Review Article

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Carbon nanomaterials enhanced cement-based composites: advances and challenges

Abstract: Carbon nanomaterials, predominantly carbon nanofibers, carbon nanotubes, graphene, graphene nanoplates, graphene oxide and reduced graphene oxide, possess superior chemical, physical and mechanical properties. They have been successfully introduced into ordinary Portland cement to give enhancements in terms of mechanical properties, durability and electrical/thermal conductivity, and to modify the functional properties, converting conventional cement-based materials into stronger, smarter and more durable composites. This paper provides a comprehensive review of the properties of carbon nanomaterials, current developments and novel techniques in carbon nanomaterials enhanced cement-based composites (CN-CBCs). Further study of the applications of CN-CBCs at industrial scale is also discussed.

Keywords: carbon nanomaterials, cement-based composites, enhancement and challenges

1 Introduction

Nanotechnology is a novel approach with applications in all areas of science, including physics, chemistry and biology, and refers to the understanding, fabrication, and manipulation of matter at nanometer scales (*i.e.* <100 nm) [1, 2]. In recent years, the construction industry has been trying to enhance conventional construction materials using nanotechnology [1, 3, 4]. The incorporation of various kinds of nano-additives into ordinary Portland cement (OPC), the most widely consumed man-made mate-

rial in civil engineering, to give nanomaterials enhanced cement-based composites with improved properties has been one of the major achievements of nanotechnology in materials science. Except for traditional nanomaterials such as nano-silica [5] and nano aluminum [6] etc., carbon nanomaterials including carbon black [7, 8], carbon nanofibers (CNFs) [9, 10], carbon nanotubes (CNTs) [11–13], graphene [14–17], graphene nanoplates (GNPs) [14], graphene oxide (GO) [14, 15, 18] and reduced graphene oxide (rGO) [16, 17, 19] have been attracting increasing amounts of research attention in terms of enhancing OPC.

Carbon nanomaterials are primarily composed of carbon atoms with a low density, a high aspect ratio or specific surface area, and unique chemical and physical properties [13, 14, 20]. Carbon nanomaterials including GO and GNPs can provide new functions including thermal/electrical interfacing [15, 16, 21], self-cleaning [15, 16, 22], self-sensing [15, 16, 23], and electromagnetic shielding [15, 16]. Carbon nanomaterials can be added to cement-based materials at very low ratios (usually lower than 0.50 wt.%) to act as extra seeding sites to produce sustainable composites with enhanced mechanical properties and durability [24, 25]. Carbon nanomaterials enhanced cement-based composites (CN-CBCs) can also perform new functions such as stress sensing and temperature monitoring, depending on the kind of nanomaterials added [26–28]. Carbon black takes the form of zero-dimensional nanoparticles that are useless in preventing crack propagation [29]; however, both one-dimensional (1D) CNFs/CNTs [24] and two-dimensional (2D) graphene-based nanosheets [25, 28] generate more interactions and stronger bonding with other materials, and are therefore increasingly employed as promising candidates for the nano-reinforcement of cement-based composites. Here, CN-CBCs is defined as the cement-based composites enhanced with carbon nanomaterials other than carbon black. By incorporating carbon nanomaterials with OPC to develop novel and advanced cement-based composites with unique material properties, improvements in the stability and longevity of various buildings is possible. The potential utilization of carbon nanomaterials in enhancing OPC has been investigated; however, most of the re-

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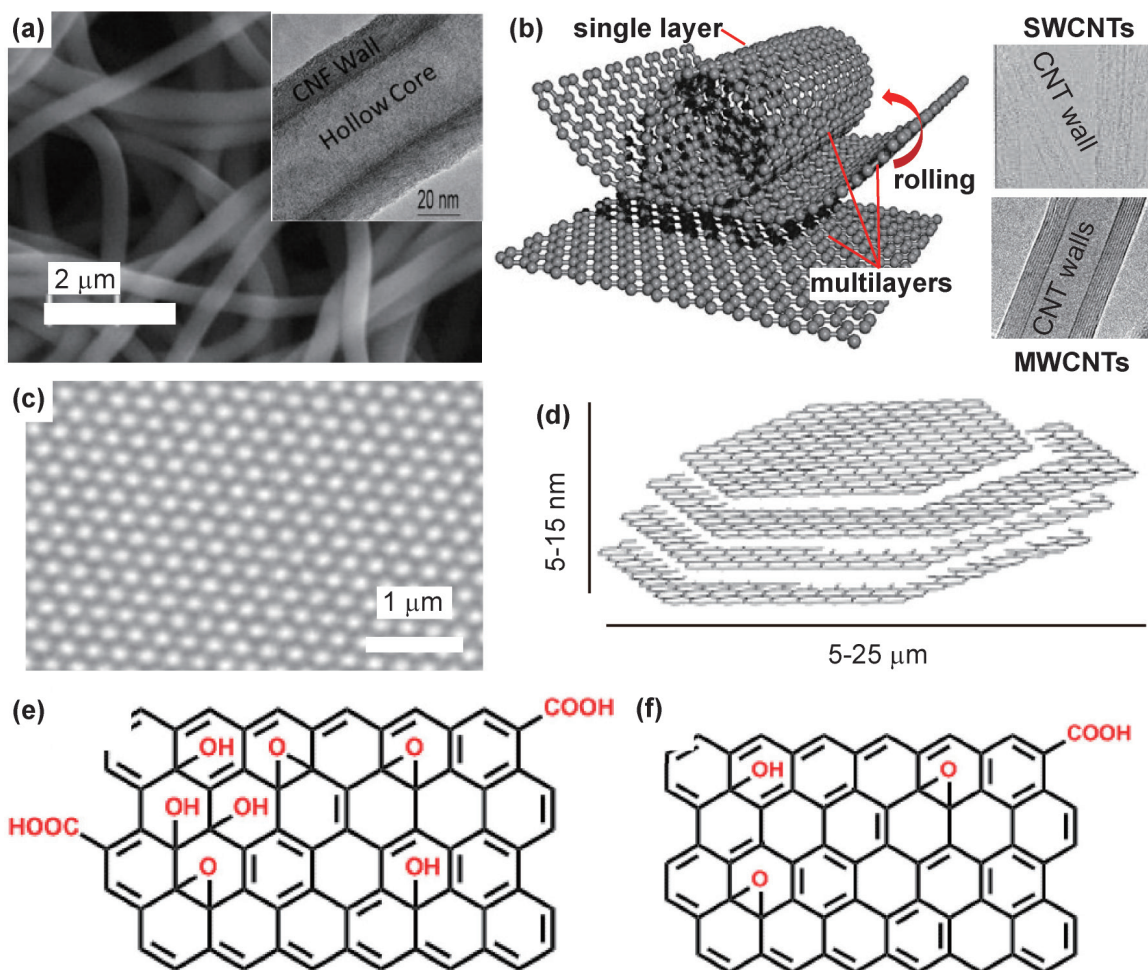
Figure 1: (a) SEM and TEM images of carbon nanofibers (CNFs) [32, 33]; (b) representation and TEM images of carbon nanotubes (CNTs) [34–36]; (c) morphology of graphene [14]; representations of (d) graphene nanoplates (GNPs); (e) graphene oxide (GO); (f) reduced graphene oxide (rGO) [25]

search into CN-CBCs is limited to the laboratory scale, and studies of its industrial-scale applications are rare. Here, the current advances in CN-CBCs are reviewed and the challenges of the large-scale usage of CN-CBCs are discussed. This paper is divided into three sections covering: (i) carbon nanomaterials and their properties; (ii) current advances in CN-CBCs; and (iii) challenges for the further development of CN-CBCs.

2 Carbon nanomaterials

In the past few years, CNFs [27, 30] and CNTs [24, 31] have been the most widely used materials for developing CN-CBCs. Graphene, a more recently studied allotrope of carbon with 2D geometry [14], has now started to challenge the dominance of CNFs and CNTs. Carbon nanomaterials

are not limited to CNFs, CNTs or graphene, and GNPs, GO and rGO have all been used to develop advanced cement-based composites [25, 28]. Before reviewing the enhancements arising from the use of carbon nanomaterials in OPC, a short review of basic knowledge about these compounds is given in this section.

Figure 1(a) shows the micro-morphology of CNFs, a kind of 1D fibrous nanomaterial [32, 33]. A hollow-core structure with a diameter range of 20–60 nm is made up of graphitic planes that are stacked on top of each other, and layers made of undulating graphitic planes are deposited in parallel on the outer surface of the original filament to form the CNF wall. CNFs are generally available with diameters averaging from 60 to 200 nm or more, and a range of as-formed lengths of 1–100 µm.

CNTs, which can be categorized as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nan-

Table 1: Carbon nanomaterials and their material properties

Material	Conductivity		Young's modulus (GPa)	Tensile/fracture strength (GPa)	Refs
	Electrical (S/m)	Thermal (W/m·K)			
CNFs	10^3	−1900	400	>3	[9, 44, 45]
CNTs	>10^3	>2500	950−1800	11−63	[46−49]
Graphene	10^7−10^8	~5×10^3	>1000	>130	[14, 20, 41, 42, 50]
GO	−	>700	23−200	0.13	[15, 16, 50, 51]
rGO	>200	>1400	>250	0.77	[17, 19, 52]
GNPs	104−105	>700	1000	~130	[16, 50, 53]

otubes (MWCNTs), are another type of 1D nanomaterial with a hollow structure and capped endings [11–13]. CNTs can be described as rolls of monolayer or multilayer graphene sheets at specific and discrete angles (Figure 1b). The diameter of a CNTs is usually less than 50 nm, and the length may be up to 50 μm, giving an aspect ratio larger than 1000.

Graphene is a honeycomb sheet structure consisting of a 2D array of carbon atoms that are covalently bonded, with few crystal defects (Figure 1c) [14, 15, 17]. As these are strictly 2D sheets with a thickness of about 0.335 nm, all carbon atoms are exposed to the environment, resulting in the highest possible surface area per unit weight. The theoretical specific surface area of a single layer of graphene is about 2360 m^2/g [37], more than twice that of CNTs [38]. When multilayers of graphene sheets (usually 10-100 layers) are packed together, GNPs can be obtained [39, 40]. GNPs are often formed with a total thickness of less than 15 nm and a diameter of several to tens of micrometers (Figure 1d).

GO is a kind of derivative of graphene, and the main difference is that the former has hydroxyl groups (-OH), epoxide groups (C-O-C), carboxyl groups (-COOH), and carbonyl groups (C=O) on its surface (Figure 1e). Owing to the existence of these oxygen-based groups, the thickness of a single layer of GO can be several nanometers, whereas the specific surface area declines to about 700–1500 m^2/g [15], and GO sheets have a wrinkled surface. With thermal or chemical reduction treatments [16, 17], these oxygen-based function groups can be partially eliminated to obtain rGO that contains fewer functional groups in its structure than GO (Figure 1f), but it is impractical to remove all the functional groups.

Current knowledge of carbon nanomaterials suggests that graphene is the basic structural unit. Graphene sheets are composed of adjacent carbon atoms linked by alternating single and double covalent bonds (sp^2 carbon bonds) [17], making them the strongest, hardest, most impermeable and most flexible nanomaterials [14, 15]. The results of atomic force microscope (AFM) nanoindentation showed that a single layer of graphene can exhibit a Young's modulus of up to 1.0 TPa, with an intrinsic strength of 130 GPa [41]. Graphene also has outstanding performance in terms of its electrical and thermal conductivity. It is estimated that the thermal and electrical conductivity of a layer of graphene are about 10^8 S/m [20] and 3000–5300W/m·K [42, 43], respectively (Table 1). As derivatives of graphene, other carbon nanomaterials also have remarkable physical, chemical and mechanical properties (Table 1).

Table 1 shows that the overall physical and mechanical properties of CNTs are better than those of CNFs because that the CNFs wall is a graphitic layer made of sp^3-hybridized carbons rather than sp^2-hybridized carbons [9]. Graphene has the best overall material properties, whereas its working efficiency declines with an increase in the number of layers (GNPs) [54]. The oxygen-based functional groups attached to GO can be treated as structural defects in pristine graphene [15], making GO almost electrically insulated, with significantly reduced thermal conductivity. rGO has properties that are intermediate between those of GO and graphene, due to its lower content of oxygen-based functional groups [16]. These unique material properties mean that carbon nanomaterials have been exploited to reinforce and provide smart functions in composites of biomaterials [55–57], ceramics [58, 59], organic polymer composites [60–62] and construction materials [24, 28, 63].

3 Carbon nanomaterials enhanced cement-based materials

3.1 Fabrication procedure

Care must be taken when fabricating CN-CBCs, as their enhanced properties can only be obtained when the carbon nanomaterials are separated as fully as possible [24, 25, 60,

Table 2: Fabrication of carbon nanomaterials enhanced cement-based composites

Matrix	Material	Fabrication process		Following procedure	Ref
		Suspensions			
		Ultrasonication	Surfactants		
Paste	CNFs	Yes, 10–20 min	polycarboxylate-based superplasticizer	Mixed with cement under stirring	[68]
Paste	CNFs	Yes	carboxymethylcellulose sodium	Mixed with cement under stirring	[69]
Paste	CNFs	Yes	polycarboxylate-based superplasticizer	Mixed with cement under stirring	[70]
Paste	CNFs /CNTs	Yes, 10–20 min	polycarboxylate-based superplasticizer	Mixed with cement under stirring for 7 min	[71]
Paste	CNFs /CNTs	Yes, 15–30 min	polycarboxylate-based superplasticizer	Mixed with cement under high-speed stirring for 7 min	[30]
Paste	CNTs	Yes, 3 hours	methylcellulose	Stirred with cement for 5 min	[31]
Paste	CNTs	Yes	polycarboxylate-based superplasticizer	Mixed with cement according to ASTM standard C1738	[72]
Paste	CNTs	Yes, 15 min	sodium dodecyl benzene sulfonate; sodium deoxycholate; cetyltrimethyl ammonium bromide; gum arabic	Mixed with cement according to GB/T1764-1999 (China)	[73]
Paste	CNTs	Yes, 30–210 min;	anionic sodium dodecyl sulfate; nonionic polyoxyethylene;	Mixed with cement under stirring	[65]
Paste	CNTs	Yes, 30 min	anionic gum arabic	Mixed with cement under stirring	[74]
Mortar	CNTs	Yes, ≥30 min	polycarboxylate-based superplasticizer	Mixed with cement under stirring	[75]
Mortar	CNTs	Yes, 40 min	polycarboxylate ether superplasticizer	Mixed with cement according to ASTM C109/C109M, 2008	[76]
Paste	GO	Yes	No need for dispersion	Mixed with cement according to ASTM C1738 [77]	
Mortar	GO	Yes, 1 hour	No need for dispersion	Mixed with cement under stirring	[78]
Mortar	GNPs /GO	Yes, 30 min	polycarboxylate-based superplasticizer	Mixed with cement under stirring	[79]
Paste	GNPs	Yes	methylcellulose	Mixed with cement under stirring	[80]
Mortar	Graphene	Yes, 90 min	polycarboxylate polymers Mixed with cement under stirring	[81]	
UHPC	rGO	Yes, 70 min	polycarboxylate-based superplasticizer	Mixed with cement under stirring	[82]

Note: The term 'UHPC' in this table refers to ultra-high performance concrete

63]. To obtain the maximum performance, all nanoparticles should be dispersed individually. The carbon nanomaterials sustain such strong Van der Waals forces that they tend to clump together to form bundles or multilayers [9, 11–15, 64]. In cement, agglomerated carbon nanomaterials can act as weak spots or may introduce new defects in the form of voids, since this agglomeration occupies the space where cement hydrates would have formed [65, 66]. In these situations, the matrix may experience sudden failure due to increased stress concentrations [63], and these micro-defects can retard the fluent transportation of phonon or electrons [67] and provide pathways for the migration and flow of water or other harmful agents [28]. To make full use of their enhancing potential, carbon nanomaterials are always introduced into cement using the following steps: (i) fabricating aqueous suspensions of carbon nanomaterials; and then (ii) mixing these prepared liquid mixtures with cement (as shown in Table 2).

High-shear mixing is helpful in separating CNFs/CNTs [83], ultrasonication has proved to be more ef-
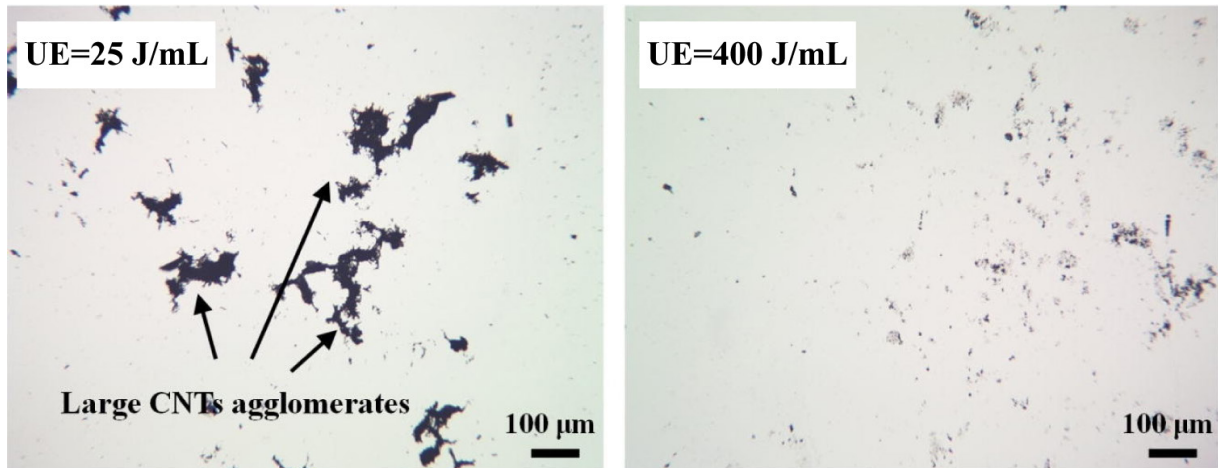
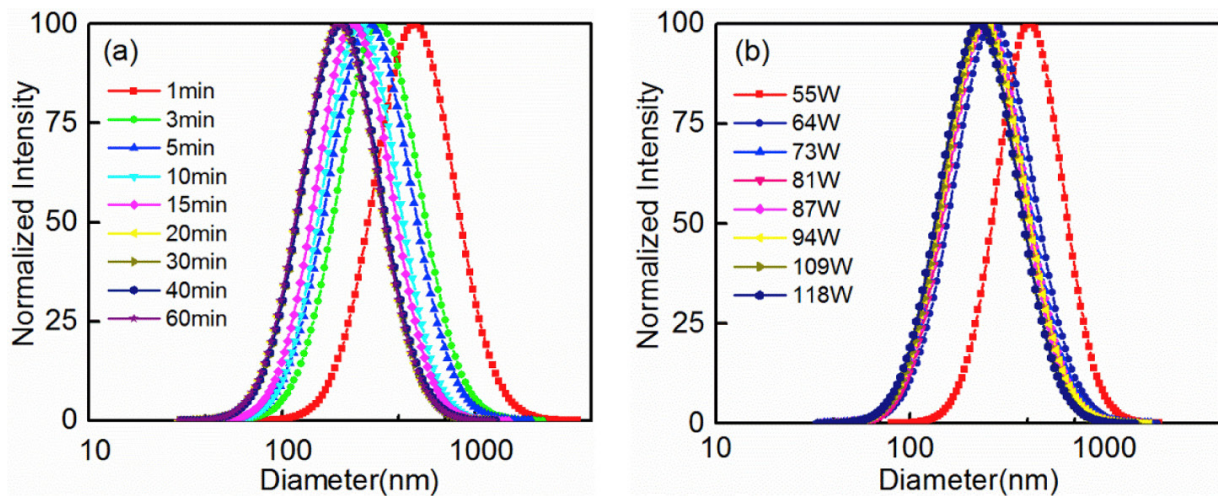**Figure 2:** Optical microscope images of CNT suspensions at different ultrasonication power [72]

Figure 3: Particle size distributions of hybrid of GO/CNT particles in suspension at different (a) ultrasonication times and (b) ultrasonication power [86]

fective, and thus has become more commonly used [24, 25]. The ultrasonication process produces rapidly collapsing cavitation bubbles in the liquid, creating high local solvent velocities that act as separating forces to overcome the attraction between nanoparticles [84, 85]. The ultrasonication process should be well designed, since insufficient ultrasonication energy (UE) is not effective for the uniform dispersion of nanoparticles (Figure 2a) [72] and excess UE tailors the nanomaterials into smaller fragments. Figure 3 presents the size distribution intensity of GO/CNT hybrid particles in water ultrasonicated for different time and at different power levels [86]. It can be seen that the particle size distribution shifts towards a smaller size with increasing ultrasonication time or power. The tailoring effect of UE limits the strength-enhancing efficiency of carbon nanomaterials, as the bridging effect of carbon nano-

materials is inversely proportional to their length [87] or equivalent radius [88]. Gao *et al.* [89] reported that hybrid GO/CNTs additives exposed to excess UE lead to deterioration of the pore structure of cement. In [73, 90, 91], high-shear mixing and ultrasonication were used in combination to prepare aqueous solutions of CNTs, rGO with a high degree of dispersion.

When preparing aqueous suspensions of carbon nanomaterials, dispersing agents are always required, such as gum arabic, polycarboxylate-based superplasticizers, etc. (Table 2). These agents can provide steric hindrance or a static charge repulsion to the nanomaterials in order to overcome the inner binding force, thus improving their degree of dispersion in liquid [63, 65]. GO and rGO sheets have hydrophilic behavior due to their oxygen-based functional groups, and can be fully separated in water even
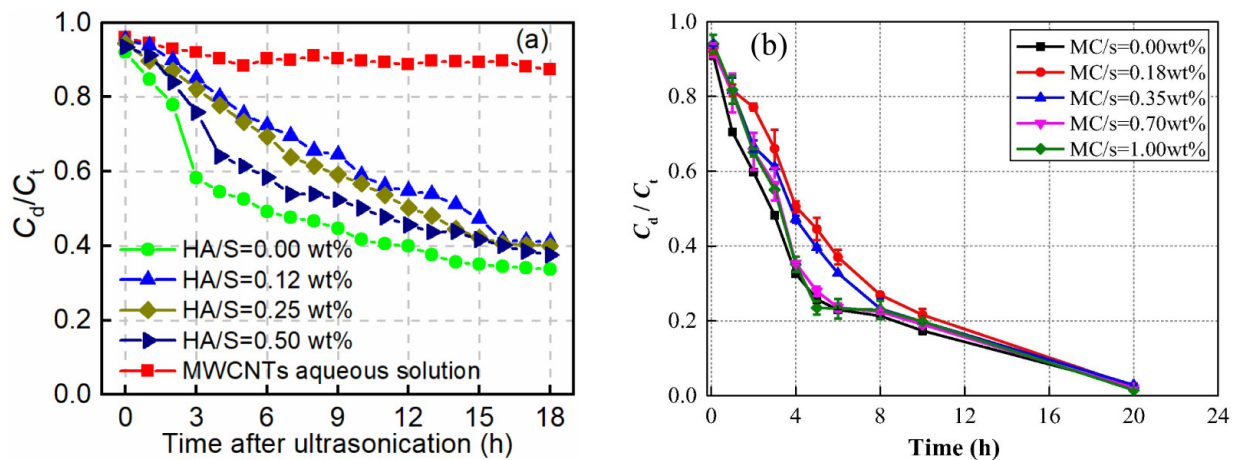
Figure 4: The dispersion degree (C_d/C_t) of CNTs in simulated cement pore solutions containing varying content of (a) humic acid (HA) [100] and (b) methylcellulose (MC) [101] over time
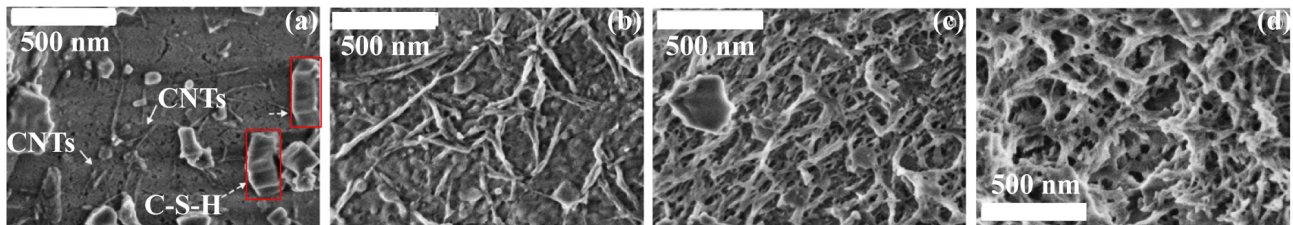

Figure 5: Distribution of calcium silicate hydrate (C-S-H) gel in a CNT-cement system after hydration for (a) 60 min; (b) 135 min; (c) 180 min; (d) 240 min [105]

without the assistance of dispersing agents [19, 43, 51, 72, 92]. Similarly, functionalized CNFs/CNTs containing carboxylic or hydroxyl groups can give a higher degree of dispersion than pristine CNTs/CNFs, although at the expense of strength [71, 93, 94]. In fresh cement-based materials, more than 95% of carbon nanomaterials are distributed in the alkaline pore solutions filled with various cations [95], and during the hardening process (which usually lasts several hours) [96], chemical or physical interactions between the cationic and carbon nanomaterials inevitably lead to the re-agglomeration of nanomaterials [97–99]. Dispersing agents are therefore added when preparing aqueous solutions of GO or rGO for the purposes of stabilization [77, 92]. In our previous studies, both humic acid (HA) [100] and methylcellulose (MC) [101] were found to be useful as extra additives to stabilize the dispersed CNTs in cementitious environments. Figure 4 shows the variation in the degree of dispersion (C_d/C_t) of CNTs in simulated cement pore solutions over time, from which we can see that C_d/C_t continuously declines and that CNT suspensions containing a moderate amount of HA or MC always have a higher C_d/C_t. Bai *et al.* [102] found that the incorporation of silica fume is capable of facilitating the dispersion of graphene in cement. The use of silica fume to improve the dispersion of

CNTs has also been reported in the literature [103]. In [104], the researchers proposed the use of polycarboxylate-acid-modified GO as an alternative to pristine GO to avoid re-agglomeration.

3.2 Improvement in the hydration reaction

The incorporation of carbon nanomaterials can promote the pozzolanic reaction of cement, and especially in the early age. In fresh cement, some of the carbon nanomaterials are absorbed by cement grains, most of which are distributed in the pore solutions [95]. There is strong evidence that these nanomaterials, whether in individual or agglomerate forms, provide nucleation sites for cement hydrates to sediment and grow. Figure 5 illustrates the process of growth of calcium silicate hydrate (C-S-H) gels on CNTs substrates for different hydration times [105]; it can be seen that once the hydration reaction has started, C-S-H gels preferentially form around CNTs and the C-S-H layer covering the CNTs becomes thicker over time, and after about three hours, a C-S-H gel network is formed. Fakhim *et al.* [76] noticed that the intensity of C-S-H gels in CNT-
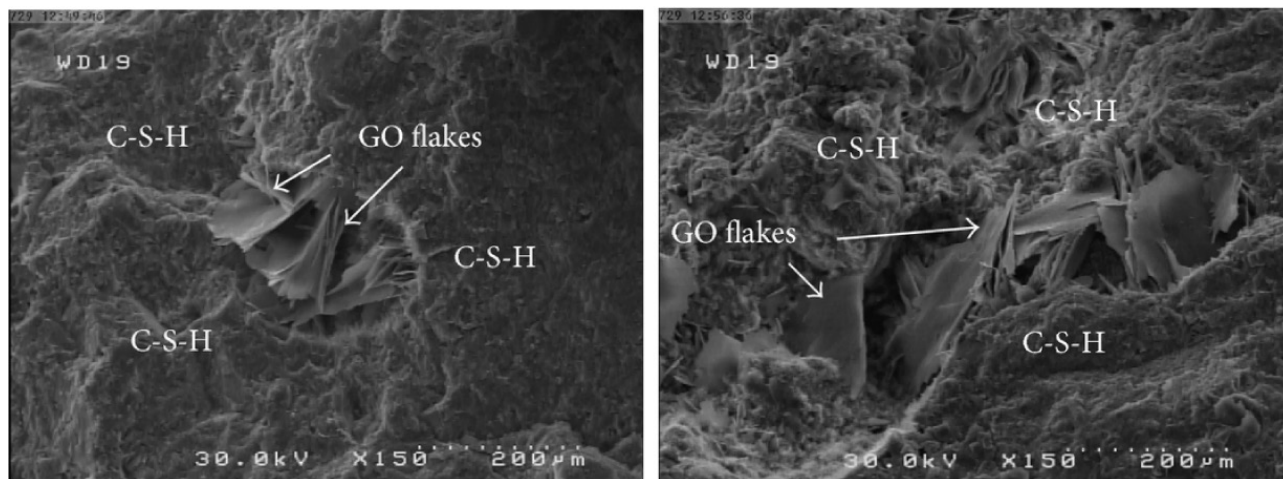
Figure 6: SEM images of cement containing GO, showing the nucleation of C-S-H by GO [106]
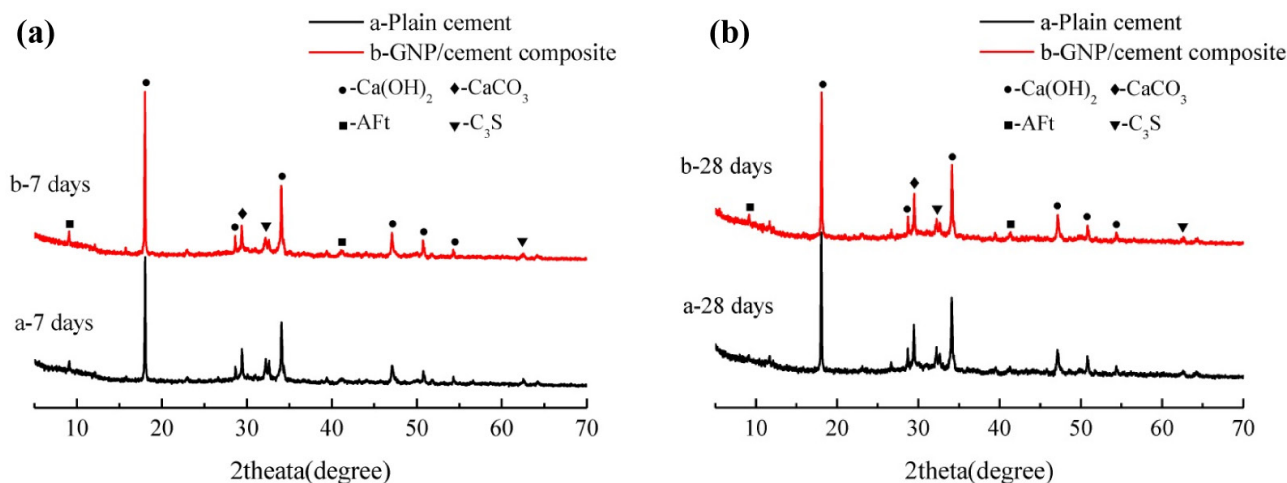

Figure 7: XRD patterns for plain and GNP-cement after (a) 7 days; (b) 28 days [80]

enhanced cement was higher than those in plain cement based on X-ray diffraction (XRD) data.

The growth of cement hydrates on GO has also been observed. In Figure 6, C-S-H deposits on the GO sheets can be seen, due to the high surface energy of GO and the hydrophilic groups on the surfaces [106]. GO acts as a nucleating substrate for C-S-H, which preferentially forms on the GO rather than solely on the surface of the adjacent cement grains. The nucleation behavior of hydrates on the nanoparticles accelerates the hydration of cement. In this study, XRD measurements were conducted and the results showed that GO-cement nanocomposites containing 1.0 wt.% and 1.5 wt.% GO had an increased intensity of C-S-H compared with plain cement. Other evidence includes the higher release rate of hydration heat [77] and the higher content of non-evaporable water [107]. In [108], the results of XRD and FTIR testing indicated that GO sheets promote

cement hydration since the water molecules on the GO surface provide a reservoir of water and transport channels for further hydration. Cement hydrates grown on GO/CNFs hybrid fibers have also been reported [109].

Wang *et al.* [80] investigated the influence of 0.05 wt.% GNPs on cement hydration products via the comprehensive use of XRD and thermal analysis (TG/DGT) techniques. The XRD patterns (Figure 7) showed that the representative phases in GNP-cement composites were calcium hydroxide ($Ca(OH)_2$) and ettringite (AFt). The intensities of the characteristic peaks with respect to $Ca(OH)_2$ and AFt in GNP-cement composite were both higher, while the intensity of the C_3S phase in the GNP-cement composite was lower. The TG/DTG curves of GNP-cement composite suggested a higher content of $Ca(OH)_2$ phase. All these observations indicate the higher hydration degree of the CNP-cement. Gholampour *et al.* [19] studied the effects of rGO
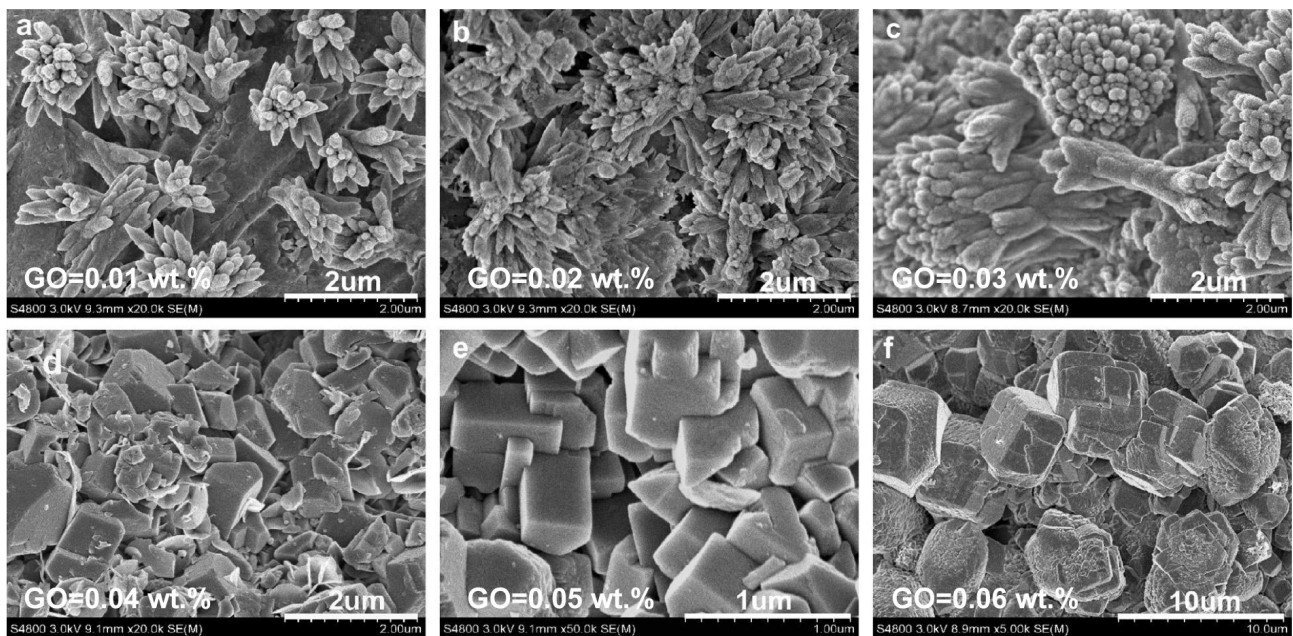
Figure 8: Effects of different proportions of GO sheets on the shapes of cement hydration crystals and their formation process [110]

on the hydration degree of cement via XRD characterization, and the results implied that at the optimum degree of reduction, the incorporation of rGO gave almost the same increase in the hydration degree as GO.

GO sheets with a high degree of dispersion and various dosages can be used to regulate the morphology of cement hydration crystals. For example, Figure 8(a)-(c) show SEM images of cement pastes enhanced by different proportions of GO (0.01–0.03 wt.%) [110], from which we can see that at proportions of 0.01–0.03 wt.%, GO sheets lead to the formation of uniformly distributed, flower-like structures from rod-like crystals, with the distribution becoming denser with an increase in the proportion of GO. In composites containing 0.03 wt.% GO, the hydration crystals exhibited a thicker, shorter rod-like shape, unlike the finer, rod-like crystals from which the flower-like structures are formed. When the proportions of GO were increased to 0.04, 0.05 and 0.06 wt.%, many densely packed regular polyhedral were observed. The authors of this study suggested that GO with smaller equivalent radius was more effective in promoting the formation of flower-like hydration crystals at low proportions, and the formation of regular polyhedral crystals at high proportions.

During normal hydration, nucleation occurs only on the surface of the adjacent cement grains, and the sediment hydration crystals form a shell structure that prevents water from coming into contact with cement clinkers [96, 111]. Due to the role of nanomaterials as nucleation sites, more hydrates that would have accumulated

beneath the shell can pass through it to enter the pore solution, resulting in thinner shell structures; the retarding effect of the shells is therefore weakened, promoting the formation of higher amounts of C-S-H. This accelerated hydration behavior has been identified as one reason for the faster hardening and the enhanced early strength of CN-CBCs [30, 112–114]. In addition, the regulating effect of GO on the morphology of C-S-H gives a more uniform distribution [110]. Both of these observations have been reported as reasons for the denser microstructure of CN-CBCs [25]. For example, Li *et al.* [31] reported that adding 0.50 wt.% MWCNTs to OPC paste could reduce the mean radius of pores by about 43.2% (from around 15.23 to 8.65 nm) and the total porosity by about 64%; the addition of MWCNTs also reduced pores with an equivalent radius of larger than 50 nm by about 82%, giving an extra filling effect. Another example is shown in Figure 9 [113], in which straight-through type cracks can be seen in plain cement, while in the paste containing GO, only fine cracks with few branches are observed. The authors of this study observed an increased volume of small and medium pores (with diameters 1–45 nm) for the GO-enhanced cement (from about 0.38 to 0.088 ml/g).

Although studies investigating the accelerating effect of CNFs on the hydration reaction of cement are rare, Mercury intrusion porosimetry (MIP) results for CNF-cement composites [68] have shown a decrease in total intrusion volumes when CNFs are added; in this study, the porosity of plain cement was 21.39%, while the porosities of cement-
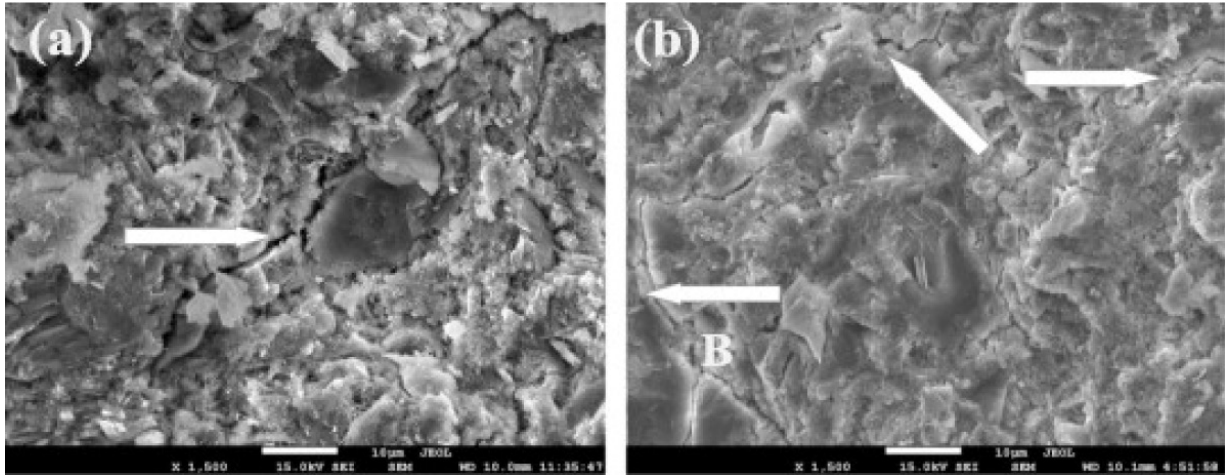
Figure 9: SEM images of the microstructure of (a) plain cement; (b) GO-enhanced cement [113]
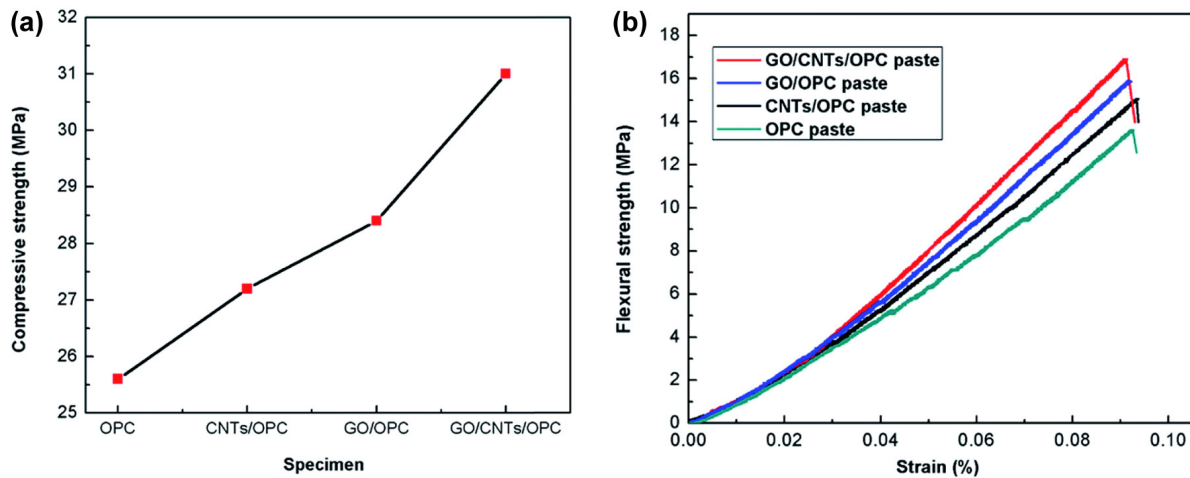

Figure 10: (a) Compressive strength; (b) flexural strength of cement-based composites containing CNTs (CNTs/OPC), GO (GO/OPC) and a GO-CNT hybrid (GO/CNTs/OPC) [119]

based materials enhanced with 0.075 and 0.1 wt.% CNFs were 19.75% and 18.33%, respectively. The median pore diameters of plain cement and cement enhanced with 0.075 and 0.10 wt.% CNFs were 77.3, 75.4, and 74.5 nm, respectively. Sanchez and Ince [115] reported that the addition of CNFs to cement promoted pore refinement and increased the pore volume in the 6–200 nm pore size range, and showed that when 2.0 wt.% CNFs was added, the total volume of accessible pores was reduced.

3.3 Improvement in mechanical properties and relevant mechanisms

The use of carbon nanomaterials as reinforcements to enhance the mechanical properties of OPC was one of the main purposes for developing CN-CBCs. Significant en-

hancements at relatively low proportions of carbon nanomaterials (usually at 0.01–0.50 wt.%) have been observed in the compressive, tensile, flexural and fracture strengths and the elastic modulus, as reviewed in previous papers [24, 25, 28]. According to [25, 28], the general enhancement in the compressive strength of the cement-based materials enhanced with graphene/GO is in the range of about 5–40%. As a comparison, the addition of nano SiO_2 (0.50–3.0 wt.%) can improve the compressive strength by about 6–10% [116, 117].

Recently, some researchers have noticed that the utilization of hybrids of carbon nanomaterials, and predominantly the combination of CNTs with GO, can give interesting outcomes. Li *et al.* [118] reported that the increases in the bending strength of cement due to incorporating hybrids with 0.50 wt.% CNTs and 1.50 wt.% GO were about 40% and 200% compared to the values from adding only
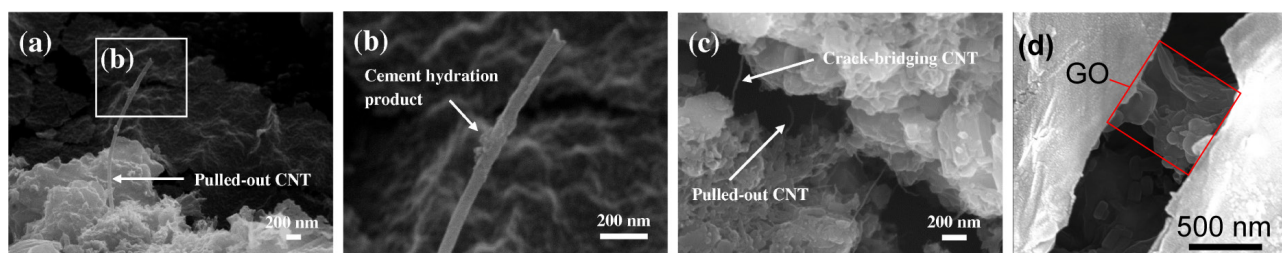
Figure 11: (a)-(c) The pull-out behavior and crack-bridging roles of CNTs in cement [72]; (d) GO sheets trapped in a nanoscale crack in cement [120]
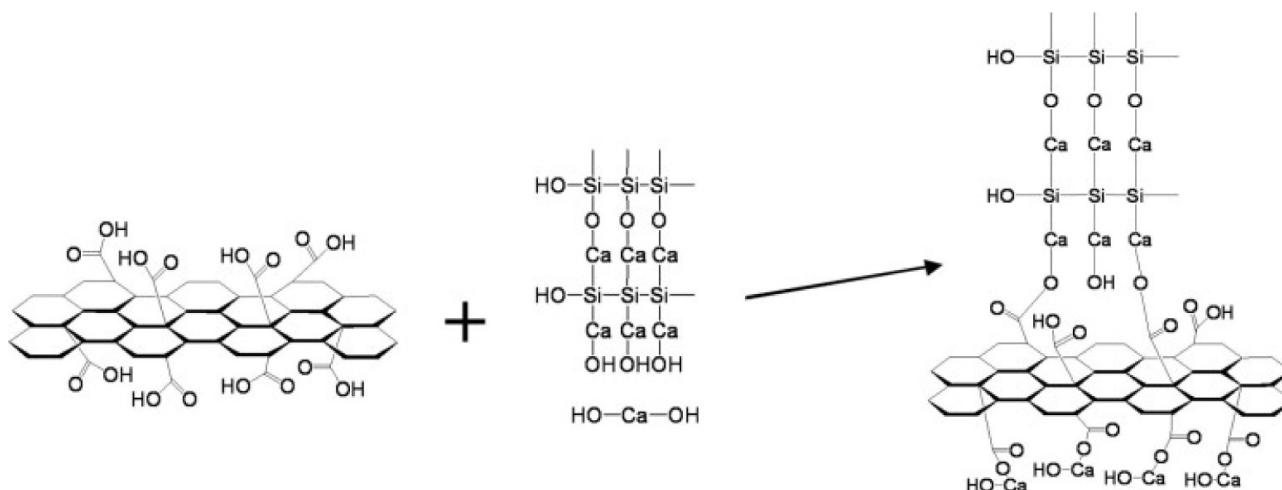

Figure 12: Schematic reaction between carboxylic acid groups and Ca(OH)$_2$, C−S−H in cement [113]

CNTs (0.50 wt.%) and GO (1.50 wt.%), respectively. As shown in Figure 10, Lu *et al.* [119] reported an increase of about 21% in the compressive strength and 24% increment in the flexural strength of OPC when a hybrid of 0.025 wt.% CNTs and 0.025 wt.% GO was added. OPC reinforced with only 0.05 wt.% CNTs gave an increase of 6.4% in the compressive strength and 10.1% in the flexural strength, and OPC reinforced only with 0.05 wt.% GO showed increases of 11.0% in the compressive strength and 16.2% in the flexural strength. In another study [109], the co-effects of CNFs and GO on the mechanical properties of cement were investigated, and the results showed that the addition of 1.0 wt.% CNFs increased the compressive and flexural strengths of cement by 20.8% and 18.6%, respectively, while replacing half of the CNFs with GO gave increases in the compressive and flexural strengths of about 31.6% and 39.8%, respectively. This is thought to be at least partially because that GO worked as an extra surfactant to improve the dispersion of CNTs in the matrices [86].

The more homogeneous and compacted microstructure of CN-CBCs has been identified as one reason for the higher mechanical properties, since the stress concentration in the matrices is reduced [24, 25]. CNFs and CNTs can also improve the load-transferring efficiency of the matrices through pulling-out behavior and crack-bridging effects at the nanoscale [24, 70, 72]. Figure 11(a)-(c) show typical images representing the pulling-out and crack-bridging roles of CNTs [72], from which it can be seen that the CNTs pulled out from C-S-H had one end standing freely, while the CNTs connecting the nano-cracks remained in the composites. In addition to CNFs/CNTs, GO sheets bridging nano-cracks were also observed (Figure 11d) [120]. According to the shear lag model [121], these nanomaterials trapped in nano-cracks share the external load, meaning that a reduced load is sustained by the matrices, thus lowering the risk of initiation and propagation of cracks and leading to enhanced strength properties.

On the other hand, some researchers hold the opinion that chemical reactions take place between the carboxylic groups attached to GO and C−S−H or Ca(OH)$_2$ during the hydration process (Figure 12) [113], and that this can provide not only covalent bonds that produce stronger interfacial adhesion but also a 3D network structure with an enhanced load-bearing capacity. This proposal is supported by Hou *et al.* [120], who noticed that plain cement showed an obvious characteristic peak of Ca(OH)$_2$ on the Raman

spectroscopy curve that disappeared after the addition of GO, indicating that Ca^{2+} had taken part in a chemical reaction with the oxygen-based groups to form $Ca(HCOO)_2$. In another study [122], based on the results of molecular dynamics simulations, the authors claim that silicate chains in the hydrophilic C–S–H substrate provide non-bridging oxygen sites and Ca^{2+}. This allows the interlayer water to dissociate into Si-OH and Ca-OH, and enables protons dissociated from the functional groups to be transferred to the non-bridging sites in C-S-H, producing carbonyl and Si-OH. Most -COOH groups are de-protonated to COO^-, so that the polarity and hydrophilicity of GO sheets are enhanced and stable COO-Ca bonds are formed. The de-protonated COO^- can also accept hydrogen bonds to form Si-OH in C-S-H, which further strengthens the interfacial connection. However, Lin *et al.* [108] have reported that after hydration for five days, the functional oxygen groups on GO remain unchanged according to results from XRD and FTIR, suggesting that GO is a catalyst rather than a reactant in cement hydration. These authors believe that GO can improve the mechanical properties of OPC-based materials by interlocking the cement hydrates more effectively.

Chen *et al.* [88] simulated the pullout process of graphene from the C-S-H matrix at the atomic scale, and reported molecular dynamics simulation results showing that the pull-out behavior is not governed solely by friction. Due to its 2D geometry, graphene has an additional constant resistance force arising from unbalanced adhesion forces near the cracking (Figure 13). In comparison to other matrixes such as aluminum [123] and polyethylene [124], the bonding between C-S-H and graphene was the weakest. This weaker bond was associated with the water molecules in the C-S-H matrix and the spaces between graphene and C-S-H acting as a lubricant.

In a previous study by the present authors [125], cement-based materials containing 0.018 wt.% and 0.036 wt.% MWCNTs were fabricated and their cohesion and friction angle were measured after 28 days of aging. The addition of 0.036 wt.% CNTs improved the cohesion and friction angle by 24% and 19%, respectively, indicating improved shearing resistance. Further research indicates that this increment can be primarily attributed to enhanced nanofriction. From molecular dynamics simulation results, it was noticed that under shearing, the MWCNTs can work as nano-pins, redirecting the propagation of a crack (Figure 14a, 14b); the internal stress is also concentrated at the MWCNT-matrix interface except at the crack (Figure 15d), resulting in larger cracking with a rougher surface morphology and thus enhanced nanoscale friction. More fracturing energy was needed to give failure of the
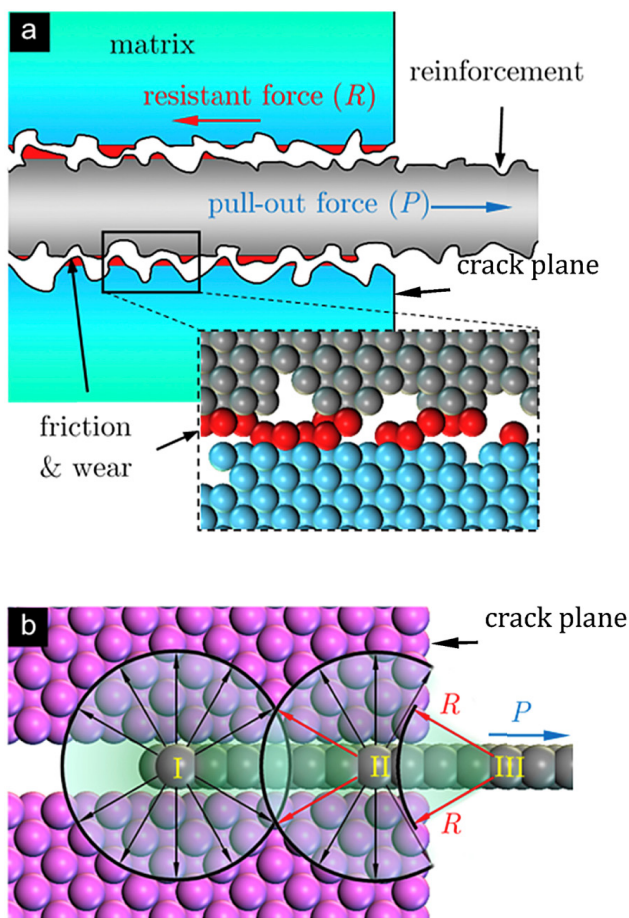

Figure 13: Schematics of (a) a friction-governed micro-/nanofiber pull-out (red areas indicate materials that are friction-damaged during pull-out); (b) crack surface adhesion resistance for ATM during pull-out (circles/arcs indicate the different force equilibria at locations I, II, and III) [88]

composites. The fracture energy of the MWCNT-enhanced matrix was about 67% higher than that without MWCNTs.

3.4 Enhanced durability

CN-CBCs performs better in terms of durability, since its refined pore structure and reduced pore connectivity can hinder the transport of aggressive ions or harmful agents. Due to their properties of impermeability [15, 16], graphene-based sheets can also prevent the migration of aggressive agents. Researchers have observed improved resistance of CN-CBCs to chloride ions, sulfate ions, or carbon dioxide molecules, and decalcification. The improvement in the durability of cement-based materials due to carbon nanomaterials is summarized in Table 3.

This enhanced durability extends the service life of concrete structures that are exposed to different severe en-
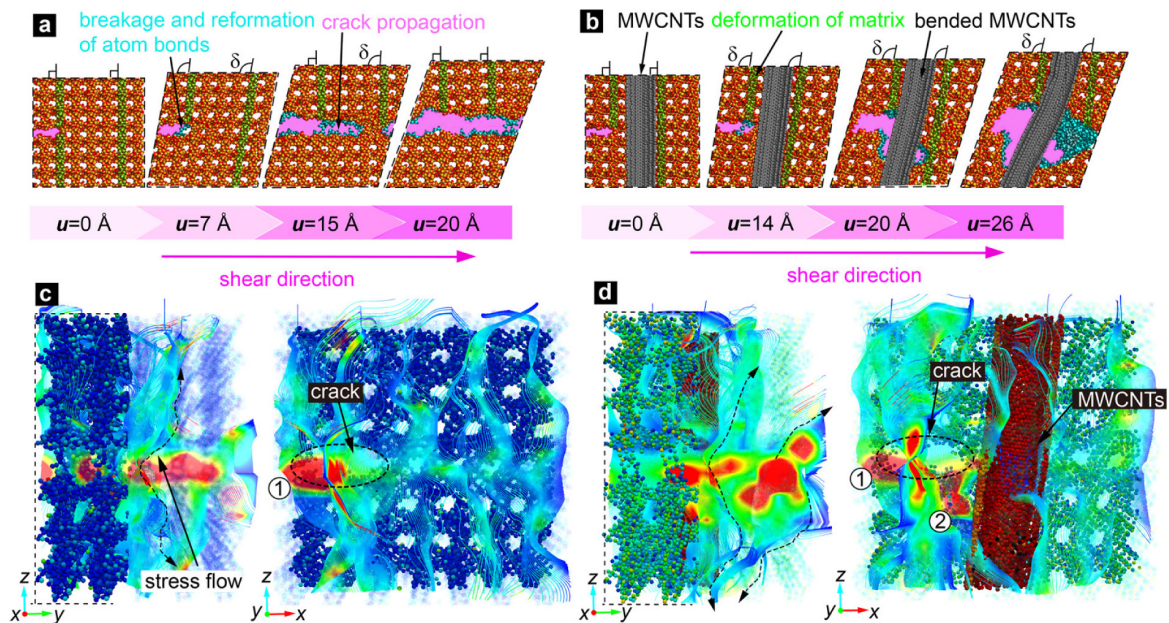
Figure 14: Nanoscale fracturing process of simulated cement matrices under shearing: (a) without MWCNTs; (b) with MWCNTs; (c), (d) the internal stress distributions [125]
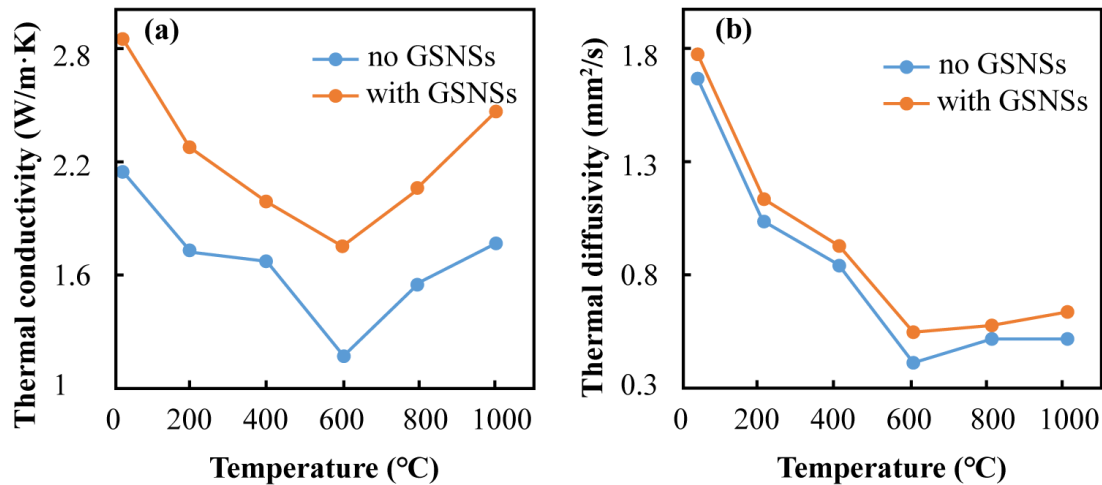

Figure 15: (a) Thermal conductivity and (b) thermal diffusivity of concrete at ambient temperature (25°C) and during exposure to high temperatures [153]

Table 3: Effect of carbon nanomaterials on the durability of cement-based materials

Nanomaterial	Improvement in durability
CNFs	Higher resistance to decalcification [126, 127]
	Higher resistance to free-thaw cycles [128]
CNTs	Higher resistance to chloride migration [129–134]
	Higher resistance to sulfate attack [130]
	Higher resistance to free-thaw cycles [128, 135, 136]
	Higher resistance to carbonation [133, 134, 137]
GNPs	Higher resistance to chloride migration [138–140]
GO	Higher resistance to carbonation [141, 142]

Table 4: Effect of carbon nanomaterials on the electrical conductivity of cement-based materials

Matrix	Nanomaterial	Content	Effect on electrical conductivity	Ref
Paste	CNFs	0.75–6.50 vol.%	Resistivity reduced from about 10^7 to 10 $\Omega \cdot$cm	[69]
Paste	CNFs	0.5–2.0 wt.%	Resistivity reduced from about 1300to 1100 $\Omega \cdot$cm	[146]
Paste	CNFs	0.048 wt.%, 0.10 wt.%	Resistivity reduced from about 2×10^6 to 0.4×10^6 $\Omega \cdot$cm	[147]
Paste	CNTs	0.048 wt.%, 0.10 wt.%	Resistivity reduced from about 2×10^6 to 0.25×10^6 $\Omega \cdot$cm	[147]
Mortar	CNTs	0.20–0.80 wt.%	Resistivity reduced from about 10^{10} to 10^7 $\Omega \cdot$cm	[148]
Paste	CNTs	0.15 wt.%, 0.30 wt.%	Electrical resistance reduced from about 10^8 to 10^6 Ω	[103]
Paste	CNTs	0.1 wt.%, 0.5 wt.%	Electrical resistance reduced from about 3300 to 1200 Ω	[149]
Paste	CNTs	0.5–1.15 wt.%	Resistivity reduced from 10^5 to 10^2 $\Omega \cdot$cm	[150]
Paste	Graphene	0.1 wt.%, 2.0 wt.%	Resistivity reduced from about 10^7 to 10^4 $\Omega \cdot$mm as the addition of graphene increases	[102]
Mortar	Graphene	0.2–1.0 wt.%	Resistivity reduced from 12000 to 4000 $\Omega \cdot$m	[151]
Mortar	GNPs	0.05–13.44 wt.%	Electrical resistance reduced from 100000 to 1 kΩ	[79]
Mortar	GNPs	4.8 wt.%	Resistivity reduced from 35 to 2 k$\Omega \cdot$cm	[54]

vironments as the improvement in durability manifests in strength properties or coefficients. For example, the flexural strength and toughness of cement-based materials containing 0.2 wt.% CNFs have been found to be about 20% and 60% higher than plain cement after decalcification for 125 days [126]. In [129], the addition of 0.03–0.10 wt.% CNTs to ultra-high-strength concrete resulted in a reduction of about 8.8–24.0% in the chloride diffusion coefficient, and a reduction of about 70% in this coefficient for cement was reported when 2.5 wt.% of GNPs was added [139]. The refined pore structure also improves the anti-permeability, and the refined pores inhibit water from freezing, as water molecules are less likely to freeze in pores with smaller volumes, and thus the resistance to free-thaw cycles is increased. Mohammed *et al.* [143] found that the weight loss of cement caused by 540 freeze-thaw cycles declined from 0.8% to 0.25% when 0.06 wt.% GO was added.

During the hydration of cement-based composites, a temperature gradient occurs between the surface and the interior, which changes the matrix strain at different locations and thus creates cracking in the matrices after hardening [96, 144]. Due to the crack-bridging effect, nanofibers can increase resistance to autogenous shrinkage. For instance, the addition of 0.50 wt.% CNTs to cement was found to increase its resistance against autogenous shrinkage by about 42.8% [131], while Blandine *et al.* [145] reported a reduction of about 50% in autogenous shrinkage for cement pastes containing 0.01 wt.% of CNFs.

3.5 Improvements in electrical and thermal conductivity

The extraordinary conductivities of some carbon nanomaterials (Table 1) are associated with the high mobility of electrons and phonons on their surfaces, meaning that both electronic charges and lattice vibrations can travel extremely fast. The results shown in Table 4 indicate that the electrical conductivity of cement-based materials can be significantly improved by adding CNFs, CNTs, graphene or GNPs.

The addition of some types of carbon nanomaterials to cement has also been shown to enhance the thermal conductivity (λ). In [67], CNTs enhanced OPC pastes were fabricated with addition ratios of 1.0, 3.0 and 5.0 wt.% and the composites were shown to have values of λ of 2.50, 2.83, and 2.65 W/m·K, respectively, *i.e.* about 58.0 %, 79.2 %, and 67.8% higher than those of plain OPC (λ = 1.58 W/m·K); based on these results, a novel self-deicing road system using solar energy was developed. Xu *et al.* [152] improved the heat transfer efficiency of cement by 42.5% by adding 0.26 wt.% paraffin/diatomite/CNTs. The thermal conductivity increased to 1.75 from 1.23 W/m·K, and cement enhanced by paraffin/diatomite/CNTs showed faster heat storage and release rates. Chu *et al.* [153] found that the value of λ for concrete containing 0.1 wt.% graphene solfonate nanosheets (GSNSs) was increased by 32.6%; this increment remained at 19.2% to 50.9% even when the temperature was increased to 1000°C (with a maximum increment at 600°C, Figure 15a), leading to increased thermal diffusivity (6.8–27.6%, Figure 15b). In [154], it was reported that the surface temperatures of cement containing
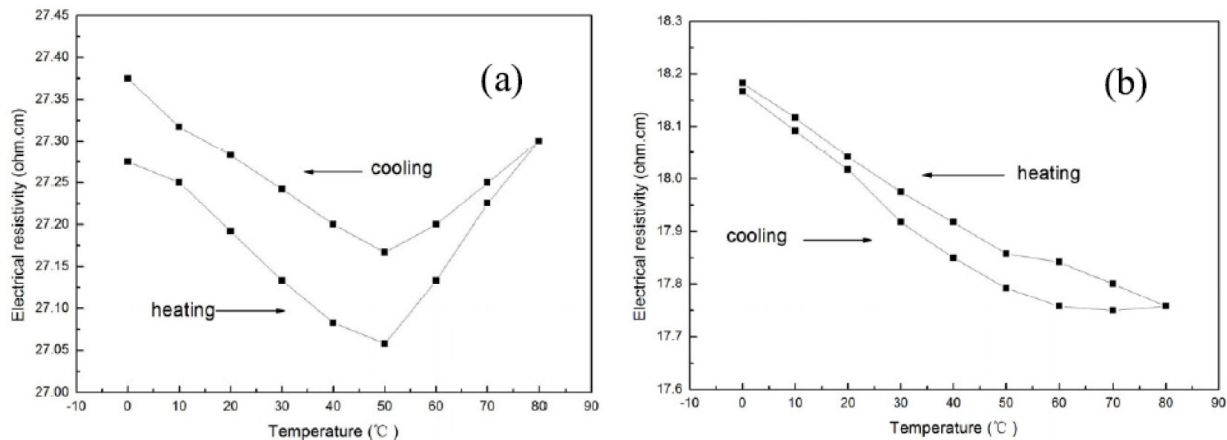
Figure 16: Resistivity-temperature characteristics during the heating and cooling of a cement paste containing (a) 0.4wt.% CNFs; (b) 0.4wt.%CNFs and 1.5wt.% CNTs [160]

expanded graphite donated paraffin and GNPs donated paraffin were lower than for plain cement, indicating an improved thermal energy storage capacity. In a study by Pisello *et al.* [155], CNTs, CNFs and GNPs were added into cement at a mass ratio of 0.25 wt.%, and GNPs were found to perform the best in terms of enhancing thermal conduction (with an increase of around 37.5%), while the other two types of carbon nano additives improved the thermal conduction by about 16.7% (CNFs) and 33.3% (CNTs).

3.6 Improvement in functional properties

When subjected to mechanical strain, CN-CBCs deforms and the thickness of the insulating regions between adjacent carbon nanomaterials is altered, causing changes in the contact resistance at nanoparticle junctions and thus in the electrical resistance. When microcracks start to grow, the percolation branches may be cut off, resulting in a sudden sharp change in the electrical resistance of CN-CBCs. These interesting observations form the basis for the use of CN-CBCs to provide smart functions [23]. In [156], CNFs enhanced cement that could detect the internal strain and damage of concrete under compression was fabricated. Coppola *et al.* [149] produced a self-sensing cement by adding CNTs that could be used to monitor concrete structures subjected to static, dynamic or impact loads, as the maximum change in the electrical resistance of the composite matched the peaks in the external load. Yoo *et al.* [150] found that compared with CNFs and graphene, CNTs provided cement with the best self-sensing capacity with minimal noise, and these authors developed a cement-based sensor with a gauge factor of 113.2 for changes in stress, much higher than com-

mercially available strain gauges. Le *et al.* [54] illustrated the damage-sensing capability of GNPs-cement composite by testing the electric potential across prisms with a known notch depth. Pang *et al.* [157] developed cement-based materials that could sense strain and damage by adding GNPs; the electrical resistance of the composites was found to decrease with increasing strain, and the normalized resistance could be described using a bilinear curve with a kink at about 400 microstrains.

CNT-cement composites can also be adopted to develop environmental monitors, as their electrical conductivity varies with moisture, chloride concentration and temperature. Jang *et al.* [158] found that the electrical conductivity of CNT-cement increased by about 300% when the volume fraction of moisture (by cement volume) was increased by 39%. In [159], it was reported that the electrical conductivity of water-saturated cement mortars containing 0.3 wt.% and 0.6 wt.% CNTs was 0.95 mS/m and 53.6 mS/m, whereas mortars with the same addition of CNTs in dry conditions had electrical conductivities of 0.40 mS/m and 43.7 mS/m. In this study, the electrical conductivity of plain mortar increased linearly with increasing chloride content at a maximum rate of 0.12 mS/m per weight content, while that of the CNTs enhanced mortars increased as a quadratic function where the maximum rates of increase were about 0.34 mS/m and 2.37 mS/m per weight content, respectively. Qin *et al.* [160] found that the electrical resistance of cement containing 0.40 wt.% CNFs declined gradually (from about 27.23 Ω·cm to 27.05 Ω·cm) as the temperature increased from 20°C to 50°C, whereas a continuing increase in temperature (to 80°C) caused the electrical resistance to increase again, and that this variation was reversible during the cooling process (Figure 16b). In [160], it was also found that the co-existence of CNTs
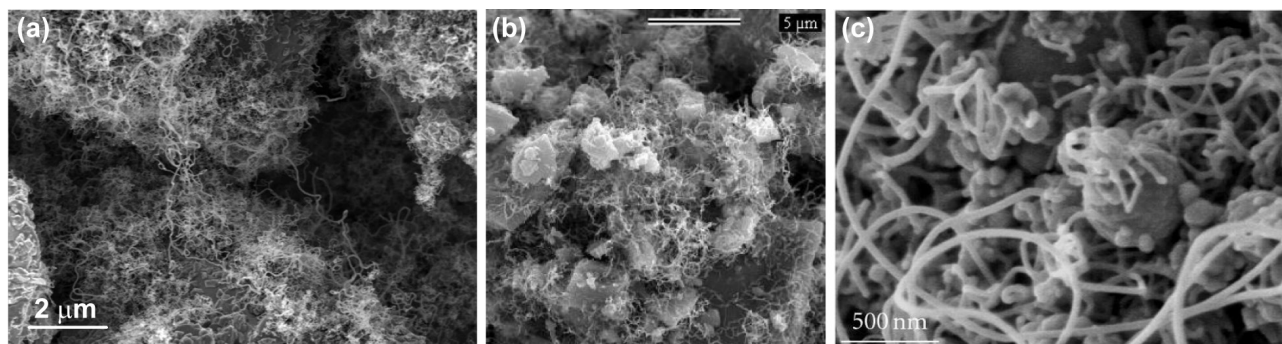
Figure 17: (a) CNFs grown on clinker [163]; CNTs grown on (b) cement clinker [164]; (c) silica [165]; the nano-hybrids in this figure were fabricated with the conventional CVD method

and CNFs in cement pastes resulted in a continuous decrease in resistance as the temperature increased from 20°C to 80°C (Figure 16b), and that the temperature sensitivity of composites containing 0.40 wt.% CNFs and 1.5 wt.% CNTs was about four times that of composites containing only 0.40 wt.% CNFs.

4 Challenges and future work

In addition to their improved hydration reactions, microstructure, mechanical properties, durability, electrical/thermal conductivity and functional properties, CN-CBCs also have sustainability benefits. Firstly, with a proper design, the incorporation of carbon nanomaterials reduces the cement content in the composites while still maintaining their engineering properties [101]. Secondly, their increased durability reduces the mean annual consumption of cement, since the service life of novel buildings is expected to be longer [25]. Thirdly, innovations in the fabrication of carbon nanomaterials, and particularly carbon nanotubes, have started to use carbon atoms from greenhouse gases such as carbon dioxide [161], which can help to reduce carbon dioxide emissions to the atmosphere. The large-scale application of CN-CBCs in civil engineering would provide a way to reduce greenhouse gas emissions.

However, some challenges remain in terms of the large-scale usage of CN-CBCs. Firstly, the preparation procedure needs to be simplified and improved, as the ultrasonication treatment is time-consuming and hard to control. Preparing aqueous solutions of carbon nanomaterials takes between several minutes and several hours (Table 2), and mixing the suspensions with cement may cause the re-agglomeration of nanomaterials. To solve the issue of the dispersion of CNTs and CNFs, one solution

that has been put forward is to manufacture CNTs/CNFs and the cement/mineral admixture as a whole by growing CNTs/CNFs in situ on the cement/mineral particles [162]. Figure 17 presents representative SEM images of CNFs or CNTs grown on grains of cement clinker or silica. These nano-hybrids have been used as alternatives to OPC to create good dispersion of CNFs or CNTs, and provide strong CNF/CNT-cement bonding for better enhancement. Grains of fly ash and silica fume can also provide substrates for the growth of CNTs [162]. Since nano-hybrids have reduced surface energy, they can be premixed with cement powders, allowing the attached mineral grains to participate in the pozzolanic reaction; as a result, CNFs or CNTs would be dispersed in the matrix individually. This offers a new method for producing CN-CBCs at an industrial scale, although more studies are needed to answer the following questions: (i) will the fabrication process tailor the nanomaterials into smaller fragments? (ii) will the nano-hybrids still provide improvements in the functional properties? (iii) are these nano-hybrids chemically stable when they are premixed with OPC? and (iv) is it possible to attach 2D carbon nanomaterials to the mineral grains, and if so, how? The SEM images in Figure 17 show that the mineral grains are at least partially surrounded by CNFs/CNTs (Figure 17c), which may provide a barrier to retard the pozzolanic reaction. If this is the case, both the dispersion of carbon nanomaterials and the hydration of the composites would be hindered.

Secondly, even if the fabrication issue could be addressed, the current cost of commercially available carbon nanomaterials remains a serious concern. Due to the novelty and complexity of nanotechnology and the equipment used to fabricate carbon nanomaterials [9, 15, 45, 166, 167], their prices are prohibitively high. For example, the current price of commercially available GO nanosheets is about 150~270 dollars per gram [168], which is about 20~30 times that of nano-Al_2O_3, and about 200~350 times

that of nano-Fe$_2$O$_3$ [169]. The costs of nanotechnology are expected to fall over the coming years as large-scale manufacturing technologies improve and the production of nanomaterials increases [18, 170]. However, even with a large reduction in price, carbon nanomaterials are most likely to be used in nice applications. Hence, cost reduction should be one of the main aims of research.

Thirdly, in civil engineering, Portland cement systems are often exposed to various complex environments, and thus numerous field trials are required before using CN-CBCs in construction sites, especially for monitoring purposes. The effects of factors such as moisture, temperature, the content of nanomaterials and even the geometry size/shape of the concrete structures on the accuracy of the monitoring results need to be fully understood in order to calibrate the instruments. An appropriate intelligent monitoring system should also be established to make use of the self-sensing capacity of CN-CBCs.

Finally, the effects of nanomaterials on the natural environment is hotly debated [1]. For example, CNTs have been unambiguously identified as the components of notorious PM$_{2.5}$ particles [171, 172]. Typical potential problems include the release of nanomaterials into groundwater or the airways via the generation of dust and exposure to potentially harmful materials. Therefore, more research and practical efforts are needed in terms of smart design and planning so that potential damage to the environment can be avoided.

5 Conclusions

Nanotechnology innovations have demonstrated the potential of carbon nanomaterials in improving the physical and mechanical properties of OPC-based composites. Studies have reported the significant improvements due to a small amount of carbon nanomaterials (CNFs, CNTs, graphene, GNPs, GO, rGO) in the hydration behavior, strength, durability, and electrical/thermal conductivity of cement-based materials. Carbon nanomaterials may allow cement-based materials to carry out smart functions like stress/damage-sensing, and CNT-cement composites can be used to monitor variations in moisture, chloride concentration and temperature. Both of these enhancements are associated with the unique material properties and morphology characteristics of carbon nanomaterials themselves. The application of carbon nanomaterials in the cement industry could also help to reduce greenhouse gas emissions in the atmosphere, and may provide sustainability benefits.

Nevertheless, certain challenges hinder the large-scale utilization of CN-CBCs. Firstly, the fabrication procedure needs to be simplified and improved, since the ultrasonication process, the most widely used method to obtain well-dispersed carbon nanomaterials in cement, is time-consuming, and the risk of re-agglomeration of nanomaterials is high. Advances in CNFs/CNTs-cement nanohybrids offer new ideas for producing CN-CBCs at the industrial scale, although some concerns remain. Secondly, the current cost of commercially available carbon nanomaterials is still a serious concern, and cost reductions should be one of the research purposes. Thirdly, field trials are required before CN-CBCs are used, and intelligent monitoring systems are needed when CN-CBCs is used for monitoring purposes. Finally, the effects of nanomaterials on the natural environment are unclear, and efforts need to be made to design CN-CBC-related engineering projects in environmentally friendly ways so that potential damage to the environment can be avoided.

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