

## Review Article

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# Application of nanomaterials in ultra-high performance concrete: A review

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**Abstract:** In the recent decades, traditional concrete poses a great challenge to the modernization of the construction industry because of low tensile strength, poor toughness, and weak resistance to cracking. To overcome these problems, ultra-high performance concrete (UHPC) with superior mechanical properties and durability is developed for broad application prospect in the future engineering construction. However, UHPC is less eco-friendly because it consumes more cement compared with the traditional concrete. The manufacturing of cement produces large amounts of carbon dioxide and therefore leads to the greenhouse effect. Nanomaterials consist of microstructural features that range from 0.1 to 100 nm in size, which exhibit the novel properties different from their bulk counterparts, including filling effect, surface activity, and environmental sustainability. This paper reviews the effect of various nanomaterials used in UHPC to partially replace the cement or as an additive on the microstructures, mechanical properties,

and other properties of UHPC. In addition, the limitations and shortcomings of the current research are analyzed and summarized, and development directions are provided for future research on the application of nanomaterials in UHPC.

**Keywords:** ultra-high performance concrete, nanomaterials, microstructure, mechanical properties, carbon emission

## 1 Introduction

Since the discovery of concrete, it has been the most common construction material extensively used in buildings, roads, bridges, and dams around the world. With the rapid development in the twenty-first century, civil engineers continue to adopt new construction materials to build higher, stronger, more durable, and esthetic structures. Following this trend, the shortcomings of traditional concrete were exposed, such as low tensile strength, poor toughness, and poor durability. To deal with the dilemma, the scientists added fibers with the superior mechanical properties as reinforcement of the concrete [1–3]. Fibers, with large elastic modulus and high tensile strength, could be used in concrete to enhance the bonding and transfer loads to improve the tensile strength and toughness. However, it is difficult to improve the cement-based materials by mixing the fibers through the hydration reaction.

In the 1970s, concrete with compressive strength exceeding 60 MPa was first obtained [4]. The application of fiber-reinforced concrete significantly improved its flexural strength and toughness, which was called high-strength concrete [5]. In 1993, Richard, a French scientific researcher, first proposed reactive powder concrete (RPC) [6]. Its main features are the absence of coarse aggregate to enhance the uniformity of the matrix, the application of pressure during the setting period to enhance the density, and the use of small-sized steel fiber to enhance the toughness, so that the concrete prepared has the characteristics of high strength and high density.

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Therefore, the raw materials used by RPC mainly include cement, silica fume, superplasticizer, quartz sand, steel fiber, etc. [7]. In 1994, De Larrard and Sedran [8] formally proposed the concept of ultra-high performance concrete (UHPC). The maximum compressive strength of UHPC could exceed 150 MPa, which is much higher than that of ordinary concrete [9,10]. Similarly, the durability of UHPC is also much higher [11–13]. To realize this, the raw materials of UHPC mainly include cement, fly ash, blast furnace slag, silica fume, water, fine aggregate etc. In some ways, RPC could be regarded as one form of UHPC. Furthermore, the water–cement ratio of UHPC is relatively small, usually controlled between 0.11 and 0.25, which results in a large amount of cementitious material usage, and the cement used in UHPC could reach up to 40% of the total materials [14,15]. At the same time, sufficient superplasticizer was required to increase the workability of UHPC. Because of the high dosage of the cement, more hydration heat was generated which caused a larger shrinkage rate compared to the ordinary concrete [16]. By adding the fiber materials with excellent mechanical properties into UHPC, the shrinkage and toughness could be improved [17]. In summary, according to the performance of UHPC, it will definitely play an important role in future construction.

Nowadays, the greenhouse effect as a major environmental problem faced by the world has brought critical challenge to sustainable development. A previous study has shown that about 5% of the total emission of carbon dioxide comes from the cement production [18]. Obviously, higher cement consumption applied in UHPC not only increases the carbon emission, but also leads to higher cost, which may hamper the application and promotion of UHPC. Therefore, how to reduce the use of cement without affecting the performance of UHPC has become a hot issue that should be considered globally.

Nanomaterials are emerging microscopic materials, which have brought great influence on the development of biology, chemistry, and other fields since discovery. In 2004, Zhu *et al.* [19] gave the definition of nanomaterials and pointed out that the size of nanomaterials ranged from 0.1 to 100 nm. However, the size of nanomaterials used in cement-based materials is usually beyond this scope [20]. When extending the research scale from the macro material to the micro level, the electrical properties and crystal core effect of the material surface continuously change till reaching a certain degree, followed by exhibition of new properties including micro-size effect and surface effect, which are unavailable to the material at the macro level. By taking advantage of the new characteristics of the nanomaterials, the hydration process of

cement can be regulated, thus affecting the mechanical properties and durability of the hardened paste [21–24]. Nanomaterials, as replacement of cement in UHPC, could reduce the CO<sub>2</sub> emissions, enhance the performance of UHPC, and even assign it with new features.

This paper focuses on the application of different nanomaterials as the ingredients of UHPC in replace of cement. The feasibility and possibility of the future research direction of nanomaterials were also explored. Because there are various types of nanomaterials and their mechanisms are quite different, this paper conducts a state-of-the-art literature review according to the categories of nanomaterials, i.e., nano-silica, nano-CaCO<sub>3</sub>, carbon-based nanomaterials, nano-TiO<sub>2</sub>, and nano-MgO. The application of nanomaterials to UHPC is still in the early stage, but it will undoubtedly lead the direction of future development.

## 2 Nano-silica

Nano-silica is an inorganic chemical material, which is non-toxic, tasteless, and pollution-free. Its microstructure is spherical, flocculent, and reticulated quasi-particle structure. Its molecular formula and structural formula are SiO<sub>2</sub> and insoluble in water [25]. It has been widely used in the research of plastics [26], resins [27], and coatings [28].

The key point of manufacturing the UHPC is to reduce the porosity, improve the particle packing density, and optimize the internal pore structure. However, in the raw materials of UHPC, the smallest particle size exceeds the nanoscale, which also leads to the existence of small holes in the raw materials after accumulation [29]. By adding nanomaterials, UHPC achieves greater density and more perfect particle size distribution. The appearance of nano-silica is amorphous white powder or silica sol, which could be easily filled into the gap between the cement particles to increase its overall density [30]. In fact, the application of nano-silica to cement-based materials has been widely studied [31,32]. Nano-silica can enhance the compressive strength, flexural strength, and durability of cement-based materials. For example, Zeng *et al.* [31] found that the manufacturing of concrete by soaking recycled coarse aggregate in the solution containing nano-silica could enhance the micro-hardness of the interfacial transition zone of concrete, thus improving its mechanical properties and corrosion resistance. Another study led by Meng *et al.* [33] proved that the particle sizes had great influence on the

properties of cement paste. They also pointed out that when the particle size of nano-silica were finer, the matrix structure could be more compact, but the larger particle size of nano-silica improved the matrix strength.

Nano-silica is attractive in applying to UHPC because of its favorable effect on ordinary concrete. Its effect is mainly reflected in the following aspects:

- (1) filling effect of nano-size, enhance the density of matrix, and reduce the porosity;
- (2) pozzolanic reaction, react with calcium hydroxide (CH) in hydration products to generate more calcium silicate hydrate (C-S-H) gel, which helps enhance the strength of cement matrix;
- (3) crystal nucleus effect (or seeding effect).

C-S-H gel grows on the surface of nano-silica, which improves the growth rate of C-S-H in the matrix and is conducive to the improvement of early strength.

## 2.1 Effect of nano-silica on UHPC performance

Table 1 shows the effect of nano-silica on the compressive strength and flexural strength of UHPC. In the study by Yu *et al.* [34], both the compressive strength and the flexural strength of UHPC showed an upward trend first and then dropped with the increase in the cement replacement rate, and the increase in flexural strength is more obvious. It was also revealed that the dispersibility of nano-silica was the main reason for the decrease in strength at high dosage. Apart from that, the content of silica fume used in UHPC also had a significant effect on the strength performance. A research led by Mendes *et al.* [35] showed that the content of nano-silica in UHPC

remained unchanged; the dosage of silica fume was increased from 10 to 20%, and the strength could be increased by about 15% at most. The curing conditions of concrete play a crucial role in improving the hydration degree and strength. The research of Li *et al.* [36] showed that the mechanical properties measured after mixing with nano-silica under different curing conditions were quite different. At high temperature, nano-silica, silica fume, and other materials in the hydration system have a higher activity, and a more sufficient reaction leads to a higher strength. The flexural performance often depends on the degree of bonding between the cement matrix and the aggregate. Jankovic *et al.* [37] studied the effect of different fine aggregates on the performance of UHPC produced using nano-silica as a replacement of cement and revealed that when the cement replacement rate was 2.0%, the combination of barite and quartz sand is better than when used alone in terms of strength.

## 2.2 Dispersibility of nano-silica

Because of the difference in hardening conditions, water-cement ratio, size of nano-silica, and mixing method, the strength enhancement effect is different. In terms of the efficiency of cement substitution in UHPC, the present replacement ratio is still very low, and agglomeration becomes the biggest obstacle restricting the increase in substituting amount. Nano-silica has strong surface adsorption and large surface energy, which can be easily adsorbed together to reduce specific surface area and surface energy. When nano silica starts to agglomerate, due to the relatively small size of the agglomerate, it still has the filling effect and releases free water in the pores. With the increase of agglomerate

**Table 1:** Effect of nano-silica on mechanical properties of UHPC

Ref.	Cement replacement	Curing conditions	Curing (age/days)	Results (improvement)	
				Compressive strength	Flexural strength
[34]	0.0–5.0%	Curing in water	28	About 15.7% (4.0%)	34.6 (4.0%)
[35]	0.0–10.0%	24 h of 22°C + 18 h of 90°C + standard curing	28	About 10.9% (0.6%)	–
[36]	0.0–2.0%	Standard curing	28	4.0 (2.0%)	12.6 (1.5%)
		2 days of 90°C + 26 days of standard curing	28	3.42 (1.5%)	34.2 (1.5%)
[38]	4.0%	Curing in water	28	10.0%	23.3%
[39]	0.0–4.0%	Curing in water	28	8.0% (3.0%)	–

The contents in “( )” show the weight percentage of nano-silica that replaces cement corresponding to the improvement rate.

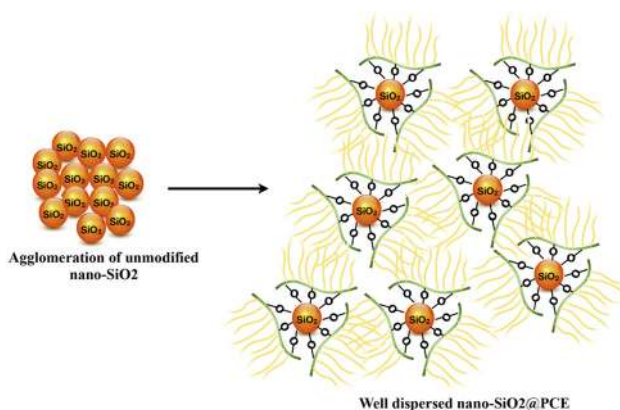
diameter, the filling effect of nano silica decreased, causing a drop in liquidity [40]. Therefore, reducing the agglomeration of nano-silica becomes an effective means to expand its replacement rate. At present, there are two main methods:

### 2.2.1 Ultrasonic dispersion

The principle is to convert electrical energy into sound energy, which generates tiny bubbles in the liquid medium, and the bursting energy of the bubbles makes the nano-materials dispersed.

### 2.2.2 Surface modification

By grafting other functional groups onto the surface of nano-silica, stable chemical bonds are formed with the hydrocarbon groups on the surface of nano-silica to form a shell core structure. Feng *et al.* [41] found that the copolymer of polycarboxylate superplasticizer with Si-OH bond on the surface of nano-silica enables nano-silica to maintain good dispersion in mechanical agitation and alkaline solution, as shown in Figure 1. It was also found that when the ratio of shell core was less than 18, by shortening the induction period and increasing the maximum heat flow, the hydration rate could be significantly accelerated, and the number of capillary pores could be reduced. After uniform dispersion, nano-silica participates in the hydration process, which also affects the microstructure.



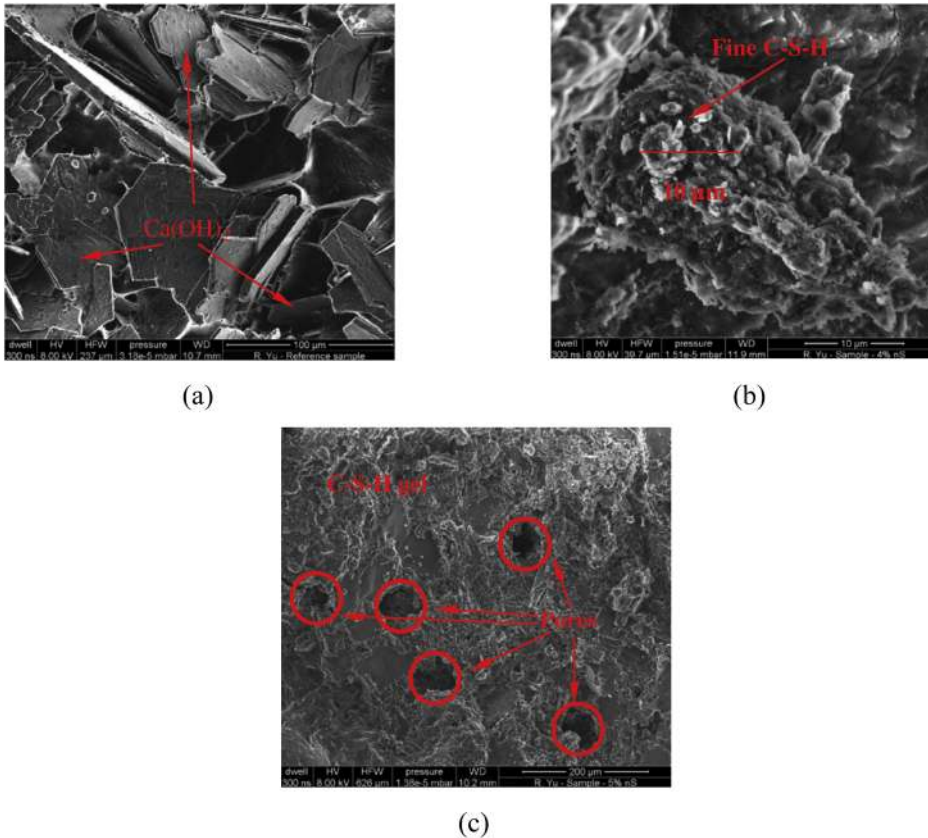
**Figure 1:** Schematic diagram of nano-silica modified by polycarboxylate superplasticizer [41].

## 2.3 Effects of nano-silica on the microstructure of UHPC

The influence of nanomaterials on hydration products can be finally reflected by the arrangement and distribution of hydration products, the density of pores, and the presence of cracks in the matrix. As shown in Figure 2, when nano-silica did not exist, the microstructure of CH crystal was disordered and had vast pore space. With the incorporation of silica nanoparticles, CH reacted with nano-silica to form C-S-H gel, which decreased porosity and increased strength. When the mixing amount of nano-silica continued to increase, the fluidity of the slurry decreased, which made it difficult to remove the air, and hence there were weakness in the C-S-H gel resulting in reduced strength [34]. The pozzolanic reaction could also effectively enhance the bonding between fine aggregate and the matrix, thereby improving the overall strength [42]. The optimization of the pore structure of UHPC with inappropriate amount of nano-silica will also improve the durability of UHPC. Studies by Ghafari *et al.* [43] showed that when the replacement ratio of cement by nano-silica is 3.0%, the corrosion resistance of UHPC increased by 41%. Another report by García Calvo *et al.* [44] revealed that functionalization of nano-silica particles by amines also optimized the pore structure, thereby improving the self-healing performance and corrosion resistance.

## 2.4 Effects of nano-silica on workability, porosity, and air content of UHPC

The addition of nano-silica also has great impact on the working performance of UHPC. There are two main mechanisms of its action. One is the beneficial effect of enhancing the fluidity because of its filling effect (smaller particles can be filled into the pores between larger particles). The other is because of its large specific surface area, nano-silica absorbs more water, which leads to a decrease in fluidity. These two functions affect the ultimate workability of the system. Yu *et al.* [38] analyzed the influence of using waste bottom ash to replace sand and nano-silica instead of cement to produce UHPC on its working performance. It was revealed that with the increase in the cement replacement rate, slump presented a gradual downward trend. This downward trend did not change with the decrease in cement dosage. In another study [34], when the dosage of cement is controlled



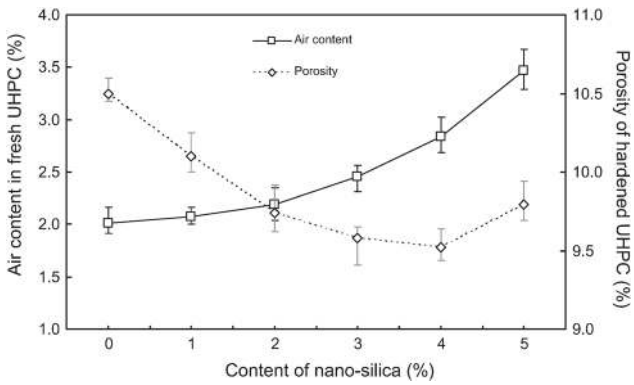
**Figure 2:** SEM images of different content of nano-silica replacement cement in UHPC: (a) 0.0%; (b) 4.0%; and (c) 5.0% [38].

below  $500\text{kg/m}^3$  in the preparation of UHPC, the substitution of nano-silica for cement would also lead to the decline of the working performance of UHPC. This tendency to decrease fluidity is also independent of the size of the nano-silica. Regardless of whether the size of nano-silica was 15 or 20 nm, the trend of fluidity reduction did not change [36–39]. It can be seen that when nano-silica is applied to UHPC, the absorption effect of large specific surface area exceeds the filling effect, thereby increasing the yield stress and viscosity of concrete, resulting in a decrease in concrete fluidity [45,46]. To solve this problem, adjusting the amount of superplasticizer and changing the mixing strategy are alternative options [45–47].

In terms of internal air content and porosity, the addition of nano-silica optimized the internal structure of UHPC and affected the porosity. The change in air content is also related to the fluidity. With the increase in nano-silica, the fluidity decreases and the viscosity of concrete increases; hence, the air in concrete is difficult to be discharged in the mixing process, and therefore the air content of concrete increased [38]. At the same time, because of the effect of nucleation of the

nano-silica and pozzolanic reaction, which makes the hydration degree of cement particles deeper, more hydration products fill into the pore of particles around resulting in decrease in porosity. When increment of hydration products is smaller than the pore volume, the porosity may increase (Figure 3) [38]. From the perspective of pores with different diameters, the incorporation of nano-silica significantly reduces the small pores with diameters ranging from 0.3 to 40 nm [39].

These studies have confirmed the potential of nano-silica as partial replacement of cement in the UHPC. The hydration mechanism of nano-silica was obtained by observing the microstructure. These studies have important implications for explaining the macroscopic performance changes in UHPC. However, there are still some aspects that need to be strengthened: (1) the optimal substitution amount of nano-silica has not been determined yet, and more extensive studies are needed to determine it; (2) although the action mechanism of nano-silica in UHPC has been studied to some extent, the current research is not comprehensive enough; and (3) the influence of modifier on nano-silica of activity and stability should be reduced.



**Figure 3:** Air content and porosity of UHPC with different quantities of nano-silica [34].

### 3 Nano-CaCO<sub>3</sub>

Nano-CaCO<sub>3</sub> mainly comes from natural calcite, marble, and limestone and is popular because of its low cost. Its performance is greatly improved compared with ordinary calcium carbonate, which is widely used in the plastic [48] and rubber [49] industries. In early studies, the addition of ordinary lime powder to alkaline cement instead of fly ash could accelerate the hydration process and improve the compressive strength of specimens after hardening [50]. Furthermore, the addition of limestone could also inhibit the transformation of ettringite (AFt) to single-sulfur calcium sulfoaluminate (AFm), and has a good chemical binding capacity for chloride ions, thereby improving the durability of chloride permeability [51].

#### 3.1 Effect of nano-CaCO<sub>3</sub> on the properties of ordinary concrete

With the development of nanotechnology, the appearance of nano-CaCO<sub>3</sub> could effectively relieve the current environmental pressure. Many people have begun to apply nano-CaCO<sub>3</sub> to ordinary concrete. Yang *et al.* [52] found that the compressive strength, impermeability, and carbonization resistance of concrete mixed with nano-CaCO<sub>3</sub> were greatly improved after molding. This was because nano-CaCO<sub>3</sub> participated in the hydration process of cement and reacted with tricalcium aluminate to produce hydrated calcium carbon aluminate. A study led by Li *et al.* [53] showed that by reducing porosity, macropore ratio, and accelerating hydration, the anti-chloride and anti-carbonation properties of autoclaved concrete are enhanced with nano-CaCO<sub>3</sub>. Nano-CaCO<sub>3</sub>

could also react with CH to form basic calcium carbonate, enhancing the interface bond strength of the transition zone, and its seeding effect effectively promoting the formation of C-S-H gel [54,55]. It can be seen that adding nano-CaCO<sub>3</sub> to ordinary concrete improves the performance indexes by promoting hydration products.

#### 3.2 Effect of nano-CaCO<sub>3</sub> on UHPC performance

In the research of applying nano-CaCO<sub>3</sub> to UHPC, it is found that its effect on concrete performance of workability is still controversial. Wu *et al.* [56] studied the results of adding nano-CaCO<sub>3</sub> to ultra-high strength concrete and found that the fluidity decreased from 220 to 160 mm. However, Camiletti *et al.* [57] found that when the weight percentage of nano-CaCO<sub>3</sub> was less than 5%, its fluidity index increased on the contrary, and strengthened the early setting and hardening effect of concrete. The difference in fluidity may be related to the filling and water absorption under different particle sizes.

The addition of nano-CaCO<sub>3</sub> also had a positive effect on the mechanical properties of UHPC. When the weight of nano-CaCO<sub>3</sub> is 1.6–4.8%, the compressive strength and flexural strength increased about 13–20% and 15–30%, respectively (Figure 4). Moreover, on 1 day, the flexural strength of UHPC was greatly improved after the addition of nano-CaCO<sub>3</sub>, but the flexural strength of 3 days was lower than that of the reference group. The later strength showed that the flexural strength of UHPC could be enhanced when the weight ratio of nano-CaCO<sub>3</sub> to replace cement is less than 4.8%. From the perspective of long-term strength, the compressive strength and flexural strength of UHPC reached the maximum when the weight of nano-CaCO<sub>3</sub> substituted cement was 3.2 and 1.6%, respectively. This is because nano-CaCO<sub>3</sub> reacted with tricalcium aluminate generated carbon aluminate and filled the pores. When the amount of nano-CaCO<sub>3</sub> is excessive, the dispersion becomes difficult and the strength will be reduced. The study by Huang *et al.* [58] showed that nano-CaCO<sub>3</sub> increased the heat release rate at the beginning of hydration by dispersing clinker particles, which also resulted in the micro-expansion of UHPC at the beginning and increased the self-shrinkage. Using nano-CaCO<sub>3</sub> and fiber materials together, carbon aluminate could be deposited on the fiber surface to improve its roughness, thus enhancing the bond between the fiber material and the matrix to improve its toughness

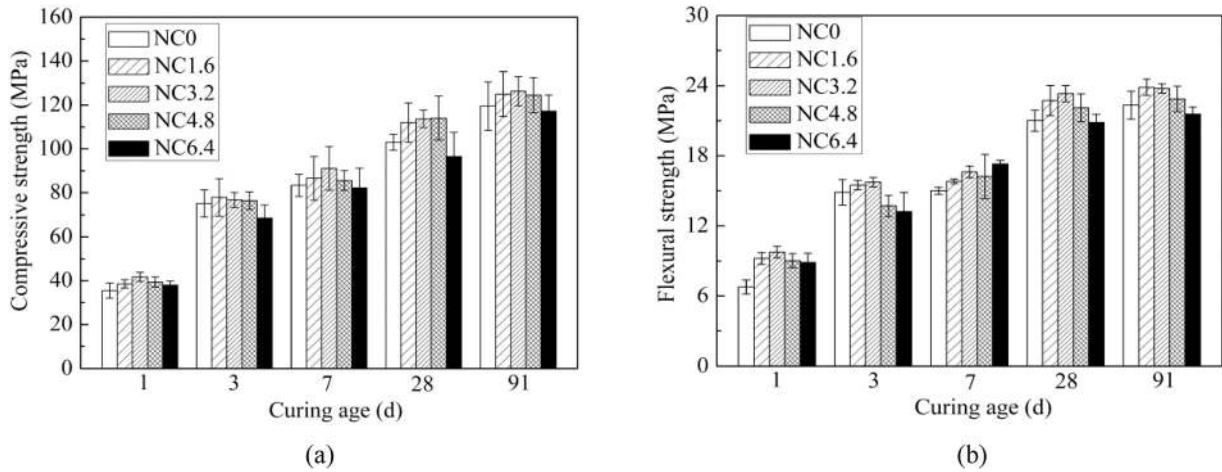


Figure 4: Effect of the content of nano-CaCO<sub>3</sub> on the strength of ultra-high strength concrete: (a) compressive strength and (b) flexural strength [56].

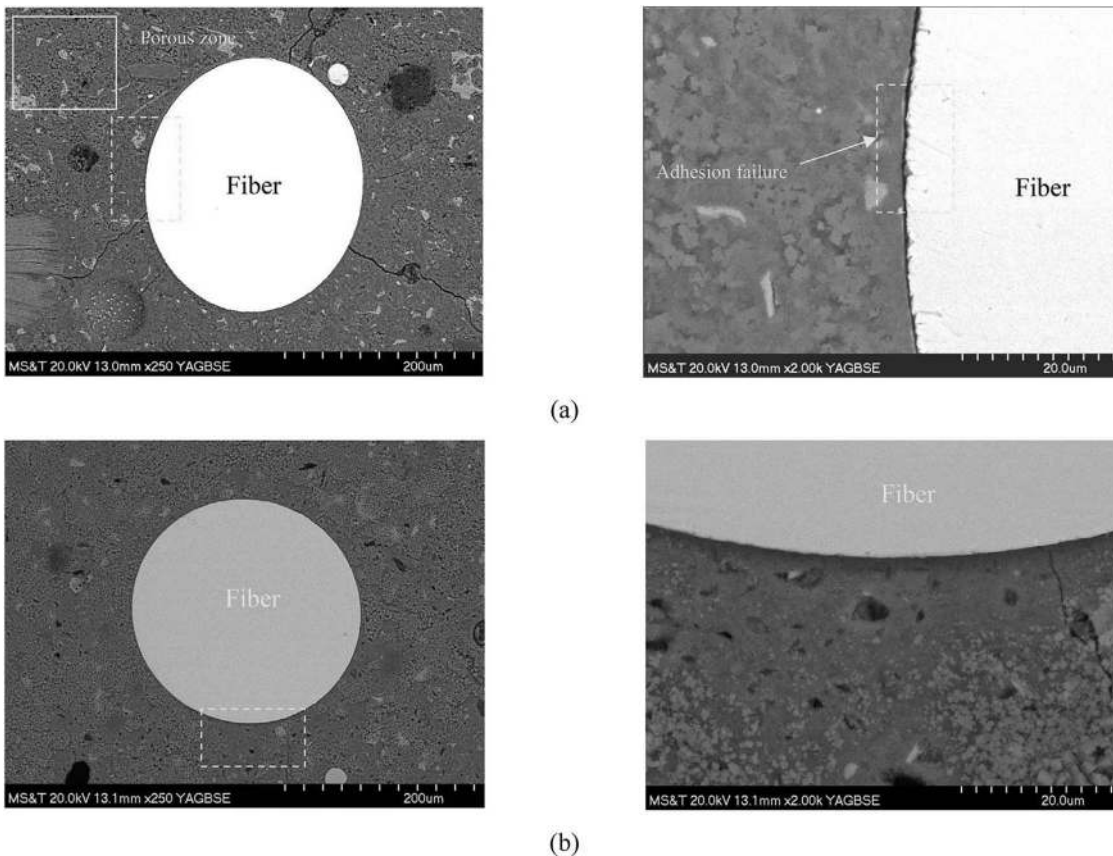


Figure 5: Effect of different content of nano-CaCO<sub>3</sub> as cement replacement on the fiber and matrix in UHPC: (a) 0.0% and (b) 3.2% [59].

and reduce self-shrinkage [59] (Figure 5). In addition, an investigation conducted by Camiletti *et al.* [60] showed that nano-CaCO<sub>3</sub> had a greater effect on the hydration rate at low temperatures, which is greater than that of micro calcium carbonate.

Both nano-CaCO<sub>3</sub> and nano-silica can promote the growth of C-S-H gel through seeding effect, but they react with different hydration products. In addition, the following problems still exist in the study of nano-CaCO<sub>3</sub> in UHPC: (1) the mechanism of nano-CaCO<sub>3</sub> in UHPC is

not clear, and the related research is still in a presumption state. Therefore, nano-indentation technology can be used to characterize the mechanical properties and structure of micro- and nanomaterials. (2) The internal optimization of nano- $\text{CaCO}_3$  on UHPC is bound to have an impact on its durability; therefore, it is necessary to conduct a comprehensive study on the change of durability.

## 4 Carbon-based nanomaterials

Unlike nano-silica, carbon-based nanomaterials tend to have excellent mechanical properties. At the same time, carbon-based nanomaterials has many features, such as super mechanical properties, surface activity, electrical properties, etc., which has been widely used in the fields of medicine [61], biology [62], ceramics [63], building materials [64], etc. Currently, the carbon-based nanomaterials applied in UHPC mainly include carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphene oxide (GO). The application of these carbon-based nanomaterials has a significant impact on the strength, durability, toughness, and electrical conductivity of UHPC.

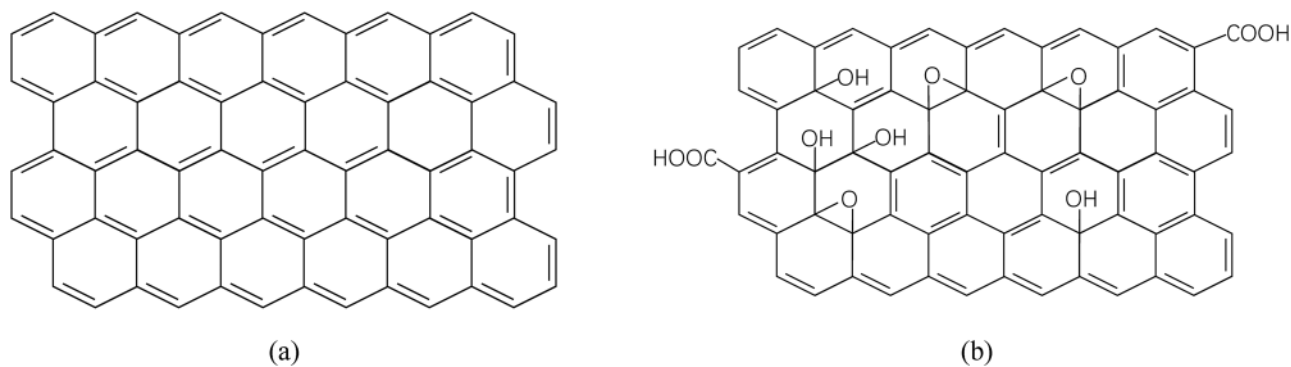
### 4.1 Graphene oxide

Graphene was first obtained in 2004 by the researchers Novoselov and Geim from the University of Manchester in the UK through a single-layer stripping method [65]. The emergence of graphene has broken the previous traditional theory that two-dimensional materials could not exist stably. It is a kind of carbon material with two-dimensional honeycomb crystal structure, which is composed of monolayer carbon atom  $\text{SP}^2$ . The ideal structure

of graphene is a planar hexagonal lattice with each carbon atom attached to its three adjacent carbon atoms in a very strong covalent bond [66]. This unique structure also showed excellent mechanical properties, with an elastic modulus of 1,000 GPa and tensile strength of 130 GPa [65–67]. However, graphene is less active and insoluble in water, making it difficult to apply directly to cement-based materials. GO is the product of strong oxidation of graphene and one of the important derivatives of graphene. The manufacturing methods of GO are as follows: Staudemaier method [68], Hummers method [69], and Brodie method [70]. The principle is that when after oxidation, graphene is linked to many oxygen-containing functional groups such as hydrocarbon group and carboxyl group in its two-dimensional plane structure (Figure 6) [71]. These hydrophilic oxygen-containing functional groups not only give GO better dispersion, but also enable GO to deeply participate in the chemical reaction process through active functional groups, which is also the reason for the booming application of GO in cement-based materials in recent years [72].

#### 4.1.1 Effects of GO on ordinary concrete performance

In the recent scientific achievements, many scholars have carried out extensive research on the application of GO in common mortar [73], concrete [74], recycled concrete [75], fly ash mortar [76], and so on. These studies confirmed the negative effect of GO on the working performance of cement-based materials. At the same time, these studies also pointed out that GO promoted the cement hydration, had a template and inducing effect on the formation of hydration products, and reduced the orientation of CH crystals, which made the cement-based material mixed with GO more dense. In addition, the nucleation effect of GO also accelerated the



**Figure 6:** Structure of (a) graphene and (b) graphene oxide [71].



generation of hydration products. The combined effect of these factors altogether enhanced the mechanical properties and durability of cement-based materials [77,78].

The surface of GO has a large number of oxygen-containing functional groups, which are easy to react with  $\text{Ca}^{2+}$  precipitated from cement hydration to form agglomeration [79]. However, the polycarboxylate superplasticizer could improve this phenomenon by increasing the dual effects of electronic repulsion and steric hindrance in the system [80]. Among them, electronic repulsion refers to the mutual repulsion between negatively charged superplastic molecules and negatively charged GO molecules, whereas spatial steric resistance refers to the addition of superplasticizer that slows down the hydration rate of the system and reduces the rate of calcium ion production, so that the cross-linking effect is blocked.

#### 4.1.2 Effects of GO on UHPC performance

Modification of fiber materials to enhance UHPC mainly depends on its own mechanical properties, but the mechanism of action of GO is quite different [81–83]. In terms of strength, a study led by Wu *et al.* [83] showed that both the compressive strength and flexural strength showed similar pattern of initial increase and then decrease with the increase in GO content. The flexural strength and compressive strength of 28 days reached the maximum when the GO content was 0.02%, which was increased by 28.7 and 25.3%, respectively, compared with the blank group (Figure 7). Wan and Zhang [84] used the molecular dynamics modeling method to analyze the hydration of GO into UHPC. Compared with OPC, the C–S–H gel layer in UHPC contained more calcium ions and hydroxide. Calcium ions combined with GO oxygen-containing functional groups, and water molecules form hydrogen bonds between GO functional groups and C–S–H gel (Figure 8). These two actions enhanced the bonding between C–S–H and GO, and improved the ductility and tensile strength of the structure. At present, the application of GO in UHPC is still in the early stage, and the mechanism of action has been preliminarily understood. However, its mechanism of action is complex, which needs more research in the future. In addition, volcanic ash reaction exists in UHPC, and therefore the influence of GO on multipole hydration should be considered.

## 4.2 CNTs

CNTs are one-dimensional nano-carbon materials discovered in 1991, and their structure can be viewed as a piece of graphene rolled up, with a hollow interior and a cylinder-cap-like seal at both ends. CNTs are nanoscale in diameter but up to micron in length [85]. According to the difference in the number of layers, CNTs can be divided into single-walled CNTs and multi-walled CNTs [86]. Its mechanical properties are similar to graphene, and it also has excellent electrical properties [87]. According to its excellent properties, it can be used in cement-based materials to produce intelligent concrete with stronger properties and pressure sensitivity [88]. The principle is to disperse nanomaterials evenly with good electrical conductivity into the cement matrix. When the structure is under stress, the pores will be compressed, and the number of the contact points of nanomaterials in the cement matrix will increase accordingly, forming an interconnected conductive network, and the resistance of the corresponding cement structure will also be changed. Measurement of this change can be used to evaluate the status, e.g., health and durability, of the structure.

### 4.2.1 Dispersion methods of CNTs

Unlike GO, CNTs have virtually no oxygen-containing functional groups on their surfaces, which makes their dispersion in cement-based materials difficult. In previous studies, the application of ultrasonic dispersion [89], surface modification [90] (the introduction of oxygen-containing functional groups on CNTs by covalent modification), and composite method [91] has been proved to be effective. However, easy to reunite after ultrasonic dispersion and the possible damage of surface modification to the structure are also important factors affecting the application. For example, Hu *et al.* [92] pointed out that humic acid enhanced the stability of dispersed CNTs in alkaline environment. When the mixture weight of humic acid and CNTs reached 5.0% of cement weight, the compressive strength and bending strength of hardened cement paste were increased by 31 and 48%, respectively. However, the possible damage of surface modification to the structure and the easy reuniting after ultrasonic dispersion are also need to be considered.

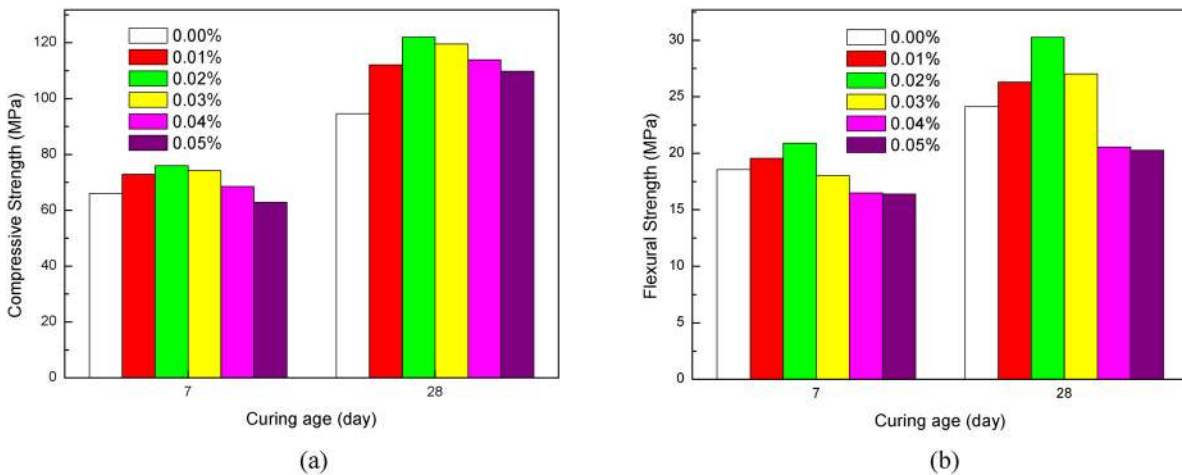


Figure 7: Effect of different content of GO application on UHPC: (a) compressive strength and (b) flexural strength [83].

#### 4.2.2 Effects of CNTs on UHPC performance

You *et al.* [93] applied CNTs to UHPC with a water–cement ratio of 0.2, and the fluidity test results showed that when the CNTs content was increased from 0.1 to 0.3%, the fluidity is basically unchanged in comparison with the control group. When the content was 0.5%, the fluidity decreased because of the difficulty in dispersing. The incorporation of CNTs reduced the compressive strength of UHPC, which may be because of the dense structure of UHPC, and when CNTs added, more defect points were created inside it. However, the conductivity of UHPC was improved by the addition of CNTs, and UHPC became conductive and pressure sensitive after compression, which was more obvious when the content

of CNTs exceeded 0.3% by volume. Lee *et al.* [94] synergistically doped CNTs with steel fibers with different shapes and different aspect ratios into UHPC, and found that CNTs had basically no effect on the compressive strength and elastic modulus, but enhanced the conductivity, which was helpful to study the strain and time response of UHPC and establish the model. Yoo *et al.* [95] added micro steel fiber and multi-wall CNTs into UHPC at the dosage of 0.5 and 2% according to the volume, and found that the mixed use of steel fiber and CNTs significantly improved the tensile properties, including strength and post-peak ductility, and also effectively enhanced the sensitivity to strain and damage. These studies confirmed that CNTs enhanced the electrical conductivity of UHPC, but the effects of the content,

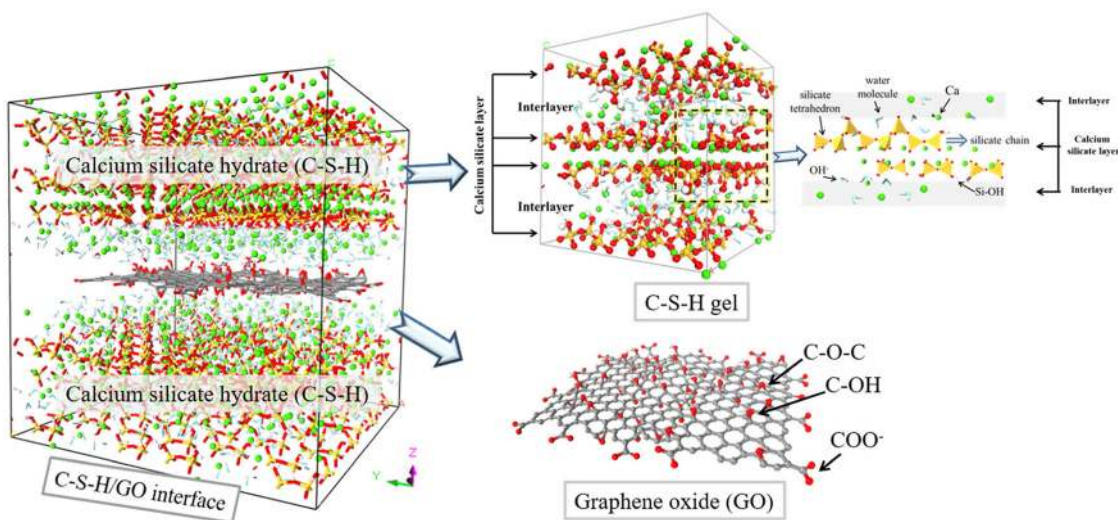


Figure 8: Model of influence of GO on C-S-H gel [84].

orientation, and pore water content of CNTs on the electrical conductivity and piezoresistivity of UHPC were still scarce.

### 4.3 CNFs

CNFs are new carbon materials between graphene and carbon 60. Its tensile strength is 2.7 GPa, elastic modulus is 400 GPa, and the diameter is between 0.5 and 100 nm [85]. CNFs can be divided into plate type, fishbone type, and tube type, depending on the way of graphene stacked [85]. In addition to excellent mechanical properties, CNFs have high electrical conductivity, and many studies have been conducted on capacitors [96] and biocompatibility [97]. Similar to CNTs, the dispersion of CNFs was influenced by surface energy, high length-diameter ratio, and van der Waals force, causing them to intertwine and difficult to disperse in cement-based materials. The dispersion in cement-based materials can also be enhanced by means of ultrasonic treatment and surface modification. In the case of uniform dispersion, CNFs can significantly enhance the toughness and strength of cement-based materials through its own structural characteristics [98,99].

#### 4.3.1 Effect of CNFs on UHPC shrinkage

As mentioned earlier, UHPC is designed with a low water-cement ratio and high cement content. The application of CNFs provides a new option to solve the self-shrinkage. The increase in the self-shrinkage would result in cracks in the matrix. Moreover, this self-shrinkage will last for a long time, even within 60–90 days [100]. The fiber material is an effective weapon to improve self-shrinkage, but more materials such as steel fiber are traditionally used [17]. The tensile strength and elastic modulus of CNFs both exceed that of steel fiber, and have the new characteristics of nanomaterials, which are of great significance for improving the performance of concrete.

#### 4.3.2 Effect of CNFs on UHPC mechanical properties and microstructure

Both CNFs and CNTs are carbon-based nanomaterials, CNFs has a larger diameter and a large surface area, which makes the bond between CNFs and cement firm

and improves the mechanical properties of UHPC [101,102]. Incorporating CNFs into UHPC has little effect on its fluidity, which also makes its mixed air content lower and denser in microstructure. At the same time, because of its strong mechanical properties, the early strength of UHPC is improved [103]. A research performed by Meng *et al.* [102] showed that CNFs greatly increased the tensile strength and flexural strength because of its fiber characters bridging microcracks (Figure 9). It also revealed that CNFs had little influence on the compressive strength and overall compactness. It can be seen that CNFs could reduce the self-shrinkage and play the same role as the steel fiber. Because of its nano-size effect, its mechanism of action is still more diverse, and its application prospects are broad. However, there are still many problems to be considered. The dispersion of CNFs is still a huge obstacle to its application in UHPC. At the same time, the compatibility of CNFs in UHPC should also be considered because of the large number of raw materials in UHPC and sometimes the addition of additives.

## 5 Nano-TiO<sub>2</sub>

Nano-TiO<sub>2</sub> is characterized by good stability, low cost, and, more importantly, photocatalysis. Photocatalytic effects can cause redox reactions and degradation reactions of nitrogen oxides in the atmosphere, producing environmentally harmless substances [104]. Concrete is an ideal carrier for nano-TiO<sub>2</sub> because of its heterogeneous porous structure, large amount of material, and frequent exposure to the air. In addition, nano-TiO<sub>2</sub> also improved the mechanical properties of cement-based materials and impermeability by optimizing the distribution and size of pores in cement paste [105,106].

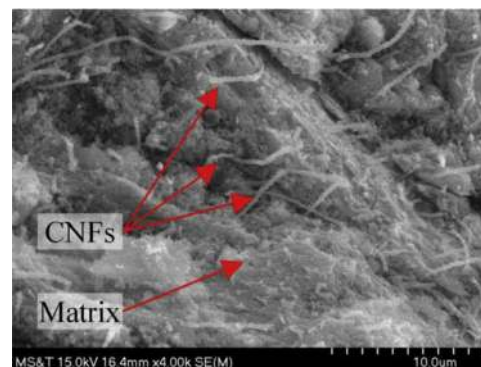


Figure 9: An SEM image of the dispersed CNFs in UHPC [102].

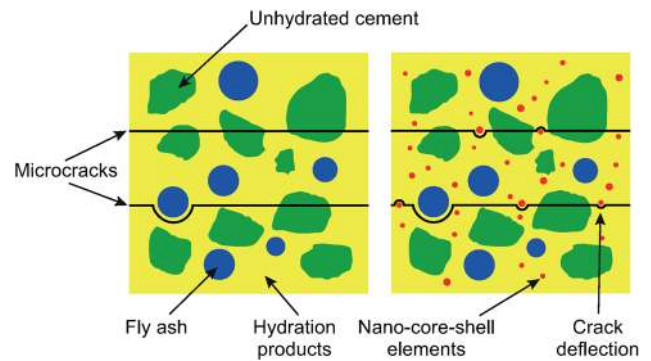
## 5.1 Factors influencing the photocatalytic efficiency of nano-TiO<sub>2</sub>

The photocatalytic efficiency of nano-TiO<sub>2</sub> is affected by many factors, such as particle size [107], light intensity [108], and temperature change [109]. Furthermore, the application of nano-TiO<sub>2</sub> in cement-based materials has the problem of getting easily detached from concrete [110]. Therefore, the firmness of the binding between nano-TiO<sub>2</sub> and UHPC becomes an important factor affecting the sustainability of photocatalysis. Similar to other nanomaterials, nano-TiO<sub>2</sub> is easy to agglomerate, and therefore it can also be assisted by ultrasonic treatment and surface modification.

## 5.2 Effect of nano-TiO<sub>2</sub> on UHPC performance

Studies by Su *et al.* [111] found that when nano-TiO<sub>2</sub> and steel fibers were added to UHPC, nano-TiO<sub>2</sub> had basically no effect on the mechanical properties of UHPC. It also revealed that when nano-TiO<sub>2</sub> acted on UHPC alone, it not only reduces the orientation of CH, but also limits the size of CH, which was also beneficial to the strength growth in the later stage. A report by Li *et al.* [112] showed that when the content of nano-TiO<sub>2</sub> weight reached 2.32% of cement, both the compressive strength and flexural strength of 28 days were increased by 18.05 and 47.07% respectively. In addition, the addition of nano-TiO<sub>2</sub> can reduce the resistivity and enhance the early strength because of the crystal nucleus effect. In another study conducted by Gu *et al.* [113], it was found that the mechanical properties of UHPC reached the highest when the content of nano-TiO<sub>2</sub> was 1.0% of the cement weight. Moreover, nano-TiO<sub>2</sub> refined the pore structure through the filling effect and nucleation effect, resulting in the increase in the density of hydration products. In addition, when fractures are generated in the tensile zone, the presence of nano-TiO<sub>2</sub> could make the fracture path grow and absorb more energy, thus delaying the spread of fractures (Figure 10). In addition, these effects reduced the dry shrinkage rate of UHPC and improved the chloride penetration resistance, frost-resistance, and carbonization resistance of UHPC.

The current research on the application of nano-TiO<sub>2</sub> to UHPC focuses on mechanical properties and durability, but there are few researches on the quantitative



**Figure 10:** Effect of nano-titanium dioxide on fracture development [113].

mechanism and influencing factors of photocatalytic efficiency after incorporation. In addition, Sha *et al.* [114] pointed out in their literature review that currently nano-TiO<sub>2</sub> caused harm to human health such as cytotoxicity, phytotoxicity, and phototoxicity through organelle dysfunction. This also limits the further application of nano-TiO<sub>2</sub> in UHPC.

## 6 Nano-MgO

Nano-MgO, which possesses high hardness, purity, and melting point, is extensively used in electronics [115], ceramics [116], etc. Recent studies have shown that it could effectively promote the formation of hydration products through its nucleation effect and filling effect. Pan *et al.* [117] found that when the replacement weight ratio of cement by nano-MgO was set at 3.0, 5.5, and 8.0%, the early compressive strength of high-performance cement mortar decreased, whereas the compressive strength of 28 days increased. The main reason for this phenomenon was that as the curing time changed, the reaction rate of MgO increased. In addition, the hydration product, magnesium hydroxide, increased as the reaction progressed and filled the pores between the cement particles. Besides, nano-MgO absorbed the free water of hydration reaction and affected the process of cement hydration reaction [118]. Another report by Li *et al.* [119] revealed that MgO promotes the formation of hydrotalcite, which was not conducive to the densification of the structure, but improved its wear resistance. Compared with other materials, there are relatively few studies on nano-MgO in UHPC, which requires more comprehensive researches on its fluidity, mechanical properties, and durability.

## 7 Impact of nanomaterial-modified UHPC on sustainable development

In the production process of cement, a variety of toxic and harmful gases such as carbon dioxide, nitrogen oxides, and sulfur oxides are released. Carbon dioxide is also the main cause of the greenhouse effect. Therefore, the sustainable development of the cement production industry has become a new research hotspot in the recent years. Shen *et al.* [120] pointed out that cleaner production, recycling, and cement substitution are effective ways to solve the current problems. The first two mainly refer to the improvement of process technology in the production process, the full utilization of various wastes, the improvement of the efficiency of resource and energy use, and the reduction of greenhouse gas emissions. The replacement of cement mainly refers to using various industrial wastes or new environment-friendly materials to reduce the use of cement.

Nanomaterials have been considered as a reliable alternative to replace cement in recent years. There are many types of nanomaterials with diverse manufacturing principles. The existing manufacturing methods of nanomaterials contributed little to carbon emissions. For example, the manufacturing methods of nano-silica include solid phase method (produced according to physical method), liquid phase method (chemical precipitation method and solution gel method), and gas phase method (chemical vapor deposition method) [121]. During the manufacturing process, no carbon dioxide is produced in the chemical products.

According to the assessment by Peng *et al.* [122], 1 kg of cement production will release 0.689 kg of carbon dioxide emission. Table 2 presents the replacement of cement with nanomaterials to manufacture UHPC using different types of cement. Based on the mix ratio and Peng's *et al.* conclusion [122], the carbon emission

reduction per cubic meter of UHPC is calculated. It can be seen that under the current low cement replacement rate, the carbon emission reduction of per cubic meter of concrete reaches up to 23.77 kg at most. The reduction in carbon emissions per cubic meter can be as high as 4.0%. Therefore, the manufacturing of UHPC using nanomaterials instead of cement is of great significance to the reduction of the greenhouse effect.

## 8 Conclusions and prospects

The effects of nano-silica, nano-CaCO<sub>3</sub>, carbon-based nanomaterials, nano-TiO<sub>2</sub>, and nano-MgO on the properties of UHPC were reviewed. It can be seen that the manufacturing of UHPC with nanomaterials instead of cement has broad prospects. The impact of these materials on UHPC is summarized as follows:

- (1) When these nanomaterials were added to UHPC, the water absorption rate of large specific surface area and filling effect became the key factors affecting the fluidity of UHPC. Except that CNFs and CNTs had little effect on fluidity at low dosage, other materials showed that the water absorption effect of large surface area was more obvious, which reduces the fluidity of UHPC. The modification of nanomaterials by admixture is one of the reliable options to solve this problem.
- (2) CNTs and CNFs mainly improved the performance of UHPC by their own mechanical properties. Other nanomaterials improved the pore structure through seeding effect, filling effect, and reaction with hydration products. These effects have played a positive role in improving the toughness, impermeability, and bending strength of UHPC.
- (3) In terms of interaction with hydration products, C-S-H gel was formed by the reaction of nano-silicon with CH, and stable carbon aluminate was formed by

**Table 2:** Nanomaterial replacement to reduce carbon emission

Ref.	Nanomaterial	Cement dosage (kg/m <sup>3</sup> )	Cement replacement (%)	Replace cement per volume (kg/m <sup>3</sup> )	Reduction in carbon emission per volume (kg/m <sup>3</sup> )
[39]	Nano-silica	950.0	3.0	28.5	19.64
[56]	Nano-CaCO <sub>3</sub>	863.2	3.2	34.5	23.77
[59]	Nano-CaCO <sub>3</sub>	863.0	3.2	34.5	23.77
[83]	Graphene oxide	453.8	0.02	0.09	0.062
[119]	Nano-MgO	800.0	2.0	16.0	11.02
[34]	Nano-silica	439.5	4.0	17.6	12.13

the reaction of nano-CaCO<sub>3</sub> with C<sub>3</sub>A. GO has a positive effect on enhancing C–S–H gel. Nano-MgO promotes the formation of hydrotalcite and has a negative effect on structure.

- (4) From the perspective of performance improvement, GO is the most promising nanomaterial. Compared with other materials, the mixing amount of GO is down to 100 times than that of other materials, but the effect of strength improvement is also outstanding. Besides, it has oxygen-containing functional groups and has better dispersion effect, but its high cost also affects its large-scale promotion. From the perspective of environmental protection, the manufacturing of UHPC using nanomaterials to partially replace the cement has a broad prospect but is limited by the manufacturing method and cost.

To better promote the sustainable development of environment-friendly UHPC, the following points can be considered:

- (1) Besides the nanomaterials listed in the paper, other nanomaterials such as nano-aluminum oxide and nano-clay particles should also be studied instead of cement to produce UHPC. Moreover, the effect of composite mixing of various nanomaterials on UHPC performance is also worth studying.
- (2) Durability, as an important index affecting the service life and maintenance cost of structures, plays an important role in the safety and durability of structures. Some durability indexes of nanomaterials mixed with UHPC has not been studied, such as fire resistance, carbonization resistance, and dynamic modulus of elasticity. These are also important to the safety and durability of the structure.
- (3) Seeding effect is one of the important roles played by nanomaterials in UHPC, but the mechanism of seeding effect has not been studied in depth and it could be further investigated by the finite element method. Meanwhile, the performance of nanomaterials is closely related to the particle size, and the effect of the different size of nanomaterials in UHPC is still unknown.

Furthermore, there are still some challenges in our application of nanomaterials to UHPC:

- (1) The proportion of nanomaterials replacing cement to produce UHPC is still low, which is mainly related to the dispersion of nanomaterials. At present, modifiers are widely used, but the influence of modifiers on the compatibility of nanomaterials should be considered. To keep the fluidity and activity of nanomaterials

under high dosage, further research should be made on the dispersion of nanomaterials.

- (2) At present, after a long period of development, the cost of cement materials is relatively low compared with nanomaterials because of the mass production. Therefore, reducing the production cost of nanomaterials is a huge problem to be solved in the future.

As one of the most promising building materials in the future, UHPC makes great significance in enhancing the structural performance. The existing researches have demonstrated that the mechanical properties and durability of UHPC using nanomaterials instead of cement have been improved. However, the replacement rate is low at present. With the progress of the research on the mechanisms of nanomaterials, lower cost, better performance, and more eco-friendly UHPC will certainly be developed in the future, which can also promote the advances of nanomaterials and building material industry.

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