]
	4% (7.5/17.5/25mm) (90d)	-	40.3%/53.3%/60.9%	
	1% (room temperature/ heating curing)		26.3%/-0%/	[99]
	3% (room temperature/ heating curing)		47.4%/-	

4.2.6 Functional properties

(1) Photocatalysis properties

Nano TiO_2 inherent with photocatalytic properties can release free radicals to react with some harmful gases (NO_X and SO_2) under UV radiation, thereby endowing cementitious composites with pollutant purifying ability [127-129]. He et al. [11] reported iron coating nano TiO_2 is more efficient for degrading vehicle exhausts than the ordinary TiO_2. Chen et al. [130] replaced cement by the hybrid nano TiO_2 of rutile and anatase crystal (30%, 10%, and 3%) to fabricate cementitious composites. They observed that tailoring cementitious composites with nano TiO_2 can effectively eliminate the stormwater pollutants after 48 hours, with enhancement efficiency for purifying NO^{3-}, H_3PO_4, and chemical oxygen demand (COD) of 16%, 25%, and 18%, respectively. What' more, the overall removal rates of the tailored group are averagely 33%, 84%, and 67% after 3 weeks, while those of reference group are only 6%, 26%, and 20%, respectively.

(2) Electromagnetic shielding and absorption properties

Electromagnetic properties of cementitious composites are extremely dependent on the content of nano TiO_2 [131]. Various types of nano TiO_2 can modify the electromagnetic properties of cementitious composites. Li et al. [132] fabricated cement paste with ten types of nano TiO_2 (anatase crystal with diameters of 5/10/15 nm, rutile crystal with diameters of 50/500/1500 nm, hybrid rutile and anatase crystal, SiO_2 coating rutile TiO_2, and Al_2O_3/SiO_2 coating rutile TiO_2). They reported SiO_2 coating rutile TiO_2 and Al_2O_3/SiO_2 coating rutile TiO_2 are efficient for enhancing the electromagnetic wave absorption performance.

(3) Self-sensing properties

The self-sensing properties of cementitious composites with nano TiO_2 under monotonic and cyclic loads have been investigated. Xiao [133] reported that the electrical resistivity of the composites with nano TiO_2 is linearly related to the pressure under monotonic load. Besides, the fatigue damage of composites under cyclic load can be reflected due to the presence of nano TiO_2, which provides feasibility for tailoring cementitious composites with nano materials to sense the fatigue behaviors.

(4) Self-healing properties

Wang et al. [10] employed different curing methods (water curing and air curing) to investigated the self-healing behavior of UHPC with nano TiO_2 through observing compressive and flexural strength. The results showed UHPC with nano TiO_2 cured in water has the largest healing efficiency, which is 34% higher than that of UHPC without nano TiO_2.

4.3 Nano ZrO_2

Nano ZrO_2 is featured by its high strength and toughness, good wear resistance and anti-corrosion performance. The phase transition of nano ZrO_2 usually appears with volume changes under pressure and high temperature, having the potential to restrain the prolongation of cracks in cementitious composites.

4.3.1 Workability

Incorporating nano ZrO_2 into cementitious composites usually makes an impact on workability because much water is absorbed by nano ZrO_2 particles during the fabrication process. The workability is largely dependent on nano ZrO_2 content and curing method. Umarajyadav and Vahini [134] indicated the flowability of concrete with 0.2% of nano ZrO_2 is acceptable, but above this value, it will decrease sharply. Nazari and Riahi [24] observed curing in saturated limewater will accelerate the C-S-H gel formation, which consequently makes fresh composites more viscous.

4.3.2 Durability

Research results in Table 4.6 demonstrate the durability of cementitious composites with nano ZrO_2 largely depends on nano ZrO_2 content and curing method. The reduction of water absorption is more obvious for concrete with nano ZrO_2 cured in saturated limewater as a result of more formation of C–S–H gel.

Table 4.6 Durability of cementitious composites with nano ZrO_2

Matrix type	Curing method	Nano ZrO_2 content	Decrease (relative values)			References
			Abrasion loss	Chloride penetration	Water absorption	
Ordinary cementitious composites	Water/ limewater curing	0.5%	-	-	3.3%/4.2%	[135]
		1.0%	-	-	3.0%/4.0%	
		1.5%	-	-	2.8%/3.8%	
		2.0%	-	-	2.7%/3.7%	
UHPC	Water curing	1%	-	-	49.6%	[136]
		2%	-	-	56.6%	
		3%	-	-	64.0%	
		4%	-	-	70.1%	
		5%	-	-	66.8%	
	Water/ heating curing	1%	33.3%/22.8%	-/47.37%	-	[99]
		3%	11.1%/48.7%	-/5.26%	-	
	Water curing	1.5%	-	32.4%	27.5%	[137]

4.3.3 Mechanical properties

(1) Static mechanical properties

Table 4.7 shows the static strength variation of cementitious composites with nano ZrO_2, confirming that optimal content of nano ZrO_2 can effectively enhance the strengths. Because excessive nano ZrO_2 can aggregate and produce weak areas in matrix, which can account for the damage of strength [138]. It can be also concluded that curing in saturated limewater is superior to curing in water for improving strength. Jiang et al. [139] indicated that cement paste with nano ZrO_2 exhibits the maximum improvement under temperature of 105°C. This may be attributed to the phase transition of nano ZrO_2 with volume changes under pressure and high temperature. Additionally, Wang et al. [22] reported the interfacial strength between aggregate and cement mortar is improved by 35.1% with incorporation of nano ZrO_2 at content of 2%. This is an explanation for the compressive, flexural, and tensile strength improvement.

(2) **Dynamic mechanical properties**

Wang et al. [94] investigated the dynamic mechanical behaviors of UHPC with nano ZrO_2. The dynamic compressive strength, impact toughness and specific energy absorption are improved by 61.3%, 23.2% and 201.3%, respectively. The main benefit of tailoring UHPC with nano ZrO_2 is increasing the ability to absorb dynamic energy. Umarajyadav and Vahini [134] found that the improvement of impact resistance is up to 549.9% when nano ZrO_2 is 0.2%.

4.3.4 Functional properties

(1) Self-healing properties

Wang et al. [10] tailored a type of self-healing UHPC with nano ZrO_2 and measured the compressive and flexural strength loss of specimen. The results showed, recovering efficiency is improved by addition of nano ZrO_2, and the air curing is more effective than the water curing.

Table 4.7 The strength variation of cementitious composites with nano ZrO_2 at 28 days

Matrix type	Curing method	Nano ZrO_2 content	Increase/decrease (relative values)			References
			Flexural strength	Compressive strength	Tensile strength	
Ordinary cementitious composites	Water/saturated limewater curing	0.5%	-	16.0%/28.5%	-	[24, 135]
		1.0%	-	18.5%/36.6%	-	
		1.5%	-	16.6%/42.7%	-	
		2.0%	-	7.6%/52.4%	-	
	Water/saturated lime water curing	0.5%	-	40.5%/45.6%	-	[25]
		1.0%	-	41.4%/47.8%	-	
		1.5%	-	40.7%/51.1%	-	
		2.0%	-	37.7%/53.4%	-	
	Water/saturated limewater curing	0.5%	13.6%/36.6%	-	-	[138, 140]
		1.0%	25%/48.8%	-	-	
		1.5%	20.5%/56.1%	-	-	
		2.0%	6.8%/65.8%	-	-	
UHPC	Water curing	1%	0%	5.7%	-6.3%	[136]
		2%	27.4%	15.2%	18.8%	
		3%	40.5%	33.9%	50%	
		4%	51.7%	49.7%	75%	
		5%	50.0%	46.5%	43.8%	
	Water curing	0.5%	16.4%	16.3%	-5.8%	[141]
		1.0%	22.1%	15.3%	-3.3%	
		3.0%	36.6%	14.5%	34.0%	
		5.0%	26.3%	14.1%	22.3%	

5 Tailoring cementitious composites with 1D nano materials

5.1 CNTs

CNTs, a representative of 1D nano carbon materials, include two main basic forms, SWCNTs and MWCNTs. SWCNTs are formed by a single sheet of graphite shaped in to a hollow cylinder, while MWCNTs are shaped by several layers of graphite. Additionally, CNTs have been modified for well dispersion or multi-function, such as functionalized and surface coating SWCNTs or MWCNTs (such as MWCNTs-COOH, MWCNTs-OH, and Ni coating MWCNTs). Researches about cementitious composites with CNTs focus on their hydration, rheology, workability, mechanical properties, durability and functional properties.

5.1.1 Hydration

Incorporating CNTs can accelerate hydration process of cementitious composites. Li et al. [142] showed that CNTs at the content of 0.1%, 0.3%, and 0.5% can decrease the time to reach maximum temperature by 3.06%, 8.69%, and 4.65%, respectively. Li et al. [143] indicated CNTs will contribute to peak hydration heat and the hydration reaction rate of cement paste at each stage, and enhance the early hydration degree.

5.1.2 Workability

The workability of cementitious composites is decided by various factors, such as type and content of CNTs, content of SP and w/c ratio. Kang et al. [144] reported the decrease of flow diameter caused by CNTs and acid-treated CNTs is 4.2% and 16.7%, respectively. It can be concluded that functionalized MWCNTs will combine or absorb more water than ordinary CNTs, and cause more obvious effect on flowability of cementitious composites accordingly. Thiyagarajan et al. [145] incorporated MWCNTs into self-compacting concrete and found that the flowability is not affected by MWCNTs. If more SP is added to wrap CNTs, CNTs will not absorb too much water. Therefore, the flowability of self-compacting concrete does not show deterioration trend. CNTs may be beneficial to water retaining ability, thus improving integrity and uniformity of cementitious composites.

5.1.3 Rheology

Jiang et al. [82] investigated the effect of w/c ratio, CNTs content, SP content and fabrication process on the rheology of cement paste. The results showed that MWCNTs lead to high yield stress, because the tubular bar makes them more liable to wrap together, and the hollow structure makes them absorb much water. Moreover, the flowability of cement paste is sensitive with w/c ratio at the range from 0.2 to 0.22, and beyond this range, flowability changes slowly. Alatawna et al. [146] investigated the effect of various CNTs on rheology. The results showed that the relative flow of oxidized-MWCNTs is lower than that of ordinary MWCNTs. And the flowability shows a decreasing trend with increase of MWCNT content.

5.1.4 Mechanical properties

(1) Static mechanical properties

Table 5.1 summarizes different trends of strengths of cementitious composites with different CNT content, diameter and length, aspect ratio, functional group, morphology (helical or tubular), and dispersing method. It can be observed, various combinations of these parameters give rise to different strength performances, justified by several arguments. Cui et al. [44] indicated CNTs with larger diameters, longer lengths, and larger aspect ratios can bond with matrix tightly, which is beneficial to load transferring. Moreover, CNTs containing functional groups also appear the superior positive effects on strength of cement paste. In contrast to the above common view, Hawreen et al. [147] indicated that CNTs with lower aspect ratio act better, and functionalized CNTs do not show significant difference from the ordinary types.

(2) Dynamic mechanical properties

Wang et al. [12] studied the dynamic mechanical behavior of cementitious composites with various CNTs (ordinary MWCNTs, MWCNTs-COOH, MWCNTs-OH, Ni coating MWCNTs, and graphitized MWCNTs). CNTs with larger diameters and longer lengths have the most favorable performance on improving dynamic compressive strength. Moreover, incorporating graphitized MWCNTs is effective than Ni coating MWCNTs in terms of dynamic strength behaviors including strength, impact toughness and energy dissipation.

5.1.5 Durability

Researches on the durability of cementitious composites with CNTs are listed in Table 5.2. It can be found that, cement mortar with CNTs presents lower chloride ion penetration, less water absorption, and higher water permeability and gas permeability, and less corrosion. Incorporating CNTs also can increase the prevention of steel rebars in concrete against chloride corrosion. Additionally, CNTs can also increase the freeze-thaw resistance of cementitious composites. Cwirzen [148] found that concrete with 0.3% of functionalized CNTs performs well after 180 freeze-thaw cycles, while the control group damages after 56 cycles.

Table 5.1 The strength performances of cementitious composites with CNTs at 28 days

Matrix type	Type of CNTs	Inner/outer diameter (nm)	Length (nm)	Dosage	Dispersing method	Increase /decrease (relative values)			References
						Flexural strength	Compressive strength	Tensile strength	
Ordinary cementitious composites	MWCNTs	2-5/<8	0.5-2	0.1%	Ultrasonic dispersion + SP	4.6%	7.8%	-	[44]
		5-10/20-30	0.5-2	0.1%		55.2%	37.6%	-	
		2-5/<8	10-30	0.1%		48.3%	23.7%	-	
		5-10/20-30	10-30	0.1%		44.8%	32.7%	-	
	MWCNTs-OH	2-5/<8	0.5-2	0.5%		21.8%	61.9%	-	
		2-5/<8	10-30	0.5%		24.1%	64.6%	-	
	MWCNTs-COOH	2-5/<8	0.5-2	0.5%		54%	43.5%	-	
		2-5/<8	10-30	0.5%		49.4%	52%	-	
	Ni coating MWCNTs	5-10/20-30	10-30	0.5%		64.4%	78.8%	-	
	Helical MWCNTs	--/100-200	1-10	0.5%		28.7%	65.3%	-	
	MWCNTs	9.5	1500	0.2%	Ultrasonic treatment + SP	-	269%	-	[149]
	SWCNT	0.5-3.0	100	0.06%	Dispersing agent: TX10	10.3	20.9%	-	[150]
	MWCNTs	5-100	100	0.12%		-	10.2%	-	
	MWCNTs	5-15/50	10-20	0.1%	Dispersing agent: TNWDIS	9.5%	21.0%	14.1%	[147]
	MWCNTs	5-10/20-40	10-30	0.05		-5.2	-2.8%	-2.0%	
	MWCNTs	5-10/20-40	10-30	0.05%		2.7	9.7%	12.6%	
	MWCNTs-COOH	5-10/20-40	10-30	0.05%		3.7	8.7%	4.1%%	
	MWCNTs-OH	5-10/10-30	10-30	0.05		6.7	6.7%	1.6%	
UHPC	MWCNTs	5-10/20-30	10-30	0.25%	Ultrasonic treatment + SP	3.6%	15.3%	-	[151]
				0.5%		20.2%	8.2%	-	
	MWCNTs-OH	2-5/<8	0.5-2	0.25%		27.2%	30.4%	-	
				0.5%		23.5%	16.8%	-	
	MWCNTs-COOH	2-5/<8	0.5-2	0.25%		25.8%	8.4%	-	
				0.5%		12.2%	8.8%	-	
Note: SP and PAP denote superplasticizer and polyacrylic acid polymer. TNWDIS is a type of polyethylene glycol aromatic imidazole agent.									

Table 5.2 Durability of cementitious composites with CNTs

Dispersing methods	CNT content	Increase/decrease (relative values)					References
		Water absorption	Water permeability	Gas permeability	Rapid chloride penetration	Chloride corrosion rate	
Dispersing agent: Viscocrete ultra 300	0.2%	-23.5%	-	28.6%	-	-	[152]
	0.4%	-35.3%	-	54.7%	-	-	
	0.6%	-35.3%	-	62.2%	-	-	
	0.8%	-41.2%	-	48.5%	-	-	
Dispersing agent: SP	0.01%	-45.3%	-	-	-51.2%	4.2%	[153]
	0.03%	-62.1%	-	-	-65.7%	-55.6%	
	0.05%	-47.4%	-	-	-56.9%	466.5%	
	0.07%	-46.7%	-	-	-49.1%	811.3%	
Dispersing agent: SDBS	0.2%	-50.1%	65.2%	15.6%	-	-	[154]
Dispersing agent: SDS	0.2%	-59.2%	42.8%	20.0%	-	-	
Note: SP, SDBS and SDS denote superplasticizer, sodium dodecylbenzene sulfonate and sodium dodecyl sulfate, respectively.							

5.1.6 Functional properties

(1) Self-sensing property

Tailoring cementitious composites with CNTs can change detect strain, stress and damage through the signals of electrical resistivity. The electrical resistivity values vary with the changing contact between CNTs and matrix. Therefore, the strain-dependent self-sensing property is related to the distribution of CNTs inside matrix and matrix attributes (such as elastic modulus).

Dispersion strategies proposed to disperse CNTs are closely related to the self-sensing properties of cementitious composites. Usually, functionalized CNTs has a stronger bond with matrix than ordinary CNTs, thereby improving the sensitivity and accuracy. The carboxyl-functionalized MWCNTs [155] and oxygen-functionalized CNTs [156] have been certified effective than the non-functionalized CNTs, in terms of sensing ability.

Usually, a 'soft' matrix is more sensitive to the same stress than the hardened. Yoo et al. [157, 158] showed the gauge factor of cement paste with MWCNTs is higher than that of strain gauge and UHPC with MWCNTs. The result certifies the strain-dependent attribute of sensing ability of cementitious composites. The w/b ratio would also affect the sensing ability. Han et al. [159] indicated the electrical resistance with w/b ratio of 0.6 is more sensitive to compressive stress, as compared to those with w/b ratio of 0.45. The possible reason is that high w/b ratio will make cement paste 'softer', meanwhile much water is easier to disperse CNTs during fabrication process.

(2) Electromagnetic properties

Factors including CNT content, functional group, size and morphology (tubular or helical), the sample thickness, and wave frequency, can govern electromagnetic performances of cementitious composites. Zhang et al. [160] reported that cement paste with 0.8% carboxylate MWCNTs achieves the best absorption performance, and the ordinary MWCNTs with larger diameter and longer length realizes the maximum shielding efficiency. Li et al. [14] studied electromagnetic wave shielding and absorption performances of cement paste with HCNTs with chirality. They reported the electromagnetic wave shielding efficiency of cement paste with 7.5% HCNTs is 1.39 times of that of control group, and the minimum reflectivity in 20 mm-thickness cement paste with 4.5% HCNTs is 2.7 times of that of control group.

(3) Damping properties

There are two views about the modification of CNTs to damping properties of cementitious composites. Luo et al. [161] believed the interface slippages between MWCNTs and matrix when bearing vibration lead to the improvement of damping ratio. They reported that the damping ratio of cementitious composites is approximately increased by 60% when 2.0% MWCNTs is added. If the improved damping property are the result of slippages between MWCNTs and matrix, the uniform dispersion will bring more enhancement to cementitious composites. Liew et al. [162] reported CNTs at content of 0.1% dispersed by TNWDIS (an aromatic modified polyethylene glycol ether) can improve the loss factor of cementitious composites by 25.9% at 1Hz. It is also noted that cementitious composites consisting MWCNTs-COOH performs better than plain group in terms of damping behaviors [163]. These investigates are the strong support behind the first view. But Zhang et al. [164] believed the enhancement is mainly attributed to the slippages between the inner-tubes of the MWCNTs rather than the interface slippages between the CNTs and cement matrix.

(4) Thermal properties

CNTs with excellent thermal conductivity widely distribute inside cementitious composites matrix, thus forming heat conduction network. Veedu [165] reported that the thermal conductivity of cementitious composites with CNTs is 1.85 times of that of control group. Hassanzadeh-Aghdam et al. [166] obtained similar conclusion based on the effective medium micromechanics-based method.

(5) Self-healing properties

CNTs can provide more nucleus sites in crack surface, thereby accelerating the self-healing of cementitious composites. Öztürk et al. [107] investigated self-healing efficiency of ECC with CNTs by observing the increase of electrical resistivity. The results showed electrical resistivity of specimen after 7 days and 90 days increases by 27.1% and 39.3%, respectively. Through macroscopic observation after self-healing for 7 days, initial microcracks close to or less than 100 μm shows complete closure at surface of ECC with CNTs.

5.2 CNFs

CNFs are promising for tailoring cementitious composites owing to their high mechanical properties, thermal stability and high electrical conductivity. Moreover, CNFs have a cost advantage compared to other nano carbon materials, thus are more likely to achieve the large-scale application of cementitious composites.

5.2.1 Hydration

Meng and Khayat [167] conducted the isothermal calorimetry test to investigate the effect of s on hydration heat of UHPC. They observed an increased cumulative heat of concrete and an accelerated hydration process with the presence of CNFs, consequently, leading to a faster setting. Yazdani and Mohanam [168] obtained similar conclusions that incorporating CNFs into cement mortar is effective for shortening the setting time by about 7.4%.

5.2.2 Rheology

The results listed in Table 5.3 show the yield stress and plastic viscosity of cement paste containing 0.1% of CNFs are about 3 times of those of plain paste. Furthermore, CNFs higher than 0.5% cause a dramatic increase of yield stress and plastic viscosity.

Table 5.3 Rheology parameters of cement paste with CNFs

Matrix type	CNF content	Yield stress (Pa)	Plastic viscosity (Pa·s)	Reference
Cement paste	0%	6.01	1.20	[82]
	0.1%	18.39	3.96	
	0.5%	292.93	7.55	
	1.0%	Over range	Over range	

5.2.3 Workability

Sbia et al. [169] indicated that flowability of fresh UHPC is not strongly influenced by the addition of CNFs. Aslani et al. [170] believed that a small content of CNFs can improve the packing density of ECC, and thus produce extra water to lubricate cement particle, consequently, contributing to the flowability. But CNFs exceeding a certain limit still cause a deterioration on flowability as too much water is absorbed by CNFs [169, 170].

5.2.4 Mechanical properties

Table 5.4 shows the strength performances of cementitious composites with CNFs at 28 days. It can be concluded that strength performances are extremely content-dependent with CNFs. Gao et al. [21] reported CNFs is more efficient for improving strength and elastic modulus of cement mortar and concrete than those of cement paste. They believed, the modification of CNFs to ITZ overweighs that to hydration products. The characterization of ITZ, where CNFs exist, shows the young's modulus at nanoscale is increased by 36.7% for ITZ in cement mortar, and by 55%-63% in concrete.

Gdoutos et al. [171] reported that the incorporating CNFs into cement mortar can effectively improve the fracture toughness, critical strain energy release rate, and critical crack tip opening displacement.

Table 5.4 The strength performances of cementitious composites with CNFs at 28 days

Matrix type	CNF content	Increase/decrease (relative values)			References
		Compressive strength	Flexural strength	Split tensile strength	
Ordinary cementitious composites	0.1%	-1.8%	-	-	[49]
	0.5%	-1.1%	-	-	
	1%	-28.7%	-	-	
	0.5%	5.1%	-	-	[172]
	1%	-1.5%	-	-	
	2%	-3.4%	-	-	
	0.02%	-	-	-4% (7d)	[173]
	0.2%	-	-	22% (7d)	
	0.1%	-	18.1%	-	[21]
	0.1%	6%	20.1%	-	
	0.1%	10%	-	-	
UHPC	10%	21.4%	-	-	[174]
	15%	12.4%	-	-	
	20%	-3.6%	-	-	
	25%	-2.6%	-	-	
	1%	-44% (7 d)			[175]

5.2.5 Durability

CNFs turn out to be effective for improving chemical attack resistance of cementitious composites. Brown and Sanchez [176] observed the cement paste with CNFs after exposed to sulfate attack for 550 days exhibits less flexural strength loss than the control group. Galao et al. [177] also confirmed that CNFs contribute to the resistance of cementitious composites against carbonation and chloride corrosion.

5.2.6 Functional properties

(1) Self-sensing properties

Cementitious composites with CNFs can detect stress, strain and damage from the electrical resistivity variation with static and dynamic load, loading duration, and environmental variation [172, 174, 178]. Wang et al. [178] reported salt freeze-thaw cycles will lead to the obvious degradation of sensing ability, demonstrating that the surrounding environment should by fully considered for application of cementitious composites with nano materials for structural monitoring. Cementitious composites with CNFs also can monitor fatigue cumulative damage, and present a two-stage trend of electrical resistivity changes, including a small increase in early stage and a sharp increase when the cumulative damage reached to 90% [179].

6 Tailoring cementitious composites with 2D nano materials

6.1 Graphene

Graphene, a representative type of 2D nanocarbon materials, are formed by stacking monolayer graphene. The tensile strength, elastic modulus, and hardness of graphene reach 125 GPa, 1.1 TPa, and 110-121 GPa, respectively. At room temperature, the electronic mobility and resistivity of graphene are 15000 $cm^2/(V \cdot s)$ and 10^{-6} $\Omega \cdot cm$, providing the smallest electronic resistivity ever known for a material. Besides, the thermal conductivity of graphene can be as high as 5300 W/m·K that is much higher than CNTs. These characteristics are beneficial to strength improvement and abrasion performance of cementitious composites. Also, graphene performs excellent electrical and thermal conductivity, which can help the cementitious composites to realize the functional properties.

6.1.1 Hydration

There still exists controversy towards the effect of graphene on hydration of cementitious composites. The first view believes graphene can accelerate the hydration process and improving hydration degree. Table 6.1 provides evidence for this observation [167], confirming that graphene diameter and content affect the hydration process. On the other hand, Jing et al. [180] concluded that graphene cause no effect on the hydration process and degree.

Table 6.1 The effect of graphene on hydration of UHPC

Graphene diameter(nm)	Graphene content	End of induction period (mW/g)	Peak of hydration (mW/g)	Cumulative heat at 72h (J/g)	Reference
25/30	0	0.258/0.258	2.001/2.001	126/126	[167]
	0.05	0.238/0.256	2.056/2.109	128/130	
	0.10	0.222/0.260	2.111/2.235	130/165	
	0.15	0.211/0.266	2.218/2.313	132/141	
	0.20	0.256/0.265	2.337/2.476	142/160	
	0.30	0.301/0.265	2.496/2.561	164/182	

6.1.2 Rheology

Rheology parameters of cement paste in Table 6.2 indicate that incorporation of graphene to cement paste increases the yield stress and plastic viscosity [181].

Table 6.2 The rheology parameters of cement paste without and with graphene

Matrix type		Yield stress (Pa)	Plastic viscosity (Pa·s)	Reference
Ordinary cementitious composites	Control group	6.64	3.10	[181]
	Graphene of 0.1%	8.18	3.27	

6.1.3 Workability

Graphene demonstrates much less flowability deterioration for fresh cement paste among nano carbon materials (GO, CNT, and graphene) [146]. Nevertheless, flowability still shows a decreasing trend with graphene increasing. Chen et al. [182] indicated the slump of concrete with graphene almost are linearly reduced with the increasing graphene content. It is also observed that the mixing process of fresh concrete becomes difficult when graphene at the content of 0.4 % is added and the slump is only 57 mm, compared with 71 mm of the control specimens without graphene.

6.1.4 Mechanical properties

(1) Static mechanical properties

Table 6.3 shows the static strength performances of cementitious composites with graphene as reported for few investigations in the literature. Incorporation of graphene can effectively increase compressive and flexural strengths of cementitious composites. Meng and Khayat [167] investigated the effect of size of graphene on tensile strength of UHPC, showing that 25 nm-graphene can increase the tensile strength and energy absorption capacity by 40% and 190%, respectively. Furthermore, UHPC with 30 nm-graphene presents higher tensile strength about 45% and energy absorption about 150% than the ordinary UHPC.

(2) Dynamic mechanical properties

Wang et al. [183] investigated the dynamic mechanical behaviors of UHPC with graphene under different strain rates (200/s–800/s). Incorporation of graphene improves the dynamic compressive strength, peak strain and ultimate strain and impact toughness of UHPC by 63.9%, 66.0%, 32.7% and 117%, respectively.

6.1.5 Durability

Chen et al. [182] reported, compared to the control group, graphene can reduce the strength loss after freeze-thaw circles, and the reduction is more obvious with the circle increasing. Fan [184] investigated the durability of cementitious composites with graphene under 300 freeze-thaw cycles and 5-month chloride corrosion, respectively, showing that the resistance of cementitious composites with graphene increased to weight loss, as well as spalling.

Table 6.3 The strength performances of cementitious composites with graphene

Matrix type	Graphene content	Increase (relative values)		References
		Compressive strength	Flexural strength	
Ordinary cementitious composites	0.2%	3.87%	-	[185]
	0.4%	28.92%	-	
	0.6%	63.93%	-	
	0.8%	75.19%	-	
	1.0%	65.76%	-	
	0.1%	19.9%	-	[184]
	0.05%	28.3%	-	[186]
	0.05%	-	82%	[187]
	0.1%	-	21%	[181]
	0.2%	154%	-	
UHPC	0.25%	3.5%	3.7%	[14]
	0.5%	21.9%	13.6%	
	0.75%	11.0%	20.7%	

6.1.6 Functional properties

(1) Self-sensing properties

Cementitious composites with graphene can act as sensors to detect strain, stress, damage and environmental changes through electrical resistivity.

In terms of sensing deformation, Sun et al. [188] reported the electrical response is not time-dependent under the same loading rate. While the sensing ability is slightly dependent on dynamic loading rate because a trend toward reduced response is observed when the loading rate increases. Under a considerable compression strain range, cement paste still presents a linear pressure-sensitive behavior when the graphene exceeds 2.4% [189]. Additionally, cementitious composites with graphene also can sense temperature changes [188, 190].

(2) Electromagnetic properties

Incorporating graphene leads to a high electrical conductivity, dielectric loss angle tangent and resonance absorption of cementitious composites, thereby, improving the electromagnetic properties. Sun et al. [188] reported electromagnetic wave shielding effectiveness of cement paste with 10% of graphene is 1.6 times of specimen without functional fillers. Additionally, the highest electromagnetic wave absorption of cement paste with the presence of 10% graphene is nearly 7 times of that of plain group.

(3) Thermal properties

Table 6.4 shows the thermal properties of cementitious composites with graphene, showing that thermal conductivity of cement paste shows an increasing trend with the increasing content of graphene. The enhancement of thermal properties of cementitious composites is attributed to the unique plate morphology of graphene, providing larger area to bond with hydration products than other nanocarbon materials (CNTs, CNFs and NCB) [51]. The improvement in thermal conductivity can reduce the thermal shrinkages and initial cracks inside matrix [184].

Table 6. 4 Thermal properties of cementitious composites with graphene

Matrix type	Graphene content	Thermal conductivity (W/(m·K))	Specific heat (J/(g·K))	References
Ordinary cementitious composites	0%	0.679	-	[190]
	5%	0.43	-	
	10%	0.947	-	
	15%	1.067	-	
	0%	1.1	1.33/	[181]
	1%	1.22	1.25	
	2%	0.3596	-	[51]

(4) Thermoelectric properties

Tailoring cementitious composites with graphene has the feasibility to achieve the energy saving purpose due to the presence of thermoelectric properties. Ghosh et al. [190] incorporated graphene into cement paste to fabricate a thermoelectric construction building material, converting the available ambient heat into electrical energy, thereby leading to a reduction of energy consumption. The experimental results demonstrated that cement paste with graphene exhibited p-type semiconductor behavior, where the charge carriers are contributed by the graphene. Although the thermoelectric efficiency up to 0.015% is small, there is still enormous available free heat energy absorbed by the building surface for conversion.

(5) Damping properties

Ruan et al. [191] incorporated graphene into cement paste to enhance its damping properties. The results showed, compared with the specimen without nano modification, the damping ratio of cementitious composites with introduction of 1% and 5% of graphene increases by 16.22% and 45.73%, respectively.

6.2 Nano BN

Nano BN, similar to graphene, is a type of 2D nano materials with plate structure. Nano BN possesses excellent performance in mechanical strength, thermal conductivity, heat resistance, lubricity, electrical insulation, and chemical stability. The tailoring cementitious composites with nano BN is to develop cementitious composites with outstanding mechanical properties, durability, and functional properties.

6.2.1 Hydration

Zhang et al. [52] reported the early hydration of cementitious composites can be obviously accelerated by incorporation of nano BN at the content of 5% and 10%, but deferred by 15% of nano BN. While at late stage, nano BN can only slightly increase the hydration degree.

6.2.2 Mechanical properties

Experimental results listed in Table 6.5 indicate incorporating nano BN with optimal content can increase mechanical performances of cementitious composites. It can be observed that UHPC containing a smaller size of nano BN has higher strength values than the larger size [52]. Moreover, heat curing is more efficient for improving strength of UHPC containing 10% and 15% of nano BN. While water curing is more preferable for UHPC with nano BN at lower content [52]. Additionally, Wang et al. [22] conducted an experiment exploring the effect of nano BN on ITZ of cementitious composites by testing bond strength of the scale-up aggregate-cement mortar interface under the three-point flexural loading. The interfacial strength is improved by 42.8% with incorporation of nano BN at the content of 0.3%. The modification of nano BN to ITZ can also account for the strength improvement of cementitious composites with nano BN.

Table 6.5 The strength performances of cementitious composites with nano BN

Matrix type	Nano BN content	Decrease/increase (relative values)		References
		Compressive strength	Flexural strength	
Ordinary cementitious composites	1%	89%	-	[6]
UHPC	1% (120 nm)	12.7%	5.1%	[52]
	3% (120 nm)	12.1%	-3.8%	
	5% (120 nm)	-5.1%	-12.2%	
	10% (120 nm)	2.1%	8.4%	
	15% (120 nm)	-6.5%	4.0%	
	1% (500 nm)	-17.2%/	-2.1%	
	3% (500 nm)	-12.3%	-6.1%	
	5% (500 nm)	-18.8%	-3.6%	

6.2.3 Durability

Zhang et al. [52] studied the durability of UHPC with nano BN, depending on different curing methods and nano BN content. The experimental results are shown in Table 6.6. It can be observed that BN can significantly decrease the chloride transportation coefficient.

Table 6.6 Durability of cementitious composites with nano BN

Matrix type	Nano BN content	Abrasion loss (kg/m^2)	Chloride transportation coefficient (10^{-14} m^2/s)	Reference
UHPC	0% (water/heat curing)	0.63/0.49	1.5/1.9	[52]
	5% (water/heat curing)	0.28/0.32	1.2/0.8	
	10% (water/heat curing)	0.4/0.42	0.8/0.02	
	15% (water/heat curing)	0.43/0.52	0.02/0.8	

6.2.4 Functional properties

(1) Oil–water separation properties

Rafiee et al. [6] reported that, through experimental analysis, concrete with nano BN at 5% content can effectively filter the crude oil from water, making the filtered water clear. They also conducted the molecular dynamics simulation to calculate the separation capacity of porous concrete composites with nano BN, based on the oil absorption results of nano BN, showing consistent comparison between simulation and experimental results.

7 Applications of cementitious composites with nano materials

Based on the excellent mechanical performance, durability and smart/multi-functional properties, cementitious composites with nano materials have gained great achievements on field of structure health monitoring (beam, column deformation and damage, structural modal identification and model-based damage detection), traffic flow detection (traffic flow, vehicle type), pollutant purification, and energy saving. Fig. 7.1 shows the typical application of cementitious composites with nano materials, and their specific introductions are stated as follows.

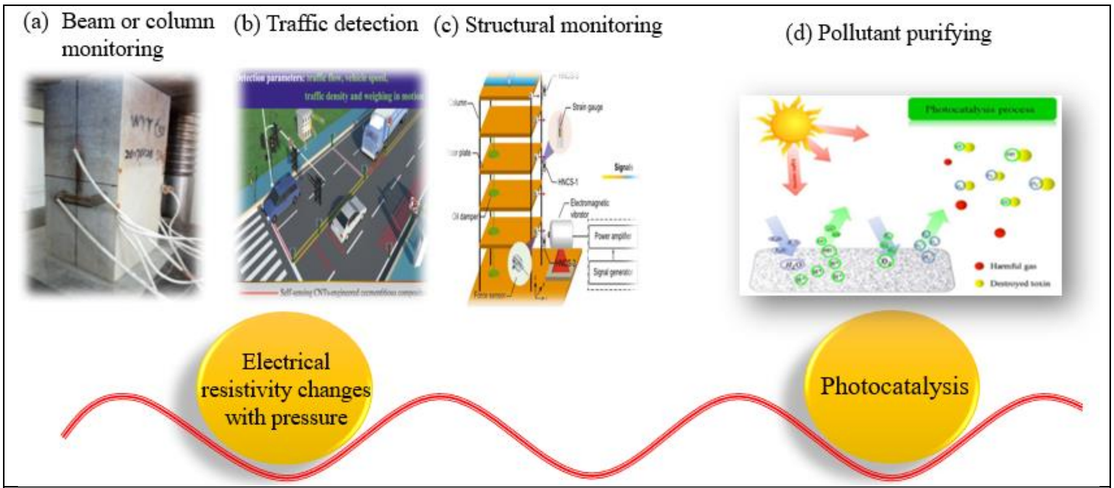


Fig. 7.1 The typical application of cementitious composites with nano materials. (a) column strain monitoring by embedded cement paste with CNT/NCB [192] (b) Traffic detection by embedded cement paste with MWCNTs [193] (c) structural monitoring by attached cement paste with CNT/NCB [194] (d) pollutant purifying through cementitious composites with nano TiO_2 [57]

7.1 Structural health monitoring

The applications of cementitious composites with nano materials have developed from structural component monitoring to the whole structural monitoring. Much researches have been conducted on monitoring structural beams and columns utilizing cementitious composites with nano materials, aiming to achieve self-sensing. The main studies are summarized in Table 7.1. Up to now, there are four methods realizing structural monitor; namely bulk, coating, bonded and embedded methods [13]. Bulk method means the whole beam or column is tailored by cementitious composites to monitor itself. It is well acknowledged that bulk method is of most simplicity in the fabrication process among other methods, and can monitor the whole life of structures but at a great higher cost. On the other hand, coating method is to place fresh cementitious composite layers on the surface of beams or columns to form an integrated structure. Bonded method is mainly achieved by bonding cementitious composite sensors to structures. Embedded method refers to embedding cementitious composites into beams or columns. These latter three methods can solve out the critical problem of high cost of bulk application of cementitious composites with nano materials, but for better monitoring through the whole life of structures, the consistency of stress and strain between the tailored cementitious composites and structures should be improved.

Table 7.1 Application of cementitious composites with nano materials on structural health monitoring

Methods	Nano materials	Parameter to monitor	References
Bulk method	CNFs	Damage of columns under reversed cyclic loading	[195]

	MWCNTs	Damage of beams with using resistor mesh mode	[196]
Coating method	CNFs	Strain of beam under four-point bending	[48]
Bonded method	CNFs	Strain of beam under four-point bending	[48]
	CNFs	Strain and damage of cylinder column under compression	[197]
Embedded method	Self-assembled CNT/NCB	Stress and strain of column under compression	[192]
	CNFs	Strain of beam under four-point bending	[48]
	MWCNTs	Crack propagation and damage accumulation of beam under three-point bending	[198]
	MWCNTs	Static and dynamic strain of full-scale reinforced concrete beam.	[199]
	SWCNTs	Crack propagation and damage accumulation under monotonic and cyclic bending	[200]

After verifying the feasibility of monitoring beams or columns utilizing cementitious composites with nano materials, the materials have been used to whole structure monitoring. Ding et al. [194] developed a L-shaped sensor utilizing cementitious composites with CNT/NCB for structural modal identification and damage detection of a five-story building model through attached method. The sensor recorded satisfactory mechanical properties and pressure-sensitive reproducibility under dynamic loading, and its results of the identified modal frequency and their changes of damage are almost the same as the results obtained from strain gauges and accelerometer.

7.2 Traffic detection

The cementitious composites with nano materials can help for traffic management on the basis of their sensing ability. Han et al. [193] conducted a road test of pavement system for traffic detection utilizing sensor of cementitious composites with CNTs. The strip sensor is embedded into pavement to judge vehicle type with assistance of five-axle semi-trailer truck and a vane, and to monitor the traffic flow. The results showed that this method has a high detection precision to monitor traffic flow rates and traffic density, vehicular speed, and vehicle classification. And the method is of great simplicity of installation and convenience of maintenance. Monteiro et al. [201] reported cementitious composites integrating NCB can also provide accurate detection for traffic flow, vehicular speed, and weight in motion.

7.3 Pollutants purifying

The utilization of cementitious composites with nano TiO_2 has been certified to be efficient for pollutant purifying. He et al. [11] utilized the tailored composites to purify the vehicle exhaust. They reported iron coating nano TiO_2 particles is more efficient than the ordinary TiO_2. Chen et al. [130] replaced cement by hybrid nano TiO_2 of rutile and anatase crystal (30%, 10%, and 3%) to design a novel fixed-bed reactor pond to purify the rainwater. The results showed, cementitious composites with nano TiO_2 is effective to the stormwater pollutant diminution, with efficiency enhancement of 16%, 25%, and 18% for NO_3^-, H_3PO_4, and chemical oxygen demand (COD), respectively. Furthermore, the overall removal rates of tailored group after 3 weeks are averagely 33%, 84%, and 67%, while those of reference group are 6%, 26%, and 20%, respectively.

7.4 Other applications

Ghosh et al. [190] incorporated graphene into cement paste to fabricate a thermoelectric construction building material, which can convert the available ambient heat absorbed from surroundings into electrical energy, thereby leading to a reduction of energy consumption. Although the thermoelectric efficiency up to 0.015% is small, there is still enormous available free heat energy absorbed by the building surface for conversion. Shukla et al. [202] tailoring cementitious composites with MWCNTs to detect smoke by observing the electrical conductivity change with smoke concentration. The responsivity in the range of 26%-46% is obtained under smoke environment with the presence of CNTs.

8 Prospects of cementitious composites with nano materials

Incorporating nano materials brings great changes in tailoring nano/micro/macro scale structures of bulk cement paste phase and ITZ in the cementitious composites through the nano-core effect, thus making cementitious composites stronger, more durable, and smart/multifunctional (e.g., self-sensing, self-healing, and pollutant purifying). Due to the nano modification to cement paste in combination with the supplement of nano scale continuity for multi-scale raw materials of cementitious composites, nano materials gradually show the potential to become the indispensable seventh component of cementitious composites besides cement, water, fine aggregates, coarse aggregates, chemical additives and mineral additives. Tailoring cementitious composites with nano materials provides a promising approach to develop the new generation of cementitious composites (e.g., ultra-high performance, smart/multifunctional and resilient) and sustainable infrastructures. For example, tailoring cementitious composites with nano materials can significantly improve dynamic mechanical properties.

Up to now, cementitious composites with nano materials have gained great achievements on application of structural health monitoring (structural deformation and damage, structural modal identification and model-based damage detection), traffic detection (traffic flow, vehicle type), and pollutant purification. Tailoring cementitious composites with nano materials has the potential to improve the bond between new and old concrete, due to the nano-core effect in bulk cement paste phase and ITZ. Therefore, cementitious composites with nano materials can become the restoring materials to repair or reinforce buildings after earthquake or impact damages. Additionally, the excellent strength performances, large deformation and toughness under dynamic impact demonstrate the prospective future for cementitious composites with nano materials applied in impact-resisting infrastructures, such as bridge pier and underwater foundation.

Although tailoring cementitious composites with nano materials has gained great achievements, it still confronts plenty of challenges in the process to achieve the large-scale applications. Further work may focus on: (1) Comprehensive understanding for the modified mechanisms and effects of nano materials to cementitious composites; (2) Methods with simplicity, economy and efficiency for large-scale dispersion of nano materials, and fabrication of cementitious composites with nano materials; (3) Development for theoretical models to predict behaviors of composites; (4) Exploration of the optimal amount of nano materials added to cementitious composites to balance properties (mechanical properties, durability and functional properties), environment, and economy; (5) Large scale-model research to achieve further engineering applications, such as smart/multifunctional constructions and resilient infrastructures.

Tailoring cementitious composites with nano materials can enhance safety of structures, prolong the life span, reduce cement and energy consumption, and improve the living comfort. It is expected and believed, tailoring cementitious composites with nano materials will bring a deep revolution to cementitious composites (e.g., ultra-high performance, smart/multifunctional and resilient) and sustainable infrastructures.

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References

[1] G. Constantinides, F.J. Ulm. The effect of two types of C-S-H on the elasticity of cement-based materials: Results from nanoindentation and micromechanical modeling. Cement and Concrete Research. 2004, 34(1):67-80.
[2] F.A. Chyad. The effects of metastable zirconia on the properties of ordinary portland cement. Dissertation for the Doctoral Degree. University of Bradford, England, 1989.
[3] L.Q. Zhang, S.Q. Ding, L.W. Li, S.F. Dong, X. Yu, B.G. Han, J.P. Ou. Effect of characteristics of assembly unit of CNT/NCB composite fillers on properties of smart cement-based materials. Composites Part A-Applied Science and Manufacturing. 2018, 109:303-320.
[4] M. Zhang. Life-cycle performance of nano-pavement concrete. Dissertation for the Doctoral Degree. Harbin Institute of Technology, China, 2007.
[5] S. Huang. Multifunctional graphite nanoplatelets (GNP) reinforced cementitious composites. Dissertation for the Master Degree. National University of Singapore, Singapore, 2012.
[6] M.A. Rafiee, T.N. Narayanan, D.P. Hashim, N. Sakhavand, R. Shahsavari, R. Vajtai, P.M. Ajayan. Hexagonal boron nitride and graphite oxide reinforced multifunctional porous cement composites. Advanced Functional Materials. 2013, 23(45):5624-5630.
[7] Q. Ye. Research and development of nano cement-based composites. Gypsum Cement Build. 2001, 25(11):4-6.
[8] J.M. Makar, J.C. Margeson, J. Luh. Carbon nanotube/cement composites-early results and potential applications. In: 3rd International Conference on Construction Materials Performance, Innovations and Structural Implications, 2005.
[9] L.Q. Zhang, N. Ma, Y.Y. Wang, B.G. Han, X. Cui, X. Yu. Study on the reinforcing mechanisms of nano silica to cement-based materials with theoretical calculation and experimental evidence. Journal of Composite Materials. 2016, 50(29):4135-4146.
[10] J.L. Wang, S.Q. Ding, B.G. Han, Y.Q. Ni, J.P. Ou. Self-healing properties of reactive powder concrete with nanofillers. Smart Materials and Structures. 2018, 27(11):115033.
[11] R. He, X. Huang, J.S. Zhang, Y. Geng, H.D. Guo. Preparation and evaluation of exhaust-purifying cement concrete employing titanium dioxide. Materials. 2019, 12(13):2182.
[12] J.L. Wang, S.F. Dong, A. Ashour, X.Y. Wang, B.G. Han. Dynamic mechanical properties of cementitious composites with carbon nanotubes. Materials Today Communications. 2020, 22:100722.
[13] S.Q. Ding, S.F. Dong, A. Ashour, B.G. Han. Development of sensing concrete: Principles, properties and its applications. Journal of Applied Physics. 2019, 126(24): 241101.
[14] L.W. Li, S.F. Dong, X.F. Dong, X. Yu, B.G. Han. Electromagnetic wave shielding/absorption performances of cementitious composites incorporating carbon nanotube metamaterial with helical chirality. Journal of Composite Materials. 2020: 002199832092313.
[15] B.G. Han, S.Q. Ding, J.L. Wang, J.P. Ou. Nano-Engineered Cementitious Composites. Chapter: Current Progress of Nano-Engineered Cementitious Composites. Dalian, China, 2019.

[16] Q. Ye, Z.N. Zhang, D.Y. Kong, R.H. Chen. Influence of nano-SiO_2 addition on properties of hardened cement paste as compared with silica fume. Construction and Building Materials. 2007, 21(3):539-545.
[17] B.G. Han, S.W. Sun, S.Q. Ding, L.Q. Zhang, X. Yu, J.P. Ou. Review of nanocarbon-engineered multifunctional cementitious composites. Composites Part A-Applied Science and Manufacturing. 2015, 70:69-81.
[18] X.Y. Wang, Q.F. Zheng, S.F. Dong, A. Ashour, B.G. Han. Interfacial characteristics of nano-engineered concrete composites. Construction and Building Materials. 2020, 259: 119803.
[19] J. Szymanowski, Ł. Sadowski. Functional and adhesive properties of cement-based overlays modified with amorphous silica nanosphere. The Journal of Adhesion. 2020, 96:207-228.
[20] J. Szymanowski, Ł. Sadowski. The influence of the addition of tetragonal crystalline titanium oxide nanoparticles on the adhesive and functional properties of layered cementitious composites. Composite Structure. 2020, 233:11636.
[21] Y. Gao, X.Y. Zhu, D.J. Corr, M.S. Konstagdoutos, S.P. Shah. Characterization of the interfacial transition zone of CNF-Reinforced cementitious composites. Cement and Concrete Composites. 2019, 99:130-139.
[22] X.Y. Wang, S.F. Dong, A. Ashour, W. Zhang, B.G. Han. Effect and mechanisms of nanomaterials on interface between aggregates and cement mortars. Construction and Building Materials. 2019, 240:117949.
[23] L.Q. Zhang. Nano-modification mechanisms and electrostatic self-assembly nano filler modification of cement-based materials. Dissertation for the Doctor degree. Dalian University of Technology.
[24] A. Nazari, S. Riahi. The effects of ZrO_2 nanoparticles on strength assessments and water permeability of concrete in different curing media. Journal of Experimental Nanoscience. 2013, 8(4):413-433.
[25] M.H. Rafieipour, A. Nazari, M.A. Mohandesi, G. Khalaj. Improvement compressive strength of cementitious composites in different curing media by incorporating ZrO_2 nanoparticles. Materials Research. 2012, 15(2):177-184.
[26] B.G. Ma, H.N. Li, J.P. Mei, X.G. Li, F.J. Chen. Effects of nano-TiO_2 on the toughness and durability of cement-based material. Advances in Materials Science and Engineering. 2015, 2015: 583106.
[27] N. Salemi, K. Behfarnia, S.A. Zaree. Effect of nanoparticles on frost durability of concrete. Asian Journal of Civil Engineering. 2014, 15(3):411-420.
[28] M.M. Salman, K.M. Eweed, A.M. Hameed. Influence of partial replacement TiO_2 nanoparticles on the compressive and flexural strength of ordinary cement mortar. Journal for Engineering Sciences, 2016, 19(2): 265-270.
[29] L.C. Feng, C.W. Gong, Y.P. Wu, D.C. Feng, N. Xie. The study on mechanical properties and microstructure of cement paste with nano-TiO_2. Advanced Materials Research. 2013, 629:477-481.
[30] L.Q. Zhang, L.W. Li, Y.L. Wang, X. Yu, B.G. Han. Multifunctional cement-based materials modified with electrostatic self-assembled CNT/TiO_2 composite filler. Construction and Building Materials. 2020, 238:117787.
[31] B.G. Han, Z. Li, L.Q. Zhang, S.Z. Zeng, X. Yu, B.G. Han. J.P. Ou. Reactive powder concrete reinforced with nano SiO_2-coated TiO_2. Construction and Building Materials. 2017, 148:104-112.
[32] Z. Li, S.F. Dong, X.Y. Wang, X. Yu, B.G. Han. Electromagnetic wave-absorbing property and mechanism of cementitious composites with different types of nano titanium dioxide. Journal of Materials in Civil Engineering. 2020, 32(5):04020073.

[33] S. Jiang. Properties and mechanisms of cement-based composites with new types of nano-fillers. Dissertation for the Master Degree. Dalian University of Technology, China, 2018.
[34] M. Oltulu, R. Şahin. Effect of nano-SiO_2, nano-Al_2O_3 and nano-Fe_2O_3 powders on compressive strengths and capillary water absorption of cement mortar containing fly ash: A comparative study. Energy and Buildings. 2013, 58:292-301.
[35] B.W. Jo, C.H. Kim, G.H. Tae, J.B. Park. Characteristics of cement mortar with nano-SiO_2 particles. Construction and Building Materials. 2007, 21(6):1351-1355.
[36] L. Senff, J.A. Labrincha, V.M. Ferreira, D. Hotza, W.L. Repette. Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. Construction and Building Materials. 2009, 23(7):2487-2491.
[37] L.A. Guefrech, P. Mounanga, A. Khelidj. Experimental study of the effect of addition of nano-silica on the behavior of cement mortars mounir. Procedia Engineering. 2011, 10:900-905.
[38] Y. Gu, Z.H. Wei, Q.P. Ran, X. Shu, K. Lv, J.P. Liu. Characterizing cement paste containing SRA modified nano SiO_2 and evaluating its strength development and shrinkage behavior. Cement and Concrete Composites. 2017, 75:30-37.
[39] A. Hanif, P. Parthasarathy, H.Y. Ma, T.Y. Fan, Z.J. Li. Properties improvement of fly ash cenosphere modified cement pastes using nano silica. Cement and Concrete Composites. 2017, 81:35-48.
[40] Y.M. Cai, P.K. Hou, X. Cheng, P. Du, Z.M. Ye. The effects of nano SiO_2 on the properties of fresh and hardened cement-based materials through its dispersion with silica fume. Construction and Building Materials. 2017, 148:770-780.
[41] J. Ouyang, B.G. Han, G.Z. Chen, L.Z. Zhao, J.P. Ou. A viscosity prediction model for cement paste with nano-SiO_2 particles. Construction and Building Materials. 2018, 185:293-301.
[42] S.W. Sun, X. Yu, B.G. Han, J.P. Ou. In situ growth of carbon nanotubes/carbon nanofibers on cement/mineral admixture particles: A review. Construction and Building Materials. 2013, 49:835-840.
[43] A.G. Nasibulin, T. Koltsova, L.I. Nasibulina, I.V. Anoshkin, A. Semencha, O.V. Tolochko, E.I. Kauppinen. A novel approach to composite preparation by direct synthesis of carbon nanomaterial on matrix or filler particles. Acta Materialia. 2013, 61(6):1862-1871.
[44] X. Cui, B.G. Han, Q.F. Zheng, X. Yu, S.F. Dong, L.Q. Zhang, J.P. Ou. Mechanical properties and reinforcing mechanisms of cementitious composites with different types of multiwalled carbon nanotubes. Composites Part A-Applied Science and Manufacturing. 2017, 103:131-147.
[45] X. Yu, E. Kwon. A carbon nanotube/cement composite with piezoresistive properties. Smart Materials and Structures. 2009, 18(5):055010.
[46] J.L. Luo, Z.D. Duan, H. Li. The influence of surfactants on the processing of multi-walled carbon nanotubes in reinforced cement matrix composites. Physica Status Solidi (A). 2009, 206(12):2783-2790.
[47] K.H. Cwirzen, V. Penttala, A. Cwirzen. Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites. Advances in Cement Research. 2008, 20(2):65-73.
[48] F.J. Baeza, O. Galao, E. Zornoza, P. Garcés. Multifunctional Cement Composites Strain and Damage Sensors Applied on Reinforced Concrete (RC) Structural Elements. Materials. 2013, 6(3):841-855.
[49] S. Jiang, D.C. Zhou, L.Q. Zhang, J. Ouyang, X. Yu, X. Cui, B.G. Han. Comparison of compressive strength and electrical resistivity of cementitious composites with

different nano- and micro-fillers. Archives of Civil and Mechanical Engineering. 2018, 18(1):60-68.
[50] M. Jin, L.H. Jiang, M.T. Lu, S.Y. Bai. Monitoring chloride ion penetration in concrete structure based on the conductivity of graphene/cement composite. Construction and Building Materials. 2017, 136:394-404.
[51] A. D'Alessandro, A.L. Pisello, S. Sambuco, F. Ubertini, F. Asdrubali, A.L. Materazzi, F. Cotana. Self-sensing and thermal energy experimental characterization of multifunctional cement-matrix composites with carbon nano-inclusions. Proceedings of SPIE. 2016, 9800:98000Z.
[52] W. Zhang, B.G. Han, X. Yu, Y.F. Ruan, J.P. Ou. Nano boron nitride modified reactive powder concrete. Construction and Building Materials. 2018, 179:186-197.
[53] G. Bastos, F.P. Barbeito, F.P. Cambeiro, J. Armesto. Nano-inclusions applied in cement-matrix composites: A Review. Materials. 2016, 9(12):1015.
[54] B. Zou, S.J. Chen, A.H. Korayem, F. Collins, C.M. Wang, W.H. Duan. Effect of ultrasonication energy on engineering properties of carbon nanotube reinforced cement pastes. Carbon. 2015, 85:212-220.
[55] Y. Gu, Q.P. Ran, X. Shu, C. Yu, H.L. Chang, J.P. Liu. Synthesis of nanoSiO_2@PCE core-shell nanoparticles and its effect on cement hydration at early age. Construction and Building Materials. 2016, 114:673-680.
[56] P. Feng, H.L. Chang, X. Liu, S.X. Ye, Q.P. Ran. The significance of dispersion of nano-SiO_2 on early age hydration of cement pastes. Materials and Design. 2020, 186:108320.
[57] Z. Li, S.Q. Ding, X. Yu, B.G. Han, J.P. Ou. Multifunctional cementitious composites modified with nano titanium dioxide: A review. Composites Part A-Applied Science and Manufacturing. 2018, 111:115-137.
[58] Y.F. Ruan, B.G. Han, X. Yu, Z. Li, J.L. Wang, S.F. Dong, J.P. Ou. Mechanical behaviors of nano-zirconia reinforced reactive powder concrete under compression and flexure. Construction and Building Materials. 2018, 162:663-673.
[59] Q.F. Zheng, B.G. Han, X. Cui, X. Yu, J.P. Ou. Graphene-engineered cementitious composites. Nanomaterials and Nanotechnology. 2016, 7:184798041774230.
[60] H. Heinz, C. Pramanik, O. Heinz, Y. Ding, R.K. Mishra, D. Marchon. Nanoparticle decoration with surfactants: Molecular interactions, assembly, and applications. Surface Science Reports. 2017, 72(1):1-58.
[61] T. Saito, K. Matsushige, K. Tanaka. Chemical treatment and modification of multi-walled carbon nanotubes. Physica B-Condensed Matter. 2002, 323(1):280-283.
[62] D.B. Mawhinney, V. Naumenko, A. Kuznetsova, J.T. Yates, J. Liu, R.E. Smalle. Infrared spectral evidence for the etching of carbon nanotubes: ozone oxidation at 298 K. Journal of the American Chemical Society. 2000, 122(10):2383-2384.
[63] S.C. Wang, K.S. Chang, C.J. Yuan. Enhancement of electrochemical properties of screen-printed carbon electrodes by oxygen plasma treatment. Electrochimica Acta. 2009, 54(21):4937-4943.
[64] M. Azeem, M. A. Saleem. Role of electrostatic potential energy in carbon nanotube augmented cement paste matrix. Construction and Building Materials. 2020, 239:117875.
[65] S. Musso, J.M. Tulliani, G.A. Ferro, A. Tagliaferro. Influence of carbon nanotubes structure on the mechanical behavior of cement composites. Composites Science and Technology, 2009, 69(1112):1985-1990.
[66] T. Qureshi, D.K. Panesar. Impact of graphene oxide and highly reduced graphene oxide on cement based composites. Construction and Building Materials. 2019, 206:71-83.

[67] A.A. Khan, E.H. Mirza, B.A. Mohamed, M. A. El-Sharawy, M.H. Al-Asmari, A. A. Al-Khureif. Static and dynamic mechanical properties of graphene oxide-based bone cementing agents. Journal of Composite Materials. 2019, 53(16):2297-2304.
[68] C. Warakulwit, S. Yadnum, V. Paluka, O. Phuakkong, M. Niamlaem, K. Pongpaisanseree, S. Sinthupinyo, J. Limtrakul. Controlled production of carbon nanofibers over cement clinker via oxidative dehydrogenation of acetylene by intrinsic carbon dioxide. Chemical Engineering Journal. 2015, 278:150-158.
[69] S. Gupta, J. Gonzalez, K.J. Loh. Self-sensing concrete enabled by nano-engineered cement-aggregate interfaces. Structural Health Monitoring-an International Journal. 2017, 16(3):1475921716643867.
[70] E. Bekyarova, E.T. Thostenson, A. Yu, B.H. Kim, R.C. Haddon. Multiscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites. Langmuir. 2007, 23(7):3970-3974.
[71] L.Q. Zhang, B.G. Han, J. Ouyang, X. Yu, S.W. Sun, J.P. Ou. Multifunctionality of cement based composite with electrostatic self-assembled CNT/NCB composite filler. Archives of Civil and Mechanical Engineering. 2017, 17(2):354-364.
[72] L.Q. Zhang, Q.F. Zheng, X.F. Dong, X. Yu, Y.L. Wang, B.G. Han. Tailoring sensing properties of smart cementitious composites based on excluded volume theory and electrostatic self-assembly. Construction and Building Materials. 2020, 256:119452.
[73] X.J. Xia, J.T. Guo, Y.K. Feng, D. Chen, Y.J. Yu, J.Z. Jin, S.Q. Liu. Hydrophobic associated polymer "grafted onto" nanosilica as a multi-functional fluid loss agent for oil well cement under ultrahigh temperature. RSC Advances. 2016, 6(94):91728-91740.
[74] Y.M. Li, X.Y. Guo, J.L. Yang, M. Li. Preparation of nano-SiO_2/carbon fiber-reinforced concrete and its influence on the performance of oil well cement. International Journal of Polymer Science. 2019, 2019:1-9.
[75] H.Z. Cui, Z.Y. Jin, D.P. Zheng, W.C. Tang, Y.B. Li, Y.C. Yun, T.Y. Lo, F. Xi. Effect of carbon fibers grafted with carbon nanotubes on mechanical properties of cement-based composites. Construction and Building Materials. 2018, 181:713-720.
[76] S. He, J.S. Qiu, J.X. Li, E.H. Yang. Strain hardening ultra-high performance concrete (SHUHPC) incorporating CNF-coated polyethylene fibers. Cement and Concrete Research. 2017, 98:50-60.
[77] Y.M. Cai, P.K. Hou, X. Cheng, P. Du, Z.M. Ye. The effects of nano SiO_2 on the properties of fresh and hardened cement-based materials through its dispersion with silica fume. Construction and Building Materials. 2017, 148:770-780.
[78] C. Chen, W. Wu, W.Z. Xu, P.A. Charpentier. The effect of silica thickness on nano TiO_2 particle for functional nanocomposites. Nanotechnology. 2017, 28(11):115709.
[79] M.H, Zhang, J. Islam. Use of nano-silica to reduce setting time and increase early strength of concretes with high volumes of fly ash or slag. Construction and Building Materials. 2012, 29:573-580.
[80] M. Oltulu, R. Şahin. Pore structure analysis of hardened cement mortars containing silica fume and different nano-powders. Construction and Building Materials. 2014, 53:658-664.
[81] P.K. Hou, S. Kawashima, D.Y. Kong, D.J. Corr, J.S. Qian, S.P. Shah. Modification effects of colloidal nano SiO_2 on cement hydration and its gel property. Composites Part B-Engineering. 2013, 45(1):440-448.
[82] S. Jiang, B.H. Shan, J. Ouyang, W. Zhang, X. Yu, P.G. Li, B.G. Han. Rheological properties of cementitious composites with nano/fiber fillers. Construction and Building Materials. 2018, 158:786-800.
[83] P. Hosseini, A. Booshehrian, A. Madari. Developing concrete recycling strategies

by utilization of nano-SiO_2 particles. Waste and Biomass Valorization. 2011, 2(3):347-355.
[84] A.N. Givi, S.A. Rashid, F.N. Aziz. The effects of lime solution on the properties of SiO_2 nanoparticles binary blended concrete. Composites Part B-Engineering. 2011, 42(3):562-569.
[85] E. Ghafari, H. Costa, E. Júlio, A. Portugal, L. Durães. The effect of nanosilica addition on flowability, strength and transport properties of ultra high performance concrete. Materials and Design. 2014, 59:1-9.
[86] M. Collepardi, J.J.O. Olagot, R. Troli, U. Skarp, R.K. Dhir, P.C. Hewlett, L.J. Csetenyi. Influence of amorphous colloidal silica on the properties of self-compacting concretes. In: Proceedings of the International Conference in Concrete Constructions, 2015.
[87] J.Y. Shih, T.P. Chang, T.C. Hsiao. Effect of nanosilica on characterization of portland cement composite. Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing. 2006, 424(1):266-274.
[88] H. Xiao. Study on the processing technology and multifunctional properties of smart concrete with super fine particles. Dissertation for the Master Degree. Harbin Institute of Technology, China, 2002.
[89] G.Y. Li. Properties of high-volume fly ash concrete incorporating nano-SiO_2. Cement and Concrete Research. 2004, 34(6):1043-1049.
[90] A.N. Givi, S.A. Rashid, F.N.A.A. Aziz, M.A.M. Salleh. Experimental investigation of the size effects of SiO_2 nano-particles on the mechanical properties of binary blended concrete. Composites Part B-Engineering. 2010, 41(8):673-677.
[91] A. Najigivi, A. Khaloo, A.Irajizad, S.A. Rashid. Investigating the effects of using different types of SiO_2 nanoparticles on the mechanical properties of binary blended concrete. Composites Part B-Engineering. 2013, 54:52-58.
[92] E. Ghafari, H. Costa, E. Julio, A. Portugal, L. Duraes. The effect of nanosilica addition on flowability, strength and transport properties of ultra high performance concrete. Materials and Design. 2014, 59:1-9.
[93] Taherkhani H, Tajdini M. Comparing the effects of nano-silica and hydrated lime on the properties of asphalt concrete. Construction and Building Materials. 2019, 218:308-315.
[94] J.L. Wang, S.F. Dong, D.N. Wang, X. Yu, B.G. Han, J.P. Ou. Enhanced impact properties of concrete modified with nanofiller inclusions. Journal of Materials in Civil Engineering. 2019, 31(5):04019030.
[95] Q.H. Li, X. Zhao, S.L. Xu. Impact compression properties of nano-SiO_2 modified ultra high toughness cementitious composites using a split hopkinson pressure bar. Engineering Mechanics. 2017, 134(2):85-92.
[96]B.M. Wang, L.J. Wang, F.C. Lai. Freezing resistance of HPC with nano-SiO_2. Journal of Wuhan University of Technology-materials Science Edition. 2008, 23(1):85-88.
[97] K. Behfarnia, N. Salemi. The effects of nano-silica and nano-alumina on frost resistance of normal concrete. Construction and Building Materials. 2013, 48:580-584.
[98] G. Quercia, P.R. Spiesz, G. Husken, H.J.H. Brouwers. Effects of amorphous nano-silica additions on mechanical and durability performance of SCC mixtures. In: International Congress of Durability of Concrete, 2012.
[99] D.N. Wang, W. Zhang, Y.F. Ruan, X. Yu, B.G. Han. Enhancements and mechanisms of nanoparticles on wear resistance and chloride penetration resistance of reactive powder concrete. Construction and Building Materials. 2018, 189:487-497.
[100] A. Nazari, S. Riahi. Abrasion resistance of concrete containing SiO_2 and Al_2O_3

nanoparticles in different curing media. Energy and Buildings. 2011, 43(10):2939-2946.
[101] S. Riahi, A. Nazari. Compressive strength and abrasion resistance of concrete containing SiO_2 and CuO nanoparticles in different curing media. Science China-Technological Sciences. 2011, 54(9):2349-2357.
[102] R.K. Ibrahim, R. Hamid, M.R. Taha. Fire resistance of high-volume fly ash mortars with nanosilica addition. Construction and Building Materials. 2012, 36:779-786.
[103] A.M. Said, M.S. Zeidan, M.T. Bassuoni, Y. Tian. Properties of concrete incorporating nano-silica. Construction and Building Materials. 2012, 36:838-844.
[104] M. Zhang, J. Islam. Use of nano-silica to reduce setting time and increase early strength of concretes with high volumes of fly ash or slag. Construction and Building Materials. 2012, 29:573-580.
[105] A. Heidari, D. Tavakoli. A study of the mechanical properties of ground ceramic powder concrete incorporating nano-SiO_2 particles. Construction and Building Materials. 2013, 38:255-264.
[106] X.D. He, X.M. Shi. Chloride Permeability and microstructure of portland cement mortars incorporating nanomaterials. Transportation Research Record. 2008, 2070:13-21.
[107] O. Öztürk, G. Yıldırım, Ü.S. Keskin, H. Siad, M. Şahmara. Nano-tailored multi-functional cementitious composites. Composites Part B-Engineering. 2020, 182:107607.
[108] C. Vipulanandan, A. Mohammed. Smart cement compressive piezoresistive, stress-strain, and strength behavior with nanosilica modification. Journal of Testing and Evaluation. 2019, 47(2):20170105.
[109] A.K.A.A. Zaidi, B. Demirel, C.D. Atis. Effect of different storage methods on thermal and mechanical properties of mortar containing aerogel, fly ash and nano-silica. Construction and Building Materials. 2019, 199:501-507.
[110] S.A.E Aleem, M. Heikal, W.M. Morsi. Hydration characteristic, thermal expansion and microstructure of cement containing nano-silica. Construction and Building Materials. 2014, 59:151-160.
[111] M. Jalal, E. Mansouri, M. Sharifipour, A.R. Pouladkhan. Mechanical, rheological, durability and microstructural properties of high performance self-compacting concrete containing SiO_2 micro and nanoparticles. Materials and Design. 2012, 34:389-400.
[112] J. Chen, S.C. Kou, C.S. Poon. Hydration and properties of nano-TiO_2 blended cement composites. Cement and Concrete Composites. 2012, 34(5):642-649.
[113] E. Mohseni, F. Naseri, R. Amjadi, M.M. Khotbehsara, M.M. Ranjbar. Microstructure and durability properties of cement mortars containing nano-TiO_2 and rice husk ash. Construction and Building Materials. 2016, 114:656-664.
[114] F. Soleymani. Assessments of the effects of limewater on water permeability of TiO_2 nanoparticles binary blended palm oil clinker aggregate-based concrete. Journal of American Science. 2012, 8(5):698-702.
[115] R. Zhang, X. Cheng, P.K. Hou, Z.M. Ye. Influences of nano-TiO_2 on the properties of cement-based materials: hydration and drying shrinkage. Construction and Building Materials. 2015, 81:35-41.
[116] A.R. Jayapalan, B.Y. Lee, K.E. Kurtis. Effect of nano-sized titanium dioxide on early age hydration of Portland cement. Nanotechnology in Construction. 2009, 3:267-273.
[117] A. Folli, I.P. Jakobsen, A.M. Shepherd, D.E. Macphee. Engineering photocatalytic cements: understanding TiO_2 surface chemistry to control and modulate photocatalytic performances. Journal of the American Ceramic Society. 2010,

93(10):3360-3369.
[118] H.Y. Li, S.Q. Ding, L.Q. Zhang, J. Ouyang, B.G. Han. Effects of particle size, crystal phase and surface treatment of nano-TiO_2 on the rheological parameters of cement paste. Construction and Building Materials. 2020, 239:117897.
[119] E. Mohseni, B.M. Miyandehi, J. Yang, M.A. Yazdi. Single and combined effects of nano-SiO_2, nano-Al_2O_3 and nano-TiO_2 on the mechanical, rheological and durability properties of self-compacting mortar containing fly ash. Construction and Building Materials. 2015, 84:331-340.
[120] T. Meng, Y.C. Yu, X.Q. Qian, S.L. Zhan, K.L. Qian. Effect of nano-TiO_2 on the mechanical properties of cement mortar. Construction and Building Materials. 2012, 29:241-245.
[121] M. Jalal, M. Fathi, M. Farzad. Effects of fly ash and TiO_2 nanoparticles on rheological, mechanical, microstructural and thermal properties of high strength self-compacting concrete. Mechanics of Materials. 2013, 61(61):11-27.
[122] H. Noorvand, A.A.A. Ali, R. Demirboga, N. Farzadnia, H. Noorvand. Incorporation of nano TiO_2 in black rice husk ash mortars. Construction and Building Materials. 2013, 47:1350-1361.
[123] A. Nazari, S. Riahi. TiO_2 nanoparticles effects on physical, thermal and mechanical properties of self-compacting concrete with ground granulated blast furnace slag as binder. Energy and Buildings. 2011, 43(4):995-1002.
[124] A. Nazari, S. Riahi, The effect of TiO_2 nanoparticles on water permeability and thermal and mechanical properties of high strength self-compacting concrete. Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing. 2010, 528(2):756-763.
[125] Z. Li, B.G. Han, X. Yu, S.F. Dong, L.Q. Zhang, X.F. Dong, J.P. Ou. Effect of nano-titanium dioxide on mechanical and electrical properties and microstructure of reactive powder concrete. Materials Research Express. 2017, 4(9):095008.
[126] A. Rahim, S.R. Nair. Influence of nano-materials in high strength concrete. Journal of Chemical and Pharmaceutical Sciences. 2016, 3:15-22.
[127] W.S. Tung, W.A. Daoud. Self-cleaning fibers via nanotechnology: a virtual reality. Journal of Materials Chemistry. 2011, 21(22):7858-7869.
[128] F. Sanchez, K. Sobolev. Nanotechnology in concrete-A review. Construction and Building Materials. 2010, 24(11):2060-2071.
[129] L. Senff, G. Ascensão, D. Hotza, V.M. Ferreira. Assessment of the single and combined effect of superabsorbent particles and porogenic agents in nanotitania-containing mortars. Energy and Buildings. 2016, 127:980-990.
[130] X. Chen, S. Rad, G. Lei, J.F. Dai, A. Shahab, S.H. You, K.H. Bai. Photo-catalytic reactor and detention pond integration: a novel technique for surface water quality enhancement via nano-TiO_2. Environmental Earth Sciences. 2019, 78(18):568.
[131] G. Xiong. Cement-based composite materials for microwave absorbing. Dissertation for the Doctor Degree. Nanjing University of Technology, China, 2005.
[132] Z. Li, S.F. Dong, X.Y. Wang, X. Yu, B.G. Han. Electromagnetic wave-Absorbing property and mechanism of cementitious composites with different types of nano titanium dioxide. Journal of Materials in Civil Engineering. 2020, 32(5):04020073.
[133] H.G. Xiao. Piezoresistivity of cement-based composite filled with nanophase materials and self-sensing smart structural system. Dissertation for the Doctor Degree. Harbin Institute of Technology, China, 2006.
[134] Umarajyadav, M. Vahini. Study of mechanical properties of concrete with nano zirconia. International Research Journal of Engineering and Technology (IRJET). 2017, 04(08):90-94.

[135] A. Nazari, S. Riahi. Limewater effects on properties of ZrO_2 nanoparticle blended cementitious composite. Journal of Composite Materials. 2011, 45(6):639-644.
[136] A. Nazari, S. Riahi. The effects of ZrO_2 nanoparticles on physical and mechanical properties of high strength self-compacting concrete. Materials Research. 2010, 13(4): 551-556.
[137] P. Jaishankar, K.S.R. Mohan. Experimental investigation on nano particles in high performance concrete. International Journal of Chemistry Technology Research. 2015, 8(4):1666-1670.
[138] F. Soleymani. The effects of ZrO_2 nanopowders on compressive damage and pore structure properties of lightweight concrete specimens. Journal of American science. 2012, 8(7):232-239.
[139] C.H. Jiang, H.W. Yuan, C.H. Lu, Z.Z. Xu, D.Y. Lu. The effect of nanoparticles on the properties of calcium aluminate cement pastes at high temperatures. Advances in Cement Research. 2017:1-9.
[140] F. Soleymani. Pore structure and flexural strength of ZrO_2 nanopowders palm oil clinker aggregate-based binary blended concrete. Journal of American Science. 2012, 8(6):187-194.
[141] B.G. Han, Z. Wang, S.Z. Zeng, D.C. Zhou, X. Yu, X. Cui, J.P. Ou. Properties and modification mechanisms of nano-zirconia filled reactive powder concrete. Construction and Building Materials. 2017, 141:426-434.
[142] Z. Li, D.J. Corr, B.G. Han, S.P. Shah. Investigating the effect of carbon nanotube on early age hydration of cementitious composites with isothermal calorimetry and Fourier transform infrared spectroscopy. Cement and Concrete Composites. 2020, 107:103513.
[143] W.W. Li, Y.R. Jia, R.X. Shen, F. Xing, J. Zheng. Compressive strength of cement mortar containing carbon nanotubes (CNTs) under sulfate attack and dry-wet cycling environment. Advances in Engineering Research. 2018, 146:219-223.
[144] S.T. Kang, J.Y. Seo, S.H. Park. The characteristics of CNT/cement composites with acid-treated MWCNTs. Advances in Materials Science and Engineering. 2015, 2015:1-9.
[145] H. Thiyagarajan, M. Mapa, R. Kushwaha. Investigation on the rheological behavior of fly ash cement composites at paste and concrete level. Journal of The Institution of Engineers-Series A. 2018, 99(2):295-301.
[146] A. Alatawna, M. Birenboim, R. Nadiv, M. Buzaglo, S.P. Damari, A. Peled, O. Regev, R. Sripada. The effect of compatibility and dimensionality of carbon nanofillers on cement composites. Construction and Building Materials. 2020, 232:117141.
[147] A. Hawreen, J.A. Bogas and R. Kurda, Mechanical characterization of concrete reinforced with different types of carbon nanotubes. Arabian Journal for Science and Engineering. 2019, 44(10):8361-8376.
[148] A. Cwirzen. Controlling physical properties of cementitious matrixes by nanomaterials. Advanced Materials Research. 2010:639-642.
[149] R.K. Alrub, A.I. Ashour, B.M. Tyson. On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites. Construction and Building Materials. 2012, 35:647-655.
[150] J.Y. Kang, S. Alsabah, and R. Theo. Effect of single-walled carbon nanotubes on strength properties of cement composites. Materials. 2020, 13(6):1305.
[151] Y.F. Ruan, B.G. Han, X. Yu, W. Zhang, D.N. Wang. Carbon nanotubes reinforced reactive powder concrete. Composites Part A-Applied Science and Manufacturing. 2018, 112:371-382.
[152] P. Alafogianni, K. Dassios, C.D. Tsakiroglou, T.E. Matikas, N.M. Barkoula.

Effect of CNT addition and dispersive agents on the transport properties and microstructure of cement mortars. Construction Building Materials. 2019, 197:251-261.
[153] H.S. Lee, B. Balasubramanian, G.V.T. Gopalakrishna, S.P. Karthick, V. Saraswathy. Durability performance of CNT and nanosilica admixed cement mortar. Construction and Building Materials. 2018, 159:463-472.
[154] B.G. Han, Z.X. Yang, X.M. Shi, X. Yu. Transport properties of carbon-nanotube/cement composites. Journal of Materials Engineering and Performance. 2013, 22(1):184-189.
[155] P.T. Dalla, P. Alafogianni, I.K. Tragazikis, D.A. Exarchos, K. Dassios, N.M. Barkoula, T.E. Matikas. The effect of different surfactants/plastisizers on the electrical behavior of CNT nano-modified cement mortars. Proceedings of SPIE. 2015, 9436:94360W.
[156] B. Del Moral, I.M. Gullón, R. Navarro, O. Galao, F.J. Baeza, E. Zornoza, B. Calderón, I. Rodríguez, N. Arnaiz, M.D.R. Sánchez, P. Garcés. The effect of different oxygen surface functionalization of carbon nanotubes on the electrical resistivity and strain sensing function of cement pastes. Nanomaterials. 2020, 10(4):807.
[157] G.Y. Li, P.M. Wang, X.H. Zhao. Pressure-sensitive properties and microstructure of carbon nanotube reinforced cement composites. Cement and Concrete Composites. 2007, 29(5):377-382.
[158] D. Yoo, S. Kim, S.H. Lee. Self-sensing capability of ultra-high-performance concrete containing steel fibers and carbon nanotubes under tension. Sensors and Actuators A-Physical. 2018, 276:125-136.
[159] D. Yoo, S. Kim, S.H. Lee. Electrical and piezoresistive sensing capacities of cement paste with multi-walled carbon nanotubes. Archives of Civil and Mechanical Engineering. 2018, 18(2):371-384.
[160] W. Zhang, Q.F. Zheng, D.N. Wang, X. Yu, B.G. Han. Electromagnetic properties and mechanisms of multiwalled carbon nanotubes modified cementitious composites. Construction and Building Materials. 2019, 208:427-443.
[161] J.L. Luo, Z.D. Duan, G.J. Xian, Q.Y. Li, T.J. Zhao. Damping performances of carbon nanotube reinforced cement composite. Mechanics of Advanced Materials and Structures. 2015, 22(3):224-232.
[162] K.M. Liew, M.F. Kai, L.W. Zhang. Mechanical and damping properties of CNT-reinforced cementitious composites. Composite Structures. 2017, 160:81-88.
[163] P. Yu, Z. Wang, S. Lu, P.F. Lai. Effects of carbon nanofibers and carboxyl functionalized multi-walled carbon nanotubes on mechanical damping behavior of cement paste. Journal of Nanoscience and Nanotechnology. 2019, 19(1):163-169.
[164] W.H. Zhang, P.P Wu, Y.S Zhang, W.C. Zeng, F.H. Yang. The effect of carbon nanotubes on the mechanical and damping properties of macro-defect-free cements. Science and Engineering of Composite Materials. 2020, 27(1):28-40.
[165] V.P. Veedu. Multifunctional cementitious nanocomposite materials and methods of making the same. U.S. Patent 7,875,211 (2011).
[166] M.K. Hassanzadeh-Aghdam, R. Ansari, M.J. Mahmoodi, A. Darvizeh, A. Hajati-Modaraei. A comprehensive study on thermal conductivities of wavy carbon nanotube-reinforced cementitious nanocomposites. Cement and Concrete Composites. 2018, 90: 108-118.
[167] W. Meng, K.H. Khayat. Effect of graphite nanoplatelets and carbon nanofibers on rheology, hydration, shrinkage, mechanical properties, and microstructure of UHPC. Cement and Concrete Research. 2018, 105:64-71.
[168] N. Yazdani, V. Mohanam. Strength, bleeding and setting time of cement mortar with carbon nanotubes and nanofibers. Advanced Science Engineering and Medicine.

2016, 8(6):490-495.
[169] L.A. Sbia, A. Peyvandi, P. Soroushian, A.M. Balachandra. Optimization of ultra-high-performance concrete with nano- and micro-scale reinforcement. Cogent Engineering. 2014, 1(1):990673.
[170] F. Aslani, L.N. Wang, M.Z. Zheng. The effect of carbon nanofibers on fresh and mechanical properties of lightweight engineered cementitious composite using hollow glass microspheres. Journal of Composite Materials. 2019, 53(17):2447-2464.
[171] E.E. Gdoutos, M.S. Konsta-Gdo. Portland cement mortar nanocomposites at low carbon nanotube and carbon nanofiber content: A fracture mechanics experimental study. Cement and Concrete Composites. 2016, 70:110-118.
[172] O. Galao, F.J. Baeza, E. Zornoza. Strain and damage sensing properties on multifunctional cement composites with CNF admixture. Cement and Concrete Composites. 2014, 46:90-98.
[173] C. Gay, F. Sanchez. Performance of carbon nanofiber–cement composites with a high-range water reducer. Transportation Research Record. 2010, 2142(2142):109-113.
[174] D. Gao, Y. Mo, L. Peng. Mechanical and electrical properties of carbon-nanofiber self-consolidating concrete. In: The Workshop on Biennial International Conference on Engineering, 2010.
[175] M. Kosson, L. Brown, F. Sanchez. Early-age performance of 3D printed carbon nanofiber and carbon microfiber cement composites. Transportation Research Record. 2020, 2674(2):10-20.
[176] L. Brown, F. Sanchez. Influence of carbon nanofiber clustering in cement pastes exposed to sulfate attack. Construction and Building Materials. 2018, 166:181-187.
[177] S. Galao, E. Zornoza, F.J. Baeza, A. Bernabeu, P. Garcés. Effect of carbon nanofiber addition in the mechanical properties and durability of cementitious materials. Materiales de Construcción. 2012, 62(307):343.
[178] H. Wang, X.J. Gao, J.Z. Liu. Effects of salt freeze-thaw cycles and cyclic loading on the piezoresistive properties of carbon nanofibers mortar. Construction and Building Materials. 2018, 177:192-201.
[179] N. Yang, Q.S. Sun. Study on the self-monitoring of bending fatigue cumulative damage for carbon nanofiber polyurethane cement. Applied Sciences. 2019, 9(10): 2128.
[180] G.J. Jing, Z.M. Ye, X.L. Lu, P.Q. Hou. Effect of graphene nanoplatelets on hydration behaviour of Portland cement by thermal analysis. Advances in Cement Research. 2017, 29(2):63-70.
[181] B.G. Han, Q.F. Zheng, S.W. Sun, S.F. Dong, L.Q. Zhang, X. Yu, J.P. Ou. Enhancing mechanism of multi-layer graphenes to cementitious composites. Composites Part A-Applied Science and Manufacturing. 2017, 101:143-150.
[182] G.F. Chen, M.Q. Yang, L.J. Xu, Y.Z. Zhang, Y.Z. Wang. Graphene nanoplatelets impact on concrete in improving freeze-thaw resistance. Applied Sciences. 2019, 9(17): 3582.
[183] J.L. Wang, S.F. Dong, X. Yu, B.G. Han. Mechanical properties of graphene-reinforced reactive powder concrete at different strain rates. Journal of Materials Science. 2020, 55:3369-3387.
[184] Z. Fan. Investigation on properties of cementitious materials reinforced by graphene. Dissertation for the Master Degree. University of Pittsburgh, America, 2014.
[185] I. Rhee, J. Lee, Y.A. Kim, J.H. Kim. Electrically conductive cement mortar: Incorporating rice husk-derived high-surface-area graphene. Construction and Building Materials. 2016, 125:632-642.
[186] N. Zohhadi, N. Aich, F. Matta, N.B. Saleh, P. Ziehl. Graphene nanoreinforcement

for cement composites. Nanotechnology in Construction. 2015:265-270.
[187] S. Huang. Multifunctional graphite nanoplatelets (MLG) reinforced cementitious composites. Dissertation for the Master Degree. National University of Singapore, Singapore, 2012.
[188] S.W. Sun, S.Q. Ding, B.G. Han, S.F. Dong, X. Yu, D.B. Zhou, J.P. Ou. Multi-layer graphene-engineered cementitious with multifunctionality/intelligence. Composites Part B-Engineering. 2017,101:104-150.
[189] A. Sedaghat, M.K. Ram, A. Zayed, R. Kamal, N. Shanahan. Investigation of physical properties of graphene-cement composite for structural applications. Open Journal of Composite Materials. 2014, 2014(1):12-21.
ites with conductive graphene nanoplatelet. Proceedings of SPIE. 2014, 9061:906126.
[190] S. Ghosh, S. Harish, K.A. Rocky, M. Ohtaki, B.B. Saha. Graphene enhanced thermoelectric properties of cement based composites for building energy harvesting. Energy and Buildings. 2019, 202:109419.
[191] Y.F. Ruan, D.C. Zhou, S.W. Sun, X.Y. Wu, X. Yu, J.L. Hou, X.F. Dong, B.G. Han. Self-damping cementitious composites with multi-layer graphene. Materials Research Express. 2017, 4(7):75605.
[192] B.G. Han, S.Q. Ding, X. Yu. Intrinsic self-sensing concrete and structures: A review. Measurement. 2015, 59:110-128.
[193] B.G. Han, K. Zhang, T. Burnham, T. Burnham, E. Kwon, X. Yu. Integration and road tests of a self-sensing CNT concrete pavement system for traffic detection. Smart Materials and Structures. 2013, 22(1):015020.
[194] S.Q. Ding, Y.W. Wang, Y.Q. Ni, B.G. Han. Structural modal identification and health monitoring of building structures using self-sensing cementitious composites. Smart Materials and Structures. 2020, 29:055013.
[195] R. Howser, H.B. Dhonde, Y.L. Mo. Self-sensing of carbon nanofiber concrete columns subjected to reversed cyclic loading. Smart Materials and Structures. 2011, 20(8):085031.
[196] A. Downey, A. Dalessandro, M. Baquera, E. García-Macías, D. Rolfes, F. Ubertini, S. Laflamme, R. Castro-Triguerog. Damage detection, localization and quantification in conductive smart concrete structures using a resistor mesh model. Engineering Structures. 2017, 148:924-935.
[197] O. Galao, F.J. Baeza, E. Zornoza, P. Garces. Carbon nanofiber cement sensors to detect strain and damage of concrete specimens under compression. Nanomaterials. 2017, 7(12):413.
[198] F. Vossoughi. Electrical resistivity of carbon fiber reinforced concrete. Dissertation for the Doctoral Degree. University of California, American, 2004.
[199] A. D'Alessandro, F. Ubertini, E. García-Macías, R. Castro-Triguero, A. Downey, S. Laflamme, A. Meoni, A.L. Materazzi. Static and dynamic strain monitoring of reinforced concrete components through embedded carbon nanotube cement-based sensors. Shock and Vibration. 2017, 2017:3648403.
[200] M. Saafi. Wireless and embedded carbon nanotube networks for damage detection in concrete structures. Nanotechnology. 2009, 20(39):395502.
[201] A.O. Monteiro, P.M.F.J. Costa, M. Oeser, P. Cachim. Dynamic sensing properties of a multifunctional cement composite with carbon black for traffic monitoring. Smart Materials and Structures. 2020, 29(2):025023.
[202] P. Shukla, V. Bhatia, V. Gaur. Multiwalled carbon nanotubes reinforced portland cement composites for smoke detection. Solid State Phenomena. 2012, 185:21-24.