

REVIEW

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Carbon-based nanomaterials engineered cement composites: a review

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Abstract

Carbon-based nanomaterials (CNMs) have been extensively used to modify cement matrix thanks to their extraordinary specific surface area, high aspect ratio, and high strength and modulus. This review focuses on the current status of research on CNMs modified cement composites, especially the progress made in the past decade (from 2011 to 2021). At first, the primary properties of typical CNMs used for manufacturing cement composites, the treatments used to effectively disperse CNMs in water and cement matrix, and the corresponding characterization methods are reviewed. And then, the effects of introducing CNMs on the properties of cement composites (both fresh and hardened) are also discussed in this work. Finally, the knowledge gaps and remaining challenges for future work are discussed.

Keywords: Cementitious composites, Carbon-based nanomaterials, Dispersion, Cement hydration, Rheology properties, Reinforcing mechanisms

Introduction

Cement concrete is the most widely used man-made material in modern civil engineering because of the low cost and long service time [1–3]. Typically, it is regarded as a type of material with high compressive strength and durability [4, 5], however, the inherently quasi-brittle behavior (e.g., poor tensile strength and crack propagation) has limited its structural applications [6–9]. Furthermore, the cement or concrete industry is high energy consumption and has a substantial environmental footprint [3, 10]. It has been reported that the global cement production was around 4.5 billion tons and the CO₂ emission was reached be approximately 1.45 Gt in 2019 [3, 11]. In 2020, the energy consumption of the cement industry in China was estimated at approximately 349.4 tons [10, 12]. These years, attempts have been adopted to develop high-performance concrete or low-carbon cementitious materials [12–14], such as partially replacing cement with supplementary cementitious materials

(SCMs) [13, 15], the application of some new cementitious binders [9, 16], and using nanomaterials to modify cement matrix [5, 17], etc. Among them, the ultra-fine particles-nanomaterials, show great potential to increase the density of microstructure and finally improve the mechanical and durability properties of cementitious composites.

Advancement in nanotechnology and nanomaterials over the past decade has provided invaluable opportunities to improve the microstructure of cementitious composites at the nanoscale [5, 18]. Typically, the introduction of nanomaterials at a very small dosage can result in a significant improvement in the performance (e.g., mechanical, chemical resistance, and transport properties, etc.) of cement-based materials [12, 19, 20], with mechanisms of nano-filling [21, 22], nucleation effect [23, 24], and pozzolanic reactivity (nano-SiO₂) [25, 26], etc. Carbon-based nanomaterials (CNMs), including carbon nanotubes (CNTs) [27, 28], carbon nanofibers (CNFs) [29, 30], graphene [31], and graphene oxide (GO) [32], are very promising candidates as additives in the cement matrix [24, 31, 33–35], which are abundant in nature and have already achieved industrialized mass production.

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For instance, the annual production of typical CNTs in China is approximately 500,000 tons. Currently, the price of CNTs is in the range of 80–120 RMB/kg, depending on the quality and number of walls, while the prices of graphene and GO are expected to be in the range of 400–450 RMB/kg and 350–400 RMB/kg in near future, respectively (<http://www.nanotubes.com.cn>). Generally, the addition amount of CNTs, graphene, and GO (by weight of cement) are 0.01–0.15 wt% [30], 0.01–2.5 wt% [36], 0.01–1.0 wt% [37], respectively. As such, it can be estimated that the addition of 0.01 wt% CNTs, graphene, and GO could increase the cost per ton of cement in concrete production by approximately 8–12 RMB, 40–45 RMB, and 35–40 RMB, respectively. According to the published literature, the addition of 0.01 wt% GO can increase the 28-d compressive strength of cement composites by about 20–30% [37], thus, it can be estimated that the cost of cement reduces by approximately 130 RMB/ton for equivalent strength (the strength of GO/cement-42.5 has roughly the same strength with cement-52.5), more than enough to cover the expense for GO addition. This could trigger a substantial economic benefit and alleviate the undesirable impacts of CO₂ emission on the ecological environment.

Unfortunately, although the application of CNMs showed great potential in cement modification, their broad application is still limited due to the poor dispersion quality, as well as the controversial understanding of the effects of CNMs on cement hydration [20, 24, 27]. Additionally, basic mechanisms for cement reinforcement of these CNMs are still under debate [20, 22, 24, 38, 39]. To this end, it is urgent to review the current knowledge related to the use of CNMs in cement composites and accelerate their practical applications. It is believed that these gaps fundamentally stem from the failure to thoroughly address the following questions: (i) how to

quantitatively assess the dispersion quality of CNMs in a cement matrix; And (ii) what types of CNMs have nucleation effect and significantly affect cement hydration. In this context, the properties of CNMs used in cement materials are introduced at first. Then the different dispersion methods employed to manufacture cement composites and the current evaluation methods are summarized. Next, we discuss the hydration and rheological properties of a fresh mixture for a better understanding of the influence of admixed CNMs in a cement hydration system. Finally, the influences of CNMs on the mechanical and durability properties of hardened cement composites are reviewed.

Properties of CNMs and their morphology

In this review work, we only discussed one-dimensional (1D) nanofibers (CNTs and CNFs) and two-dimensional (2D) nanosheets (graphene and GO), the properties of which are presented in Table 1 and Fig. 1, because they are the most studied CNMs in enhancing cement materials during the last decade [19, 20, 50–54].

CNT (or CNTs) has a 1D concentric tubular structure with a hexagonal arrangement of carbon atoms and they were firstly reported by Iijima in 1991 [55]. The quality, property, and production of CNTs were continuously improving since then. The diameter and length of CNTs are typically in the range of 1–100 nm and 1–100 μ m, respectively, resulting in a very high aspect ratio and thus severe entanglement with each other [56–58]. These physical crosslinking, together with Van der Waal's interaction between CNTs, making their dispersion very challenging in water or cement matrix [28, 59]. It is well known in the CNTs community that, for a given dispersion method, the dispersion quality is highly dependent on the CNTs tortuosity and aspect ratio, both of which largely determine the entanglement degrees [59, 60].

Table 1 The primary properties of CNMs used for preparing cement composites

Component	CNTs	CNFs	Graphene	GO
Diameter/thickness (nm)	0.4–2.0 (SWCNTs) ^a 1.0–100 (MWCNTs) ^a	0.5–100	~1	~0.67
Aspect ratio	1000–10,000	100–1000	600–600,000	1500–45,000
SSA ^a (m ² /g)	20–1315	100–1000	700–1500	2000–2600
Elastic modulus (GPa)	>1000	6–200	>1100	>300
Tensile strength (GPa)	50–200	400–600	~125	>112
Resistivity (Ω ·cm)	~10 ⁻²	0.1	-	-
Thermal conductivity W/(m·K)	~6600	20–1950	-	-
Special applications	For structural health monitoring [28, 40–43].		Electromagnetic protection [31, 44, 45].	Accelerating cement hydration [20, 24, 39, 46].

^a SWCNTs and MWCNTs are single-wall CNTs and multi-walled CNTs, respectively. SSA is a specific surface area

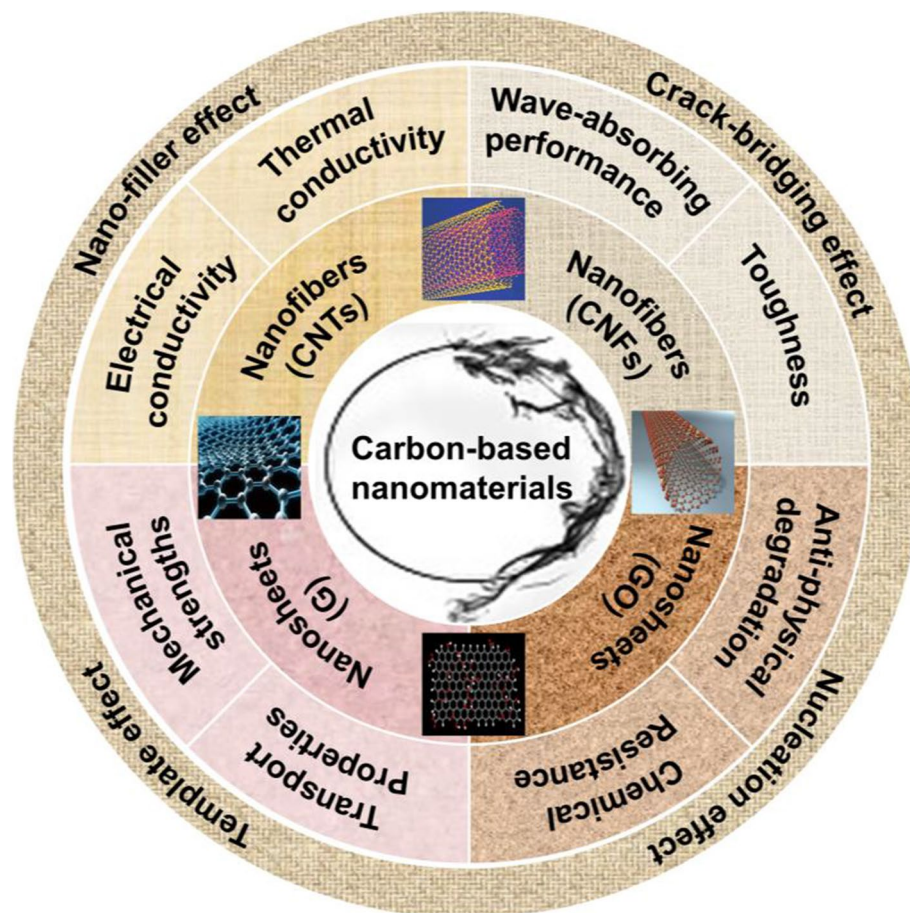


Fig. 1 The roles of the typical 1D nanofibers (CNTs and CNFs) and 2D nanosheets (graphene and GO) in cement composites [19, 22, 28, 34, 39, 45, 47–49]. G represents graphene

CNFs are cylindrical nanostructures with graphene layers arranged as stacked cones, which can be viewed as fiber-shaped nanomaterial with a length ranging from 50 nm to 200 nm [45, 61]. CNFs have similar geometrics and physical properties with CNTs, yet with much lower price (generally one-fifth of the price of CNTs), and thus also extensively employed as an additive for cement matrix modification [30, 62]. Owing to the potential micro (and nano) improvement of the interfacial transitional zone (ITZ), CNFs demonstrate a great potential to improve the mechanical strengths of cement materials [34]. Additionally, CNMs (especially graphene, CNTs, and CNFs) demonstrate great potential to develop smart cement composites in the future.

Strictly speaking, graphene is a one-atom-thick flat nanosheet of sp^2 bonded carbon atoms, it is arranged in a honeycomb-like lattice [63–65], which is the mother of all graphitic materials, such as fullerenes, CNTs, and graphite [64, 66]. Note that, most of the excellent physicochemical characteristics of graphene, such as excellent

strength, high modulus, and outstanding electrical conductivity, are in-plane properties, essentially resulted from the in-plane sp^2 carbon-carbon bonds [63, 67]. Interestingly, because of the extremely small thickness of graphene, it can also be considered to be soft matter. According to the previous reports, GO has a similar bending stiffness with graphene (assuming a similar thickness), is in the order of 2 kT [63, 68, 69], meaning that these single-layer 2D materials can be easily buckled and a considerable amount of wrinkles will be naturally formed [63, 64, 66]. Such features could affect the interaction between graphene (and its derivatives) with matrix materials [36, 59, 70, 71]. Because single-layer graphene with atom thickness and perfect crystal structure, which cannot be yielded at a large scale currently, the commercially available materials claimed as “graphene” are actually multi-layers thin graphite [63, 64, 68]. They are mostly synthesized by exfoliation of graphite either by intercalation followed by mechanical shearing [63, 64, 72]. According to classical plate theory, the bending

stiffness of plates is inversely proportional to the cubic thickness [63–65]. Implying that the bending stiffness of multi-layer graphene with ~30 nm (corresponding to 100 layers), which is six orders of magnitude higher than that of the single-layer graphene [63, 64, 68, 72]. Such huge different bending stiffness could significantly change graphene-cement interactions.

Another strategy to synthesize graphene is to chemically reduce GO [64, 73, 74], which can be readily obtained by oxidation of graphite in strong acid, as firstly reported more than a century ago [64, 68, 72, 74]. Fig. 2 illustrates the GO synthesis process. In short, the gap between adjacent layers in graphite greatly increased due to the functionalization of graphene, mainly by carboxylate and epoxy groups, thus effectively decreased Van der Waal's interaction between graphene layers, allowing easy exfoliation into single layers in water [64, 65]. Therefore, single-layer GO dispersion with high quality was easy to prepare. More importantly, its oxygen-containing functional groups fancy involving chemical/physical interactions [20, 24, 75], and then enhancing the bond strength [73, 76]. Based on these characteristics, it has been generally accepted that GO can accelerate cement hydration [20, 53, 75, 77, 78], improve the polymerization

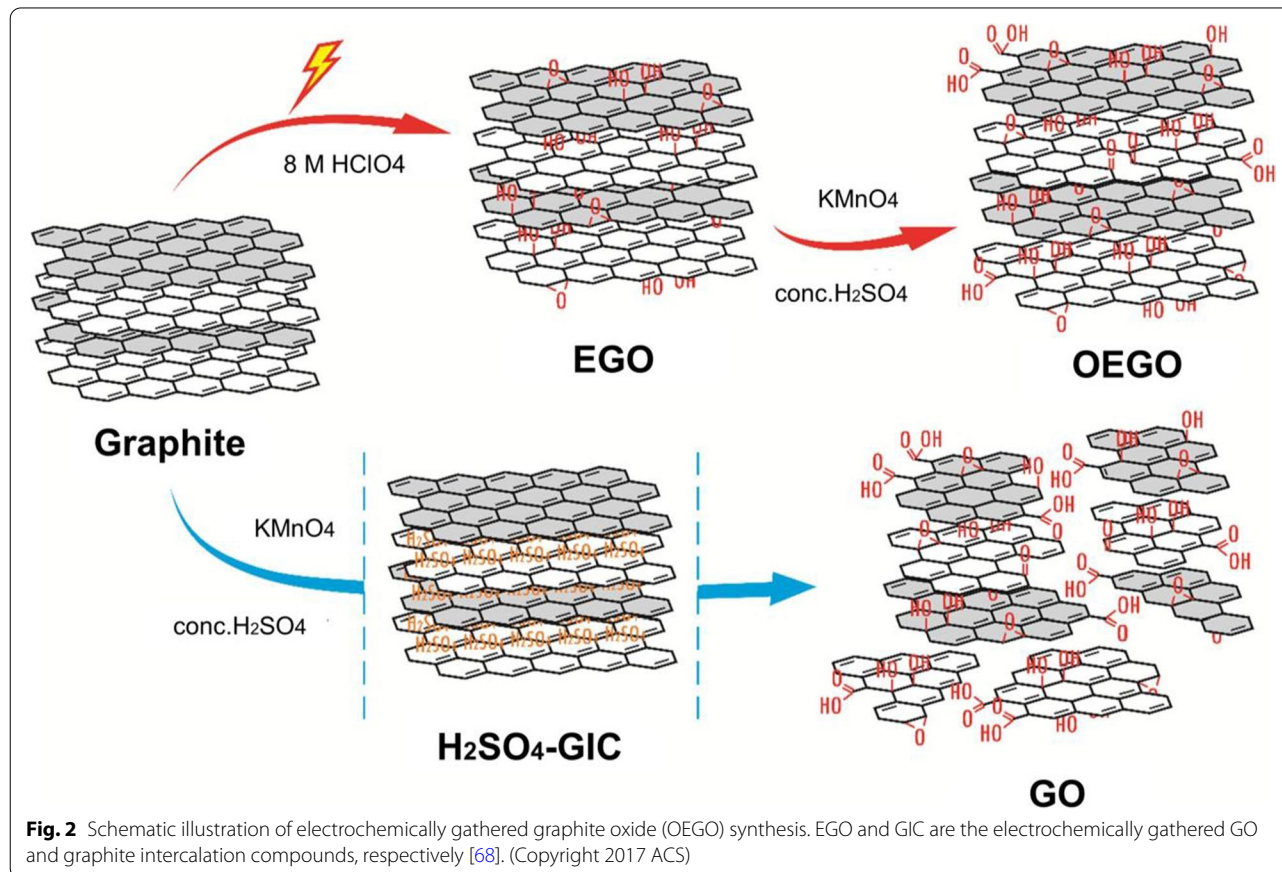
degree of cement hydrates [20, 24], and regulate the formation of hydration crystals [46, 79, 80]. With these advantages, GO has been the most studied CNMs for the modification of cement materials during the past decade (as depicted in Fig. 3).

Dispersion and characterization of CNMs in water and cement matrix

Challenges for CNMs dispersing

As mentioned above, the possible agglomeration of CNMs in the cement matrix are defects and negatively affect the properties of cement composites [19, 28, 53, 81–83]. That is, a high dispersion quality of CNMs is a prerequisite for the effective reinforcement of cement-based materials [8, 44]. However, it is still very challenging to realize an excellent dispersion of CNMs in the cement matrix, since the strong Van der Waal's attraction between CNMs, as well as the complex electrolytic environment provided by cement pore solution (in the presence of divalent ions) [29, 82, 84, 85].

Table 2 summarizes the dispersion methods of CNMs in the water and cement matrix. According to the published literature, acid treatment and surfactant wrapping are generally the most used strategies to overcome



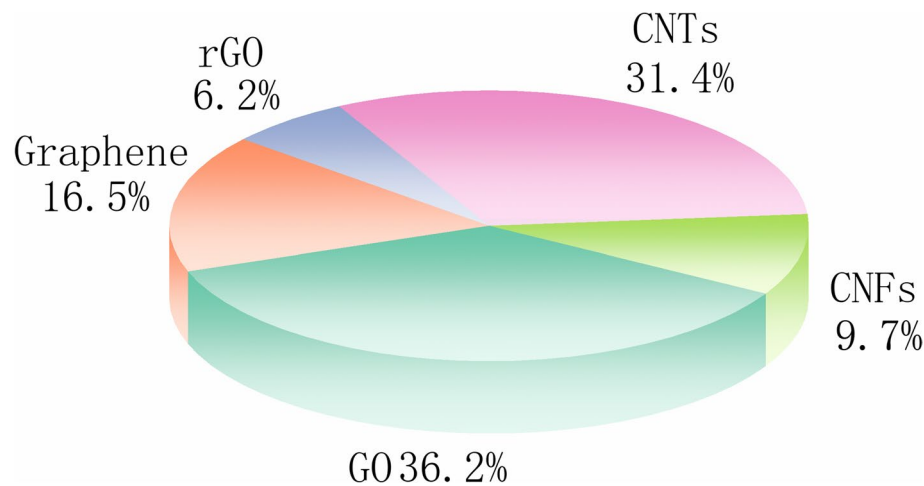


Fig. 3 The relative number of published articles of various CNMs used for manufacturing cement composites, rGO is reduced GO. (Data collected from Google Scholar from 2011 to 2021, total of 14206 published literature)

Table 2 Dispersion methods of CNMs in water and cement matrix

Dispersion methods	System	Description	Ref.
Ultrasonic dispersion	Water	Ultrasonic waves/energy can cavitate and exfoliate the CNMs.	[28, 86, 87]
Acid treatment	Water	The strong steric hindrance effects can separate CNMs from charged ions.	[38, 65]
Surface modification	Water/cement pore solution		[82, 84, 85, 88]
Mechanical dispersion	Mechanical agitation	Applying shearing force created by mechanical friction, collision, and crush on CNMs.	[19, 51, 89–91]
	Ball milling		
Integrated dispersion method	Cement matrix	The combined usage of the aforementioned methods.	[21, 22]
Silica fume or nano-silica	Cement matrix	Using spherical particles to prevent agglomeration of CNMs.	[84, 85, 94–97]

attractions between CNMs [52, 82, 85, 88, 92]. Specifically, acid can endow charges on the surface of CNMs at the cost of some detrimental effects on their structure [65], while surfactant wrapping can make CNMs more compatible with water, with the mechanism of either charge repulsion or steric repulsion depending on the molecular structure of surfactant [29, 82, 85, 88]. However, the high ionic concentration of cement pore solution (high alkalinity and di-covalent Ca ions), could severely screen charge repulsion interaction [84, 98]. Therefore, considering the highly complex electrolyte environment of pore solution in cement hydration, the achievement of uniform dispersion of CNMs in cement matrix is still very challenging. Since CNMs are typically dispersed in water before mixing with cement, this review work summarized CNMs dispersion in water, cement pore solution, and cement matrix, separately, to clarify the main mechanism and related colloidal behavior in each step.

Dispersion of CNMs in water

At present, admixtures are indispensable constituents in modern cement concrete applications [5, 12, 36, 37, 44, 99]. Surface active chemicals, including superplasticizers, shrinkage reducing admixtures, and air-entraining surfactants, etc., are prepared in the form of an aqueous solution before mixing with cement powder [82, 84, 85, 100]. Along with this idea, the preparation of uniform aqueous dispersion of CNMs can facilitate their practical applications [9, 101].

Currently, the dispersion methods of CNMs in water mainly include mechanical shearing and ultrasonication, and surface physiochemical modification [19, 91], as presented in Table 2. For a given material, the dispersion capability of shearing is mainly dependent on the shearing stress, which in turn, are determined by the shearing rate and viscosity of the dispersion [51, 52, 89]. Since the viscosity of CNMs dispersion is typically in the same range of water [102], the maximum shearing

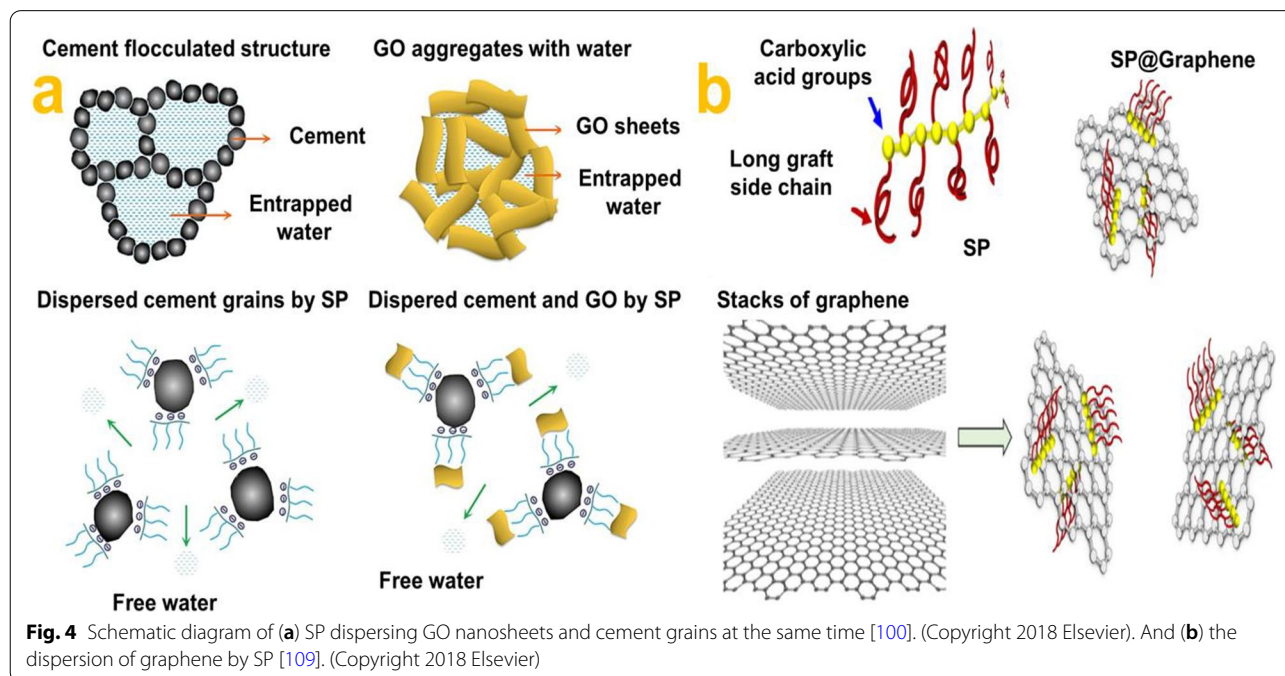
stress and dispersion quality that can be realized is very limited. Ultra-sonication is a process based on cavitation (about 200 W and the frequency of 30 kHz), with high local energy, and has been extensively employed for CNMs dispersion [21, 22, 28]. The effectiveness of ultra-sonication can be optimized by a proper combination of sonication power and sonication time [19, 21, 22]. Note that, because of the high cavitation energy, the crystal structure and aspect ratio of CNMs may be destroyed and reduced, both of which will decrease the reinforcement efficiency of CNMs [22, 99]. Besides, for a given material and sonication power, the dispersion quality will be saturated with time, as reported by Coleman et al. [103]. Therefore, proper optimization of sonication conditions is required to further promote the dispersion quality of CNMs.

To further promote the dispersion quality, CNMs can be grafted with hydrophilic functional groups, both physically and chemically [81, 82]. GO, which has been extensively used to modify cement matrix past the last decade [20, 24, 77, 82, 104, 105], can be considered as graphene that is chemically grafted with a significant amount of oxygen-containing groups [64]. CNTs treatment by strong acid is also commonly used to facilitate its dispersion in water [38, 65]. As explained above, such a dispersion method relies on the surface charge repulsion, which can be easily screened out by ions if there is any [20]. This means that even CNMs can be well dispersed in water after chemical modification, they might still agglomerate when mixed with cement,

because of the high ionic strength resulted from cement dissolution.

Another surface modification method is to wrap CNMs with surfactants [37, 82, 84, 85, 88, 100]. Broadly, the surfactants can be divided into categories of anionic [82], cation [106], and neutral type [82], all of them have been studied for CNMs dispersion. As matter of fact, organic admixtures, including water-reducing admixtures, air-entraining admixtures, superplasticizers, shrinkage reducing admixtures, are all surfactants that can be potentially employed to disperse CNMs [82, 88, 107]. Polycarboxylate superplasticizer (SP), which is currently the most used surfactant, has been extensively investigated to disperse CNMs and enhance the stability of the resulted dispersion upon increasing ionic strength [82, 85, 88, 100, 107, 108]. As illustrated in Fig. 4, using SP in a GO-cement system can disperse GO nanosheets and cement grains at the same time (Fig. 4a). Similarly, a good dispersion quality of graphene in an aqueous solution can be achieved with the help of SP (Fig. 4b). However, it should be noted that the absorbed surfactant itself could also be stripped off when the ionic strength is high enough [82, 110]. For instance, Zhao et al. [100] reported that the GO could aggregate again when the Ca ions concentration was reached 1 M (NaOH solution) or higher [82].

Interestingly, the stability of surfactants that are wrapped around CNMs in the various electrolyte has been systematically investigated since more than two decades ago in environmental science [80–82, 85, 111],

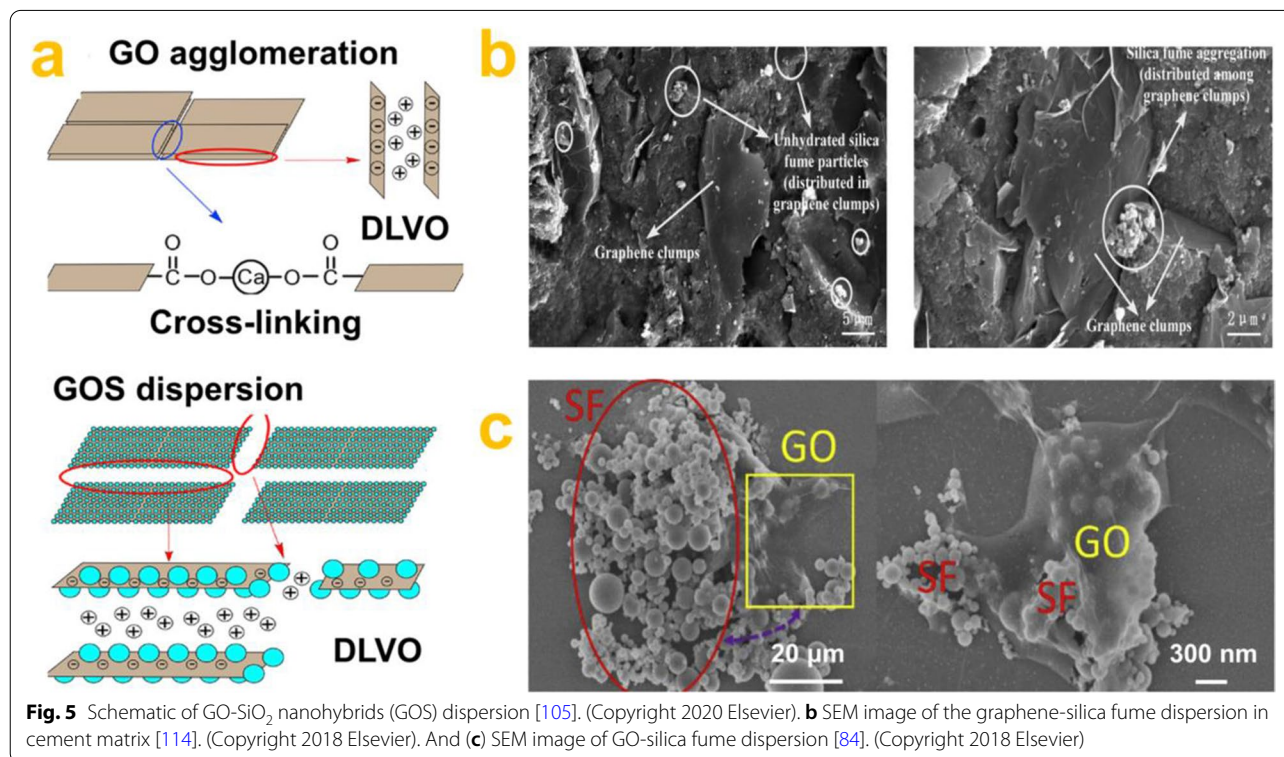


in which, the agglomeration of particles is one of the key research topics. However, the exact chemical structures of most SP are generally confidential, blurring the optimization of the CNMs dispersion. Because SP is synthesized for cement property modification through SP-cement grain interaction, a new surfactant should be designed and prepared specifically for the CNMs dispersion. Moreover, the stability of surfactants for CNMs dispersion still needs to be studied and clarified [85]. As reported by Birenboim et al. [22], the introduction of surfactants can retard the cement hydration and entrap substantial air in cement paste. It has been pointed that caution should be exercised when using surfactants in the aqueous matrix, as it can lead to foaming [12, 22]. Therefore, there might be a trade-off between the positive effects of CNMs and the negative influences of surfactants.

Dispersion of CNMs in the cement matrix

CNMs can also be considered to be an admixture in the form of dry powders, and directly mixed with cement, similar to silica fume, fly ash, and slags [19, 28, 29, 51, 89]. Typically, CNMs are mechanically mixed with cement particles for several minutes to obtain a homogeneous mixture and then mixed with water and other raw materials to manufacture cement composites [16, 20, 24]. For example, as indicated by Mohammed et al. [112],

0.01 wt% GO and cement were mechanically stirred for about 5 min to obtain a uniform mixture, while they failed to achieve good dispersion when the GO amount was 0.06 wt% GO, due to the physical cross-linking and Van der Waal's forces between GO nanosheets. It is almost impossible to dis-entanglement CNMs agglomerations just by normal shear mixing apparatus. Recently, silica fume/nano-SiO₂ with extremely small particle size and spherical particles, have been employed to disperse CNMs in the cement matrix by a pre-mixing process [84, 85, 97, 105, 107, 113], as illustrated in Fig. 5. Because of the high SSA of CNMs, the effectiveness of using silica fume as carriers to disperse CNMs, mainly depends on the available surface area of the carriers. For instance, Kim et al. [115] investigated the effect of silica fume content (0-30%, mass by cement) on the dispersion of CNTs in a cement matrix, and found that 20 wt% silica fume and 0.3 wt% CNTs were mixed for 4 min could facilitate the dispersion of CNTs. We can roughly estimate the maximum concentration of well-dispersed nano-SiO₂ that can be realized by this strategy as follows. Assuming that the silica fume particles with a typical size of 50-300 nm can be well separated and completely covered by a single layer of closely compacted nano-SiO₂ (with a typical size of 4-20 nm), the concentration of nano-SiO₂ in the cement matrix could reach obtain an optimal value. Note that, this method in fact realizes a uniform



distribution of nano-SiO₂ throughout the whole matrix, at the cost of local severe agglomeration specifically at the surface of silica fume. Therefore, such nano-SiO₂ can in principle only modify the local chemistry and micro-structure around silica fume. Also, the pre-mixing time of silica fume and CNMs is another key factor that affects the dispersion of CNMs in the cement matrix. For example, Akarsh et al. [94] and Bai et al. [114] pointed out the GO-cement and graphene-cement should premix for approximately 3 min and 10 min, respectively, to obtain a uniform mixture. A similar pre-mixing time for nano-SiO₂ and CNMs was also reported in other studies [85, 97, 105].

To increase the shearing stress significantly, high-energy ball milling can be applied [52, 92, 93, 116]. For instance, Ghosh et al. [117] proposed that the graphene and cement grains were blended using a planetary ball mill via 30 g Zirconia balls, which is an efficient approach to obtain a homogenous distribution of graphene with cement grains. Jing et al. [92] used X-ray diffraction (XRD) and scanning electronic microscope (SEM) to verify this hypothesis. A similar beneficial role of ball milling on dispersion graphene was reported in another report [89], in which the graphene and cement were dry mixed for 72 h. Chiranjikumar et al. [118] using a high-energy planetary ball mill method (at 500 rpm for 8 h) to disperse GO in the matrix, and found that adding 0.1 wt% GO in 100% recycled concrete could be an alternative way to achieve sustainability in the construction industry.

As discussed above, ball milling provided an alternative method for dispersing CNMs in a cement matrix and showed great practical significance to fabricate CNMs-cement composites [93]. Note that, the ball-milling process can also result in cement powder fining, which increases the reactivity of cement particles [92, 116]. Thus, cautions should be taken when evaluating the true effects of CNMs on the performance of the obtained cement composites.

Dispersion quality assessment

Table 3 summarizes the current techniques are adopted to evaluate the dispersion quality of CNMs in water or cement matrix. As can be seen, much evidence reported the CNMs dispersion quality in water by techniques of UV-vis spectroscopy [82, 99], laser particle size analysis [9, 84], dynamic light scattering [8, 119], zeta potential [82, 109], optical microscope [82, 85], and SEM observation [21, 28, 120, 121]. However, noted that the high dispersion quality of CNMs in water before mixing with cement is not necessarily resulting in high dispersion quality in the cement matrix.

Because cement is highly heterogeneous, including multiple phases and pores at multiple scales, the dispersion quality of CNMs in a cement matrix is very difficult to evaluate [12, 30, 36, 44, 100]. And the extremely low CNMs concentration (e.g., 0.01–0.1 wt%) typically used further makes this task formidable. SEM equipped with energy dispersive spectrometer (EDS) has extensively been used to characterize the dispersion of CNMs in cement matrix [21, 28, 43, 122], although it is difficult to locate and even confirm that it is indeed CNMs due to the complexity of the hydration products. However, SEM cannot achieve quantitative characterization of CNMs dispersion in the cement matrix. The complete evaluation of CNMs dispersion and distribution in cement matrix is critically important for the design and optimization of the CNMs-cement interaction, and effectively promotes the effectiveness of CNMs. Recently, Cui et al. [99] found that the UV-Vis absorbance value of the GO suspension increased from 0.72–0.95 when ultrasonication energy increased from 15% to 60%, indicating that higher ultrasonication energy resulted in a higher degree of GO dispersion. Additionally, they found that the ratio of Raman intensity of D band G band (I_D/I_G ratio) rose with increasing sonication energy. Therefore, the energy input of 30% was selected to obtain a balance between the GO dispersion [99]. This provides new possibilities

Table 3 Techniques are adopted to evaluate the dispersion quality of CNMs in suspension or cement matrix

Methods	System	Description	Ref.
UV-vis spectroscopy	Suspension/ cement matrix	Employing the Beer-Lambert Law to calculate the content of CNMs according to the absorbance.	[4, 82, 99]
Laser particle size		Smaller particle size indicates better dispersion	[9, 84]
Dynamic light scattering			[8, 119]
Zeta potential		Higher zeta potential value (absolute value) means better dispersion	[82, 109]
Optical microscope		Assessment of dispersion based on directly observed dimensions	[82, 85]
SEM			[21, 28, 120, 121]
Transmission electron microscope			[22, 32, 87]
X-ray photoelectron spectroscopy			[22, 24, 86, 105, 107, 119]
Raman spectrum			[86, 120]

for a more refined characterization of CNMs dispersion in the cement matrix. However, such analysis is severely limited by the resolution of the laser point. Again, hydration products including ettringite (AFt), monosulfate (AFm), and calcium hydroxide (CH), all have their own shape factor (geometrically, AFt has nano-needle shape, while AFm and CH have nano-plate shape) [123, 124], which make it very difficult to distinguish them from the added CNMs. For instance, Meng et al. [125] used SEM to locate the distribution of graphene nanoplates, which as matter of fact, could also be AFm. Therefore, the employment of elemental mapping or other complementary techniques is necessary to confirm that the focused materials under SEM are indeed CNMs.

Influence of CNMs on the performance of cement composites

Properties of fresh cement composites

In this review work, the main properties of interest of fresh cement mixture including hydration kinetics and rheology properties, both of which will affect the

subsequent mechanical and durability properties of hardened cement composites.

Despite the substantial research effort devoted to fulfilling the nucleation effect potential of the CNTs, previous reports of CNTs accelerate cement hydration are somewhat contradictory [22, 24, 27, 38], with some studies demonstrating an obvious acceleration effect [20, 24] and others no effects or even retardation [27, 38], as illustrated in Fig. 6. For instance, an investigation was conducted by Sobolkina et al. [38], who indicated that the addition of either 0.25 wt% HNO₃-oxidized CNTs hardly affects C₃S hydration, and they argued that the insignificant effect was mainly due to the limited adsorption sites present on CNTs surface (Fig. 6a). It was hypothesized that some functional groups on the CNTs surface or other CNMs may stimulate cement hydration as the generation of additional calcium silicate hydrate (C-S-H) [38]. Tafesse et al. [27] reported that pure CNTs are not capable of activating or delaying cement hydration, based on the results of nonevaporated water (Fig. 6b), rather, they only provide nano-filler effect in cement composites.

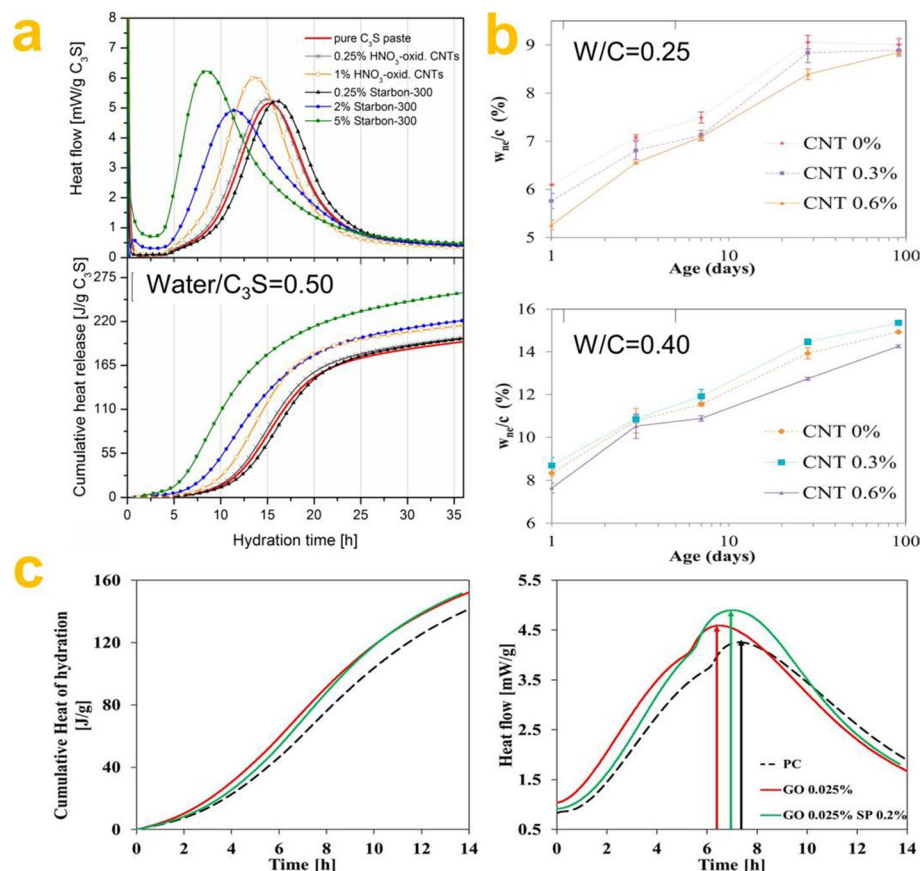


Fig. 6 **a** Isothermal calorimetry results for the C₃S pastes [38]. (Copyright 2016 Wiley). **b** Hydration results were determined indirectly from the nonevaporated water [27]. (Copyright 2019 Elsevier). And **(c)** isothermal calorimeter results for cement paste [24]. (Copyright 2018 Elsevier). SP is a polycarboxylate superplasticizer

In contrast, Jung et al. [28] reported that the surface of the dispersed CNTs can contribute to precipitate cement hydrates. These inconsistent findings may be attributed to the dispersion quality and surface chemical affinity of CNTs. Note that the high surface area of CNTs cannot guarantee seeding effect, as reported by many groups [27, 38, 126]. It has been generally accepted that GO can accelerate cement hydration because of the rich oxygen-containing functional groups on its surface [20, 22, 100]. A recent study found the incorporation of 0.025 wt% GO resulted in an earlier heat flow peak [24], as illustrated in Fig. 6c. A similar accelerating effect of GO on cement hydration was found in other studies [79, 127], in which the introduction of 0.025–0.10 wt% GO can significantly increase the heat flow of cement composites. Unfortunately, direct evidence for the seed effects of CNMs is still missing, which will be elaborated in the following.

Generally, adding CNMs to the cement matrix can lead to an improvement of viscosity (decreased workability), since the super-high SSA of nanoparticles requires more water for surface wetting [5, 31, 36, 44, 100]. The low viscosities of the fresh mixtures have a negative influence on the mixing and casting process and then affect the final mechanical and durability properties [5, 9]. According to the rheological parameters of paste obtained from the Bingham curve [128], the plastic viscosity (η) of the cement mixture ($w/c=0.36$) incorporating 0.03 wt% GO (by weight of cement) was approximately 40% higher than that of the plain cement. Similarly, the admixing 0.3 wt% CNFs resulted in increased plastic viscosity of paste ($w/c=0.20$) by approximately 35% [29].

Surfactants may be an ideal candidate to overcome this issue because of their steric hindrance and electrostatic

repulsion [29, 44, 97, 107], which prevent the agglomeration of cement grains. As provided in Fig. 7, Li et al. [135] found that the introduction of SP significantly decreased the yield stress ($\sim 80\%$) and minimum viscosity ($\sim 70\%$) of cement pastes ($w/c=0.24$) in the presence of graphene (at a dosage of 0.75 wt%). However, in the presence of SP, especially the content over 0.75 wt%, the admixing graphene can hardly influence the yield stress and minimum viscosity of cement pastes. Note that, the admixed CNMs may affect the compatibility between cement materials and surfactants thus affect the rheological properties of cement mixture [29, 136]. In addition, a few studies reported that CNMs can lubricate solid particles in cement composites, which improved the flowability of the mixture [22, 29, 125]. Such knowledge gaps constrain the wider acceptance of CNMs in developing cementitious composites and drive the need for further research to advance the understanding.

Properties of hardened cement composites properties

Mechanical strengths

Mechanical properties of cementitious composites are generally regarded as the most important performance in practical applications [12, 30, 31, 36, 44, 101]. During the past decades, it had been generally accepted that admixing a small dosage of CNMs to cement can result in remarkable improvement in the mechanical strengths (e.g., compressive, flexural, and tensile strength) [20, 28, 32, 114, 128, 137].

Table 4 illustrates the experimental findings collected from the published reports related to the enhancement of CNMs to the mechanical strengths. As can be seen, GO (generally 0.01–0.10 wt%, by weight of cement) is typically

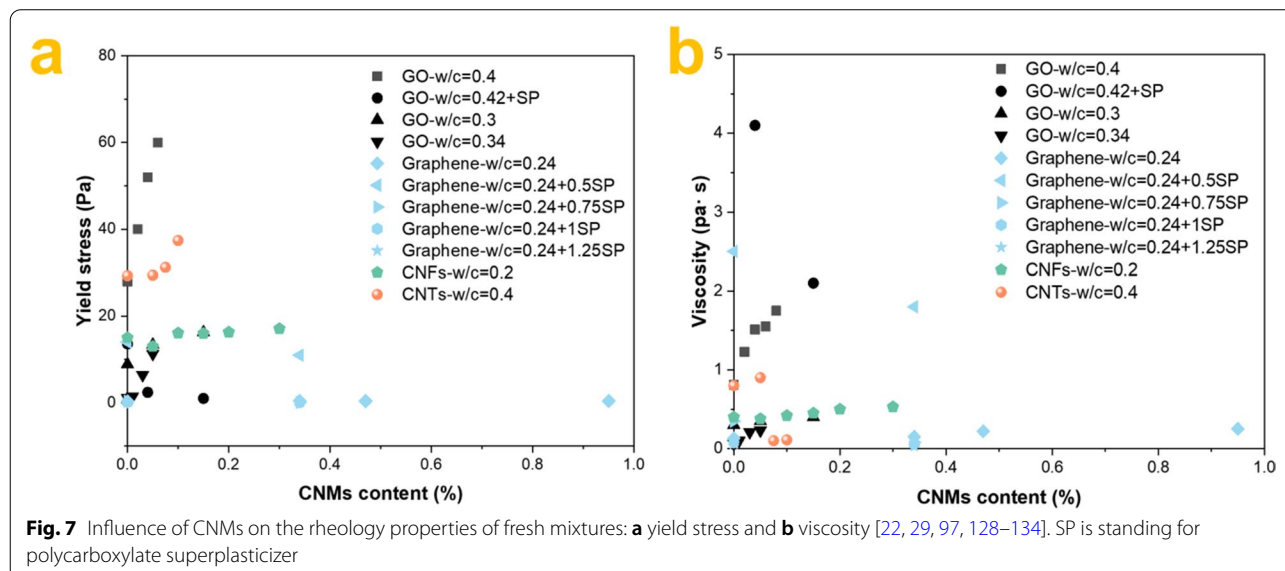


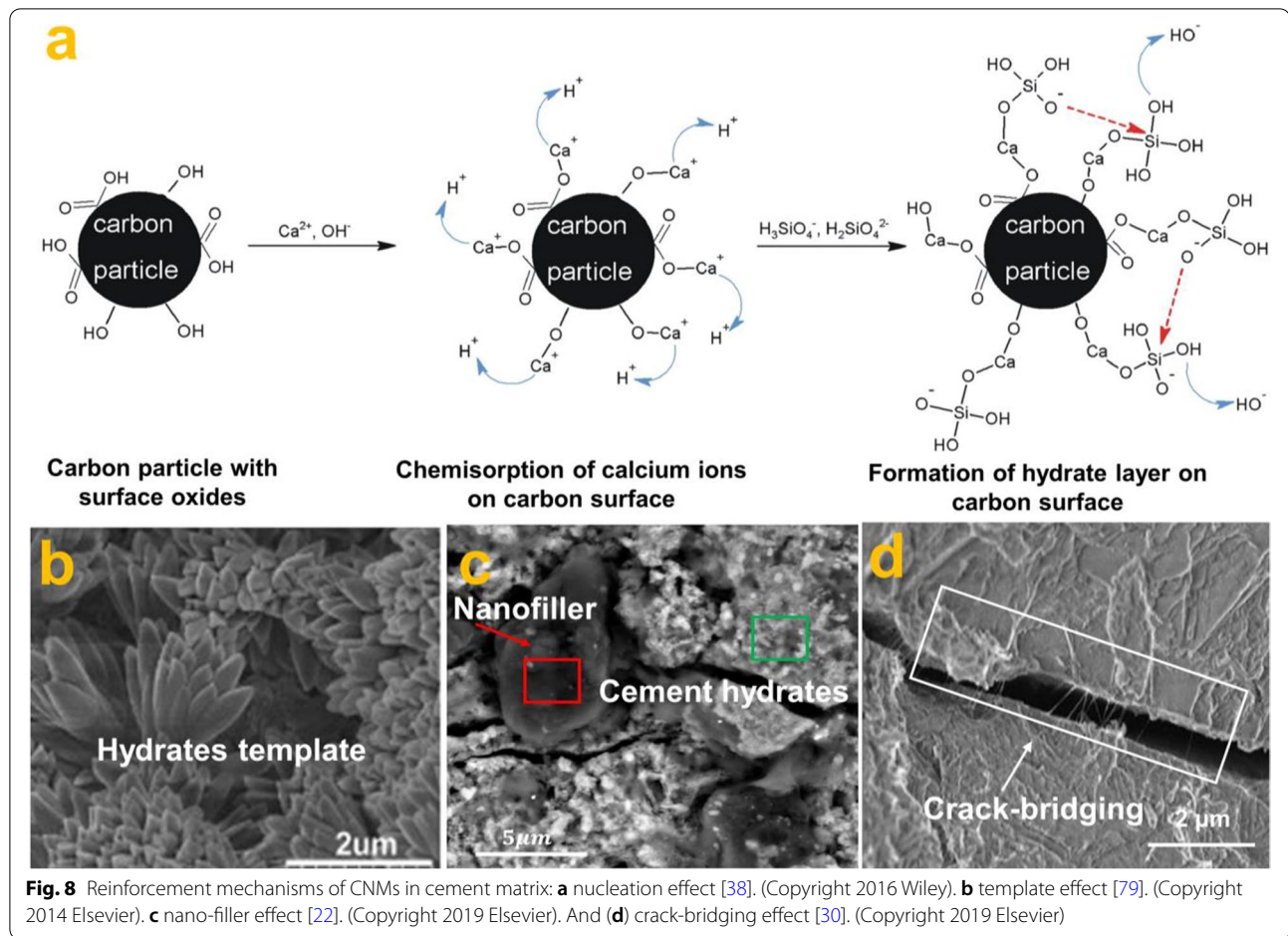
Table 4 Improvement of CNMs to mechanical properties of cement-based materials cured at 28 days

Matrix	CNMs types (by weight of cement)	w/c	Increment in mechanical strengths			Ref.
			Compressive	Flexural	Tensile	
Paste	Graphene (0.05 wt%)	0.35	3-8%	15-24%	-	[138]
Paste	Graphene (0.025 wt%)	0.40	14.9%	23.6%	15.2	[139]
Paste	Graphene (2 wt%)	0.38	-33.3%			[140]
Paste	GO (0.05 wt%)	0.35	29.0%		-	[20]
Paste	GO (0.01 wt)	0.30	10.0%	15.6%	-	[79]
Paste	GO (0.03 wt)	0.30	20.1%	27.3%	-	
Paste	GO (0.05 wt)	0.30	27.5%	30.7%	-	
Paste	CNFs (0.1 wt%)	0.485	-	20%	-	[34]
Paste	CNTs (0.15 wt%)	0.40	14.3%	3%	-	[141]
Mortar	GO (0.022 wt%)	0.42	34.10%	30.37%	33.0%	[88]
Mortar	GO (0.1 wt%)	0.48	27.7%	-	-	[142]
Mortar	Graphene (0.05 wt%)	N.A.	8.3%	15.6%		[143]
Mortar	GO (0.15 wt%)	0.35	13.7%	14.5%		[94]
Mortar	GO (0.01 wt%)	0.37	13.4%	51.7%	47.0%	[80]
Mortar	GO (0.03 wt%)	0.37	38.9%	60.7%	78.6%	
Mortar	GO (0.05 wt %)	0.37	47.9%	30.2%	35.8%	
Mortar	CNTs (0.3 wt%)	0.40	-2.7%	-	-	[43]
Mortar	CNTs (0.5 wt%)	0.60	-1.8%	-	-	
Mortar	CNFs (0.1 wt%)	0.485	6.15	-	-	[34]
Concrete	CNFs (0.30 wt%)	0.20	60.0%	10.1%	55.0%	[29]
Concrete	CNTs (0.002 wt%)	0.23	-1.1%	-	-	[28]
Concrete	CNTs (0.005 wt%)	0.23	5.5%	-	-	
Concrete	CNTs (0.008 wt%)	0.23	-0.8%	-	-	
Concrete	CNTs (0.01wt%)	0.23	-4.9%	-	-	
Concrete	CNFs (0.1 wt%)	0.51	8.13%	-	-	[34]
Concrete	CNFs (0.10 wt%)	0.51	6.16%	-	-	[144]
Concrete	Graphene (0.30 wt%)	0.20	40%	59%	-	[125]
Concrete	Graphene (0.10 wt%)	0.16	62.25	9.25	-	[145]

used to manufacture cement paste and cement mortar, while CNFs and CNTs are generally used to fabricate cement concrete, especially used to prepare ultra-high-performance concrete. For improving the compressive strength of cement-based materials, the addition of GO is more effective than other CNMs, while CNTs and CNFs seem more effective for improving the flexural and tensile strengths of cement-based materials.

As illustrated in Fig. 8, the reinforcement mechanisms proposed by the current literature include i) acting as a nucleation site to promote cement hydration [20, 22, 24]. For instance, Sobolкина et al. [38] indicated that the CNMs with high SSA and rich in oxygen-containing functional groups on their surfaces have a nucleation effect on early C_3S hydration, as illustrated in Fig. 8a. Also, Birenboim et al. [22] reported that admixing a low concentration of GO (<0.05 wt%) can increase the compressive strength of paste by 40%, mainly due to the nanosize of GO act as a nucleation site. Interestingly,

a large number of flower-like hydration crystals were grown on GO sheets (Fig. 8b), this phenomenon is possibly explained by the template effect of GO, inducing hydrates growth in a specific space [79, 146]. Notably, the nucleation effect is a prerequisite for the template effect and this phenomenon merely occurs in a cement matrix incorporating GO sheets, which has been observed by many reports [39, 46, 79, 80]. ii) The nano-filler effect reduces the porosity and refines the microstructure [5, 88]. A recent study was carried out by Konstantopoulos et al. [147], who showed that introducing 0.5 wt% CNTs resulted in higher density hydrated phases and lower total porosity, this phenomenon was explained by nanoindentation as enhanced C-S-H connectivity in the porous network. Besides, Birenboim et al. [22] found that a dense microstructure was achieved with the addition of 0.03 wt% GO, mainly due to the admixed GO nanosheets that can act as a nanofiller that refined the microstructure (Fig. 8c). However, considering the small number of



CNMs that are utilized, typically less than 0.1 wt%, purely physical filler effects are probably negligible. And iii) the bridging effect to inhibit microcracks propagation [8, 27–29]. Silvestro et al. [91] indicated that the incorporation of 0.1 wt% CNTs increased the 28-d compressive and tensile strengths of a cement paste by up to 30% and 50%, respectively. The microcracks were eliminated with the addition of CNTs and CNFs [148, 149], and the admixing CNMs plays a dominant role in enhancing the flexural strength and tensile strength of cement composites because of their larger aspect ratio (Fig. 8d), as discussed in section 2.

Recent work was conducted by Xu and Shi et al. [20], who found that the admixing 0.02 wt% GO promoted cement hydration to generate Si-rich phases (tobermorite-like hydrate) and Ca-rich hydrates (jennite-like structure), instead of ordinary C-S-H gel. This seems to provide a new possibility to explain the possible mechanisms of GO-reinforced cement composites. Note that the reported experimental evidence mainly comes from SEM images of fractures cement composites samples, where CNMs are exposed and hydration products can be

observed to be attached on CNMs. Note that, this phenomenon can be also induced by the growth of hydration products far away from CNMs, and CNMs are merely passively embedded inside. Recently, we have employed CNTs sponges, with unique nano-pores microstructure, as a platform to in-situ separate pore solution from cement grains [71]. The experiments directly prove that CNT with and without strong acid treatment are all inert for cement hydration, and there is no seed effect.

Durability

Durability is critical to guarantee the reliability and stability of cement composites [5, 12, 31, 36, 37, 101]. Typically, their durability is evaluated in terms of transport properties and chemical resistance [30, 37]. It is an issue attracting wide interest in the application of cementitious composites as it relates to the safety, service life, and maintenance costs [30, 150–153]. Currently, the durability of CNMs reinforced cement composites has not been sufficiently studied, compared to the comprehensive studies concerning their mechanical properties. This section summarized the findings brought out by CNMs in

the durability of cement composites in recent literature, including transport property and chemical degradation.

Transport properties of cement composite reflect its resistance to the ingress of aggressive agents (e.g., water and ions, etc.) to pass through inside [12, 30, 36, 150, 151], which can be improved by introducing well-dispersed CNMs [122, 152]. For instance, an investigation was carried out by Qureshi et al. [153], who reported that the maximum water vapor adsorption at 98% relative humidity increased up to 2% in the 0.06% GO-cement composites, suggesting additional C-S-H gel was formed in the cement composites, which can induce a denser microstructure (see Fig. 9). A similar result has been observed by others [53, 112], who found that the water absorption and gas permeability of a cement composite could be reduced by 10–20% with the addition of GO. Similar to the role of GO in the cement matrix, CNTs or CNFs possess the nanofiller effect and bridging effect to improve the microstructure of cementitious materials [28–30, 122].

Chemical degradation of cement-based materials generally includes sulfate attack, carbonation, and acid attack [12, 30, 36, 37]. As discussed above, the addition of CNMs also showed great potential to improve the chemical resistance for cement composites. For example, the introduction of 0.03 wt% GO reduced the carbonation depth due to the movement of CO_2 molecules into the cement matrix was restricted by GO, that is, the reduction of carbonation depth of GO-reinforced cement composites is related to the reduced porosity [53, 154]. Also, Long et al. [53] found that the introduction of 0.2 wt% GO could reduce the carbonation depth by approximately 40% after 28 days, mainly due to the reduced porosity and refined pore structure, as presented in Fig. 10a. According to Mohammed et al. [155], who reported that a considerable decrease (from 11 mm to 2 mm) of carbonation depth in a cement specimen incorporating 0.06 wt% GO after 15 months, this result has attributed the benefit to the increased air content and the decreased mesopore volume (see Fig. 10b and c). Similarly, a recent study was

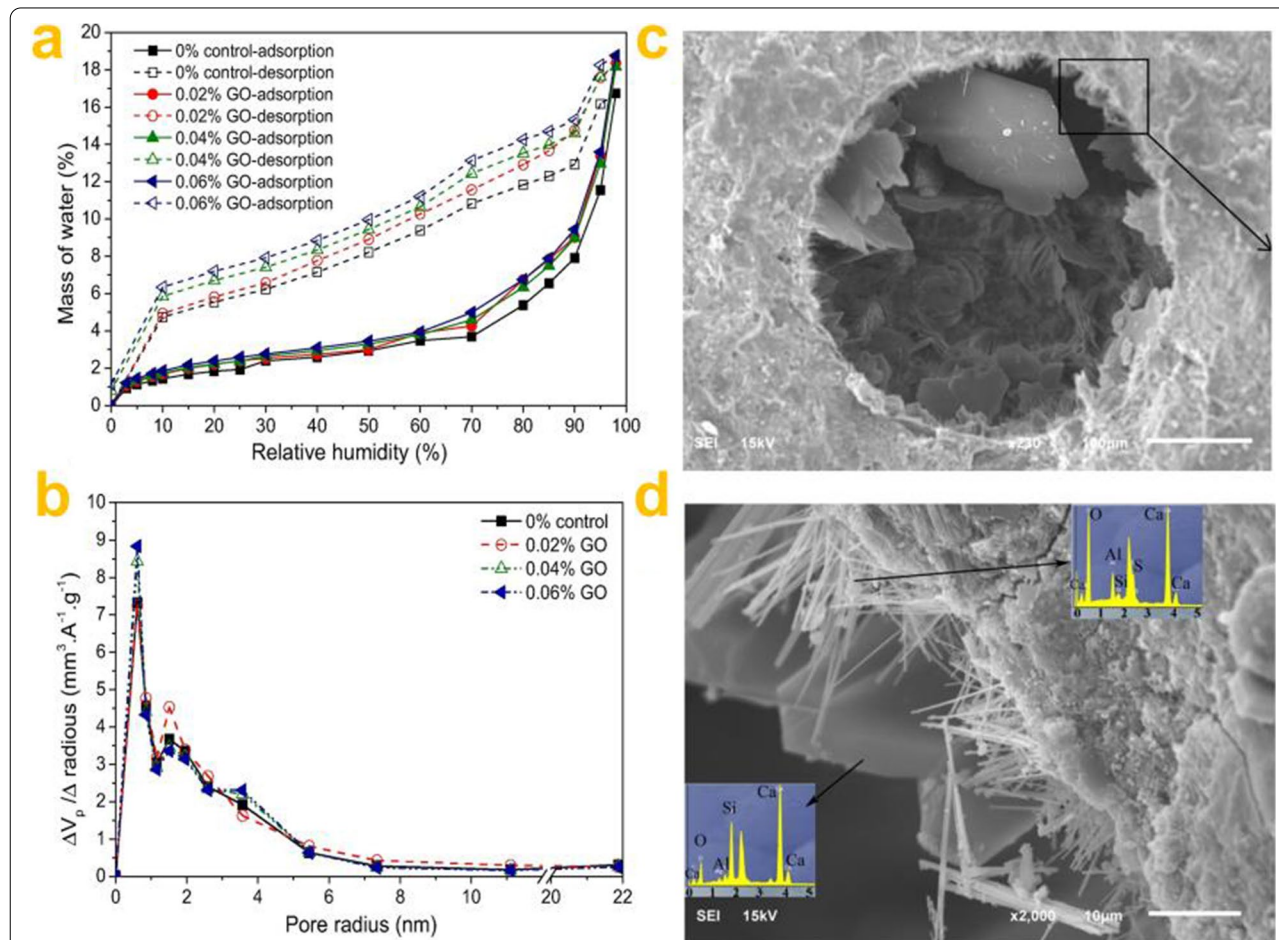


Fig. 9 Properties of cement composites with the addition of GO: **a** mass loss **b** pore size distribution **c** SEM images of mixture with 0.06 wt% GO, and **d** magnification of black rectangle indicating the surface growth nature of flake structures and AFT [153]. (Copyright 2019 Elsevier)

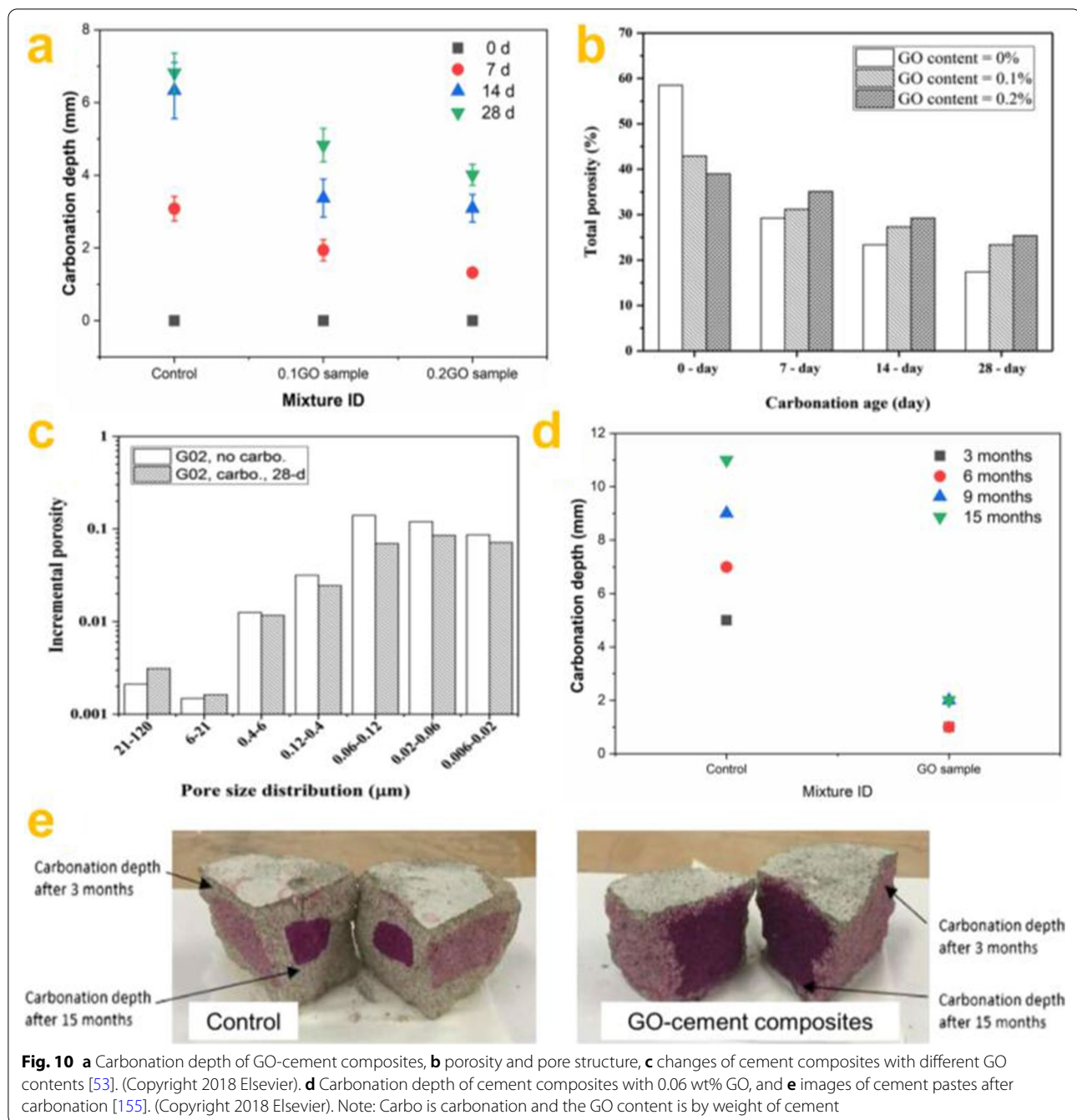


Fig. 10 **a** Carbonation depth of GO-cement composites, **b** porosity and pore structure, **c** changes of cement composites with different GO contents [53]. (Copyright 2018 Elsevier). **d** Carbonation depth of cement composites with 0.06 wt% GO, and **e** images of cement pastes after carbonation [155]. (Copyright 2018 Elsevier). Note: Carbo is carbonation and the GO content is by weight of cement

carried out by Li et al. [47], who reported that the weight loss of a paste specimen incorporating CNTs decreased by 13.3%. A similar beneficial role of CNTs or CNFs on the chemical resistance of cement composites was also found in other studies and attributed this benefit to the refinement microstructure [21, 22, 27–29].

Overall, the addition of CNMs has demonstrated a promising durability performance for cement materials. Compared with CNTs or CNFs, GO has a much higher

SSA and abundant hydrophilic functional groups, enabling it to perform better in improving the durability of cement-based materials. Currently, although the consensus is that the durability of cement-based materials strongly relies on both strength and microstructure, the fundamental mechanisms underlying the durability damage of CNMs-reinforced cement-based materials are not fully unraveled. To this end, more in-depth studies should be explored in the future to verify this hypothesis.

Conclusions and remaining challenges

Over the past decade, the addition of a small dosage of CNMs has demonstrated great potential to improve the mechanical and durability properties of cement composites. We summarized the relevant publications in the last decade (from 2011 to 2021), and the main findings and remaining challenges identified from the literature review can be drawn as follows:

- 1) The dispersion quality and distribution of CNMs in the cement matrix are the keys to understand their roles in the cement matrix. Although previous studies on the admixed CNMs have achieved some satisfactory achievements in terms of reinforcement efficiency [20, 22, 29, 88, 104, 156], the effective dispersion of CNMs in the cement matrix is still a top challenge. Also, semi-quantitative or quantitative evaluation of the dispersion and distribution of CNMs in cement composites faces great challenges, which constrains their feasibility to be widely utilized in the construction industry.
- 2) It has been generally accepted that the addition of GO can accelerate cement hydration, where admixed GO mainly demonstrated the nanofiller and hydration template roles. In addition, the negatively charged GO could consume Ca ions, thereby affecting the degree of polymerization of the cement hydrates. However, direct evidence is still very limited, more detailed investigations need to proceed to investigate the influence of admixed GO on the formation of cement hydrates. Especially the cement hydration lasts for a long time and a variety of hydrates are produced at different times, and how (when) the admixed GO affects cement hydration is still needs to be further in-depth studied.
- 3) Pure CNTs or CNFs are generally not capable of activating or delaying the hydration products, rather, they offer a nanofiller and cracking-bridging capability in cement composites. Interestingly, it has been found that the CNTs rich in oxygen-containing functional groups demonstrated the potential to promote cement hydration. Overall, the admixed CNTs that accelerated the cement hydration have not yet been unanimously agreed upon. Although previous studies claimed that the nucleation effect of the admixed CNMs in the cement hydration, direct evidence is still missing. Note that recently, we have utilized CNTs sponge as a platform to investigate the true effects of CNT on the growth of cement hydration products, and the results indicate that CNT with and without acid treatment have no seed effects.
- 4) For the fresh mixtures, the introduction of CNMs results in higher viscosity, that is, the admixed CNMs

harm the setting time and workability of the mixtures, which is not conducive to the later transportation, casting, and compaction process. Fortunately, this may be compensated by employing some SCMs, such as fly ash.

- 5) At present, the research of CNMs-engineered cement composites is a booming field and there are many handicaps to be overcome. The admixing an extremely low concentration of CNMs has a positive influence on the mechanical strengths of cement-based materials, on the premise of effective dispersion. More attention should be paid to investigate the effects of various CNMs on the formation of multiple cement hydrates. Additionally, CNMs demonstrate great potential to develop smart cement composites in the future.

Abbreviations

SCMs: Supplementary cementitious materials; CNMs: Carbon-based nanomaterials; CNTs: Carbon nanotubes; CNFs: Carbon nanofibers; G: Graphene; GO: Graphene oxide; 1D: One-dimensional; 2D: Two-dimensional; ITZ: Interfacial transitional zone; OEGO: Electrochemically gathered graphite oxide; EGO: Electrochemically gathered graphene oxide; GIC: Graphite intercalation compound; SP: Polycarboxylate superplasticizer; SSA: Specific surface area; AFt: Ettringite; AFm: Monosulfate; CH: Calcium hydroxide; C-S-H: Calcium-Silicate-Hydrate; SEM: Scanning electron microscopy; TEM: Transmission electron microscopy; XRD: X-ray diffraction; EDS: Energy dispersive spectrometer.

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Authors' contributions

Dong Lu: Data processing, Writing-Original draft preparation, and Writing-Reviewing and Editing. Jing Zhong: Conceptualization, Methodology, Supervision, Writing-Reviewing and Editing. The authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this article.

Declarations

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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