DE GRUYTER Nanotechnology Reviews 2021; 10: 779–792

Review Article

Zhong Xu*, Zhenpu Huang, Changjiang Liu*, Hui Deng*, Xiaowei Deng, David Hui*,
Xiaoli Zhang, and Zhijie Bai

Research progress on key problems of nanomaterials-modified geopolymer concrete

https://doi.org/10.1515/ntrev-2021-0056
received July 27, 2021; accepted August 1, 2021

Abstract: The raw materials of geopolymer come from industrial wastes, which have the advantages of lower carbon emissions and less energy consumption compared with traditional cement products. However, it still has the disadvantages of low strength, easy cracking, and low production efficiency, which limit its engineering application and development. At present, with the application and development of nanotechnology in the field of materials, it is found that nanomaterials have a good filling effect on composites, which greatly improves the integrity of the composites. It has become a very popular research direction to optimize and improve the engineering application performance of geopolymer concrete (GPC) by nanomaterials. The modification of nanomaterials can further improve the properties of GPC and expand its application fields in engineering and life. Based on people's strong interest in nanomaterial-modified GPC and providing the latest and complete research status for further related work, this paper summarized the key technical problems in the field of nanomaterials-modified GPC in the past decade. Those include the modification mechanism, dispersion mode, and mechanical properties of nanomaterials. At the same time, the application bottlenecks and key problems of nanomaterials-modified GPC are comprehensively analyzed. Finally, the prospects and challenges of future work in this field are discussed.

Keywords: nanomaterials, geopolymers, modification mechanism, mechanical properties

1 Introduction

Nanomaterials-modified geopolymer concrete (GPC) has become a research hotspot in recent years because of its good application performance and various modification mechanisms [1]. Researches show that nanomaterials have a significant impact on the fluidity, mechanical properties, and microstructure of concrete. At the same time, some scholars pointed out that some modification effects are not necessarily positive. At this stage, many key problems in the field of nanomaterials-modified GPC have not been completely solved, and the research results of key technologies are still full of controversy [2,3].

Since cement was invented in 1824, the use of it has continued to increase. With the growth of population, statistics show that the annual global cement production will increase to 6.1 billion tons by 2050. China and other developing countries account for a high proportion, and China accounts for about half of the global cement production in 2019 [4]. The production of ordinary Portland cement needs to consume a lot of nonrenewable resources, such as natural gas, oil, coal, and so on. At the same time, mass production of cement can also lead to ultrahigh CO_2 emissions (7% of global carbon emissions) [5]. Based on the needs of environmental protection and sustainable development, it is urgent to find alternatives to traditional cement.

In 1978, J. Davidovits, a French material scientist, put forward the concept of geopolymer. Geopolymer is a kind of cementitious material with more environmental benefits than traditional cement materials. Due to lower carbon emissions and less energy consumption, geopolymer is

---

*** Corresponding author: Zhong Xu,** College of Environment and Civil Engineering, Chengdu University of Technology, Chengdu 610059, China, e-mail: xuzhong@cdut.edu.cn
*** Corresponding author: Changjiang Liu,** School of Civil Engineering, Guangzhou University, Guangzhou 510006, China, e-mail: cjliu@gzhu.edu.cn
*** Corresponding author: Hui Deng,** College of Environment and Civil Engineering, Chengdu University of Technology, Chengdu 610059, China, e-mail: dh@cdut.edu.cn
*** Corresponding author: David Hui,** Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, United States of America, e-mail: dhui@uno.edu
Zhenpu Huang, Xiaoli Zhang, Zhijie Bai: College of Environment and Civil Engineering, Chengdu University of Technology, Chengdu 610059, China
Xiaowei Deng: Department of Civil Engineering, The University of Hong Kong, Pokfulam, Hong Kong 999077, China

an important alternative to replace traditional cement products [6]. Different from ordinary concrete produced by cement, GPC uses geopolymer as cementitious material, which can be produced from waste industrial products and cheap minerals, such as fly ash [7], slag [8], high territory [9], and waste glass powder [10]. The production and preparation of GPC requires alkali activator to carry out polymerization and forms a stable aluminosilicate network structure, which has excellent mechanical properties and engineering application properties [11]. Alkali activators can come from chemical reagents or industrial wastes, such as red mud and cement kiln ash [12], which are materials with environmental benefits.

GPC has many advantages, and its reaction mechanism has been studied more thoroughly at present, but it still has some bottleneck problems, such as high porosity, low interfacial bond strength, and slow strength growth in the later stage, which limit its wide application in practical engineering [13]. In recent years, with the latest progress of nanomaterials' research, the use of nanotechnology to solve the bottleneck problem of GPC has become a hot spot and has formed some technological exploration, but it is still one-sided and controversial, which is worthy of further thinking innovation and technology research and development.

Nanomaterial is a new type of material developed in the early 1980s. Nanomaterials refer to ultrafine materials with nanometer size (1–100 nm), including various powder materials, such as metal, nonmetal, organic, inorganic, and biological nanomaterials [14], which have obvious application value in engineering. Nanomaterials can play an obvious filling role in concrete because their particle size is less than 10 nm, the proportion of surface atoms reaches 20%, and the number of atoms distributed on the particle surface increases sharply with the decrease of particle size, as shown in Figure 1 [15]. Due to the size characteristics of nanomaterials, it can well fill the gaps in GPC, play the role of filling and bridging, accelerate the formation of aluminosilicate network and hydration process, and improve the mechanical properties of GPC [16]. The application of nanomaterials in GPC is still in its infancy, and there are still many controversies on the mechanism, dispersion mode, and comprehensive performance evaluation of nanomaterials-modified GPC.

There are many kinds of selection and dispersion methods, but it is difficult to achieve the convenience of operation and uniformity of dispersion at the same time, which forms a big obstacle for the research and engineering application of nanomaterials' modification effect. At the same time, the factors affecting the mechanical properties of GPC are the focus of the research, and the solution of these problems undoubtedly needs to be supported by a lot of exploration. However, through literature review and carding in this field, it is found that the research on nanomaterials-modified GPC lacks systematism; no effective summary and evaluation of previous work has been made by scholars. As a result, it makes many scholars' understanding not comprehensive enough, suffers from lack of navigation aids, and restricts further development.

In order to ensure scholars have a more comprehensive understanding of the working basis, research status, and application prospect of nanomaterials-modified GPC, the author wrote this paper to explore the influence of nanomaterials on the properties of GPC and analyze the

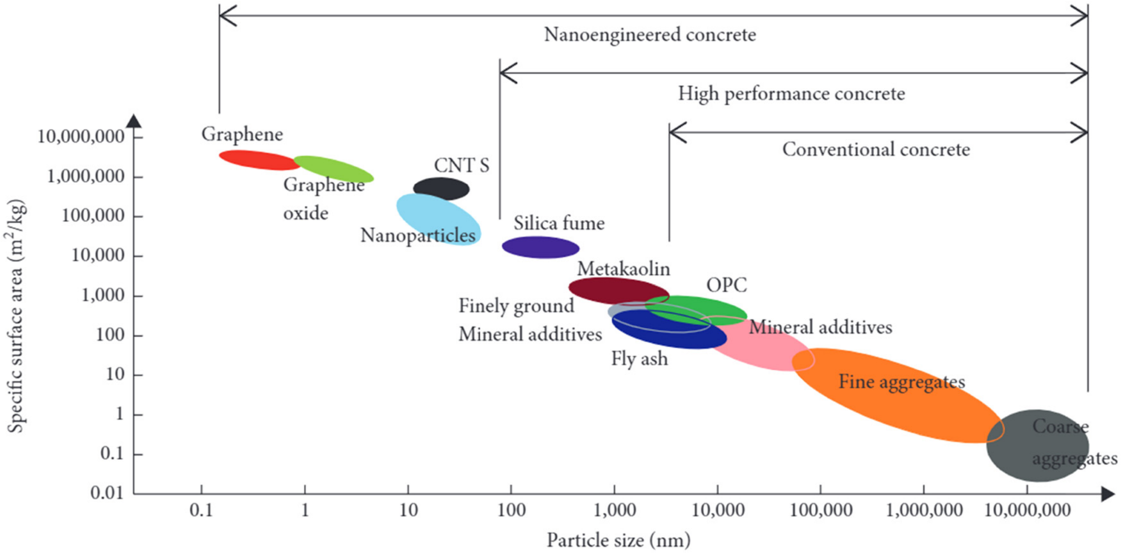

Figure 1: Relationship between particle size and specific surface area of concrete [15].

corresponding mechanisms and key problems. The types of material selections, the research progress of the properties, and dispersion of nanomaterials in the field of GPC modified by nanomaterials in recent ten years were reviewed, the mechanical properties of GPC modified by nanomaterials were comprehensively analyzed, and the application prospects and possible challenges of nanomaterials in GPC were prospected.

2 Types and properties of the selected nanomaterials

Studying the properties of nanomaterials can help scholars to analyze the modification mechanism of nanomaterials. The research on the properties of nanomaterials should start with the selection of materials; a brief introduction will be given below. At the same time, the types and physical and chemical properties of nanomaterials will be introduced in detail, to help readers quickly establish the system framework of modified nanomaterials.

2.1 Nanomaterials selection used in modified concrete

The research shows that the workability, mechanical properties, durability, and microstructure of concrete can be effectively improved by adding nanomaterials [17]. At present, materials such as nano-SiO_2 (NS), nano-$CaCO_3$ (NC), nano-Al_2O_3 (NA), nano-Fe_3O_4, nano-TiO_2 (NT), nano-ZnO_2, carbon nanotubes (CNTs) and nano-metakaolin, and graphene oxide (GO) are often used as admixtures [18–25], to improve the engineering properties of concrete. The first step to prepare Nanomaterial-Modified GPC is to select suitable nanomaterial as additive. There are various nanomaterials on the market with different characteristics and functions. As shown in Figure 2 [26], it can be seen that NS is the most commonly used nanomaterial to modify GPC at present, which has a significant impact on the fluidity, mechanical properties, and microstructure of concrete. Other nanomaterials have many advantages, but the main limiting factors of other nanomaterials are high price, not easy to disperse, and so on [25].

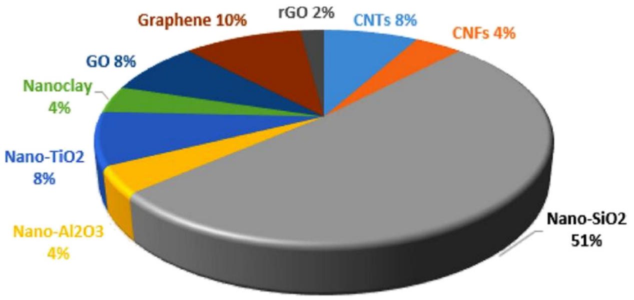

Figure 2: Research on the use of various nanomaterials in geopolymers [26].

2.2 Physical properties of nanomaterials

According to their morphology, nanomaterials can be divided into three types, nanoparticles (such as NS, NA, and NT), nanotubes/fibers (with one-dimensional linear characteristics, such as CNTs), and nanoflakes (with two-dimensional flake characteristics, such as GO nanoparticles). Table 1 lists the main characteristics of the representative products of these three types of nanomaterials.

Nanomaterials have high specific surface area, which enables them to act as the main components of concrete modification, produce additional hydration products and dense interfacial transition zone (ITZ) in concrete, and form more favorable microstructure to promote engineering performance. The research results of Sato and Diallo [33] show that due to the presence of NC in the geopolymer matrix, the rapid formation of calcium silicate hydrate gel (C–S–H) on the surface of tricalcium silicate is observed. The formation of additional hydration products and the filling effect of nanomaterials improve the performance of ITZ and the permeability resistance of concrete.

On the other hand, the high aspect ratio of CNTs and other nanomaterials makes it suitable for improving mechanical properties of concrete. CNTs enhance the connection ability of various parts of concrete material on the nano scale and produce obvious bridging effect, thus improving the mechanical properties of material and reducing the generation of cracks.

2.3 Chemical properties of nanomaterials

Nanomaterials increase the rate of aluminate formation by accelerating the hydration reaction of tricalcium aluminate, which is confirmed in the studies of Sato and Diallo [33]. They found that adding nanomaterials shortened the curing cycle of concrete and increased the heat of hydration. On the other hand, nanomaterials can also react with tricalcium silicate to shorten the setting time of

Table 1: Main properties of nanomaterials

Types	Nanomaterials	Main features	References
Nanoparticles	NS	1. It is globular and mainly amorphous with high volcanic ash activity 2. The diameter is usually 2–100 nm and the specific surface area is about 10–200 m^2/g	[21]
	NA	1. It is mainly globular or sub-globular and is characterized by volcanic ash activation 2. The diameter is usually less than 100 nm and the specific surface area is about 10–100 m^2/g	[7,13,27]
	NT	1. NT particles have several structures, including rutile, anatase, hydrotalcite, TiO_2 (B), TiO_2 (H), TiO_2 (R), and cubic phase. Mainly high crystalline phase, no volcanic ash reactivity 2. The diameter is generally 1–200 nm and the specific surface is 10–150 m^2/g	[28,29]
Nanofibers	CNTs	1. The diameter of nanotubes is 0.4–2 nm and the specific surface area is 20–1,315 m^2/g 2. Tensile strength is usually between 50–200 GPa, modulus of elasticity is higher than 1,000 GPa, and conductivity is higher than 1,000 S/cm	[30,31]
Nanoflakes	GO	1. The main functional groups fixed on GO surface are –OH and –COOH, which can be detected by FTIR method 2. The tensile strength of GO is above 112 GPa, the modulus of elasticity is above 300 GPa, and the resistance is high	[32]

concrete and improve its early strength [34]. However, for materials like NS, the improvement of mechanical properties of concrete is more due to the increase of silica content than to the chemical reaction between NS and concrete base [35].

It's worth noting that the effect of concrete composites modified by nanomaterials will also be affected by the dispersion degree of nanoparticles in the composite matrix. The improper dispersion of nanomaterials will lead to the agglomeration of nanomaterials, resulting in the formation of weak areas in the matrix and the corresponding reduction of mechanical properties, which means that the doping number of nanomaterials needs to be appropriate.

It is not difficult to find out from the above discussion that how to effectively utilize these nanomaterials and fully utilize their special potential in GPC is a matter of concern. For this reason, academia and industry should devote themselves to solving the problem of complete dispersion of nanomaterials in GPC, and at the same time, improve the basic understanding of the mechanism of properties modification of GPC modified by nanomaterials.

3 Dispersion technology and characterization method of nanomaterials

Nanomaterials have large specific surface area and surface activity. Due to the existence of Van der Waals force (VDW), nanomaterials tend to agglomerate in the natural state, resulting in uneven distribution and reducing the application performance of GPC. Therefore, it is necessary to discuss the influence of dispersion methods and characterization methods of nanomaterials on GPC.

3.1 Dispersion methods of nanomaterials

The dispersion of nanomaterials is a very important link in the research field of nanomaterial-modified GPC, which can directly affect the performance of GPC. Therefore, the selection of appropriate dispersion mode is a very basic and important step in the research of nanomaterial-modified GPC.

At present, the most popular dispersion method is ultrasonic dispersion. Ultrasonic vibration provides a strong shear force, which can effectively counteract VDW and make the aggregated nanomaterials disperse more effectively to prepare a uniform suspension [36]. However, some scholars believe this method has obvious disadvantages. Suzuki *et al.* [37] and others mentioned that this method is time-consuming, too complex, and expensive when using ultrasonic to disperse nanomaterial. In order to solve this problem, Saafi *et al.* [38] studied the combined application of ultrasound and polycarboxylate surfactants to prepare more thoroughly dispersed suspensions in a shorter time. Abbasi *et al.* [39] used a similar method to disperse the mixture of NMK. Xu *et al.* [40] used Darex super 20, a high-water reducing superplasticizer based on naphthalene sulfonate, combined with ultrasonic wave for 30 min to obtain effectively dispersed GO suspension, as shown in Figure 3 [41].

Figure 3: Ultrasound combined with Darex Super20 dispersion effect [41].

The dosage of superplasticizer and ultrasonic power should also be considered in the comprehensive dispersion method; there is a lack of systematic and unified understanding in this aspect. In the exploration of reducing the water dosage, Zhao *et al.* [42] suggested that the dispersion effect is best when the mass ratio of dispersant to nanomaterial is 10:1. Lu *et al.* [43] believe that when the mass of the dispersant is 15% of nanomaterials, it is most conducive to dispersion. In terms of ultrasonic power, it is generally believed that it will have a great impact on the dispersion state of GO. Too small power will lead to poor dispersion effect, and too much power will damage the structure of GO. Li *et al.* [44] pointed out that GO/PVA composites have better dispersion when the ultrasonic energy is 15 Wh/L. Liu *et al.* [45] found that GO/nano-silica composite had the best dispersion when the ultrasonic power was 100 W; the mechanical properties of GO/metakaolin are the best, when the ultrasonic time is 15 min and the power is 81–94 W. Considering the different composites studied, the parameters of ultrasonic equipment and the corresponding treatment methods are different. It is therefore impossible to generalize the rule of universality from their studies. Ultrasound power and time also need to be determined according to the object of study of each test, and on the premise of many experiments, to find the best dispersion scheme.

In addition, methods such as chemical additives, covalent functionalization, *etc*. can be used to disperse nanomaterials [46–48]. However, in fact, most of the above decentralization methods are too costly and some of them are cumbersome; they are difficult to be widely applied in practical engineering projects. There is no dispersion method with strong applicability at present; it can be inferred that future research on this field will continue to deepen and finally find a dispersion method with strong adaptability.

3.2 Methods for characterizing dispersion

In trial-preparation vessels, it is often possible to observe the dispersion of nanomaterials with the naked eye and check whether nanomaterials have precipitation and agglomeration, *etc*. However, there is no widely applicable and convenient method for evaluating the dispersion of nanomaterials in hardened GPC. Scanning electron microscopy (SEM) is the most commonly used method to directly study the dispersion of nanomaterials [49]. Due to the existence of active particles in the hydration process of cementitious materials, it is difficult to separate the hydration products of geopolymer from those of reacted nanomaterials, so this method is often disturbed by many factors. Some tests use the engineering properties of hardened GPC, such as mechanical strength, water absorption, and gas permeability, to indirectly evaluate the dispersion of nanomaterials, but so far there is no direct evidence and relevant details to confirm the reliability of this method [50].

As discussed above, characterizing the dispersion of nanomaterials in suspensions is much easier, and these methods are potential options to accurately predict the distribution of nanomaterials in hardened GPC. In the past research, there are many methods to characterize the dispersion of nanomaterials in suspension, and they have been fully studied, such as ultraviolet-visible

Table 2: Characterization of dispersion of nanomaterials in suspensions

Method	Criteria of judgment	References
Laser particle size analysis	The smaller the particle size, the better the dispersion	[51]
ATR-FTIR spectroscopy	The larger the particle spacing, the better the dispersion	[52]
Zeta potential	The higher the particle potential, the better the dispersion	[37]
SEM	The smaller the particle size, the better the dispersion	[25]

spectroscopy, laser particle size analysis, dynamic light scattering, zeta potential, Attenuated Total Reflectance - Fourier Transform Infrared spectroscopy (ATR-FTIR), SEM, confocal laser scanning microscopy (CLSM), and atomic force microscopy. The specific methods are shown in Table 2.

The research on dispersion mode and characterization method mainly focuses on tentative exploration, but there is no relatively uniform understanding at present. Existing research and exploration have been accumulated in quantity; the author believes that with the deepening of the research, breakthroughs will be made.

4 Working properties of nanomaterials-modified GPC

It is not difficult to find from the above analysis that the micro-physical properties of nanomaterials obviously have a significant influence on the working performance of GPC. The condensation time of GPC is very short, which is not conducive to transportation and construction on site; the application of GPC in engineering is greatly limited and it is often used to prepare precast concrete [53].

Many scholars try to use different nanomaterials to study the change of concrete performance. Wu *et al.* [54] found that the workability of concrete was greatly improved after the addition of NC, and the slump increased slightly when the content of NC varied between 0 and 1.5%. The study found that the optimum content of NC was 1.5%. A study found that ref. [55] the water demand decreased with the increase of NC content, and when the NC content was 2, 5, and 8%, the water demand decreased by 0.4, 1.8, and 3.2%, respectively.

Several studies have found that NS has a negative effect on GPC slump. Hani *et al.* [56] added 0.75% NS to study the influence on the slump of three different water-cement ratios of concrete, which decreased by 15.2, 15.5, and 14.1%, respectively, compared with the standard group; thus it can be seen that NS reduced the slump and flow of concrete mixtures with different water-cement ratios, and these changes were more obvious with the increase of nanoparticle content. They believe this is related to the increase in the surface area of concrete after adding nanomaterials, which will require more mortar to wrap NS, resulting in a decrease in its fluidity. Similarly, Adesina [57] found that adding NS up to 1.5% could significantly reduce the slump at different water-binder ratios. As shown in Figure 4 [57], the decrease in the slump of concrete with NS can be attributed to the formation of a high water-retaining microstructure, which results in an increase in the viscosity of the mixture.

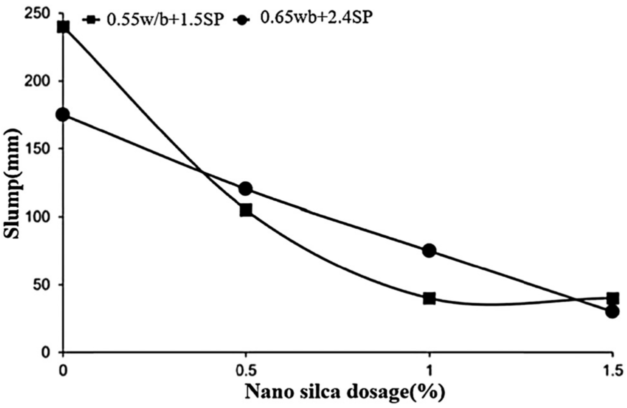

Figure 4: Relationship between NS content and slump [57].

Adjusting the water-binder ratio can improve the performance of GPC, but it has little effect on mechanical properties and durability of hardened GPC. Sun *et al.* [58] studied the influence of CNTs on the workability of concrete through experiments. The research found that when concrete is not mixed with CNTs, the slump can reach 150 mm. With the increase of CNTs content, the slump of concrete mixtures gradually decreases, and the fluidity becomes poor. Adding water reducer (<1.0%) into concrete mixtures with different CNT contents can make the slump of the mixtures up to 150–160 mm, which meets the construction requirements. Although surface modification of nanomaterials and geopolymers with water reducers or high-efficiency water reducers can improve the working performance of fresh mixtures, the effectiveness of high-efficiency water reducers may be affected by strong alkali, which will undoubtedly increase the difficulty of GPC preparation [59], as alkali activators are required for the polymerization of GPC.

The influence of nano magnetite on the working performance of concrete is negligible [60]. This phenomenon is attributed to the highly hydrophobic and porous morphology of nano magnetite. Therefore, it is important to understand the physical properties of nanomaterials and their possible influence on their working properties before they are applied to concrete composites.

According to the existing literature, there are still few articles on the performance of nanomaterials-modified GPC. The selected test materials have a certain randomness, and there is a lack of unified understanding of the performance improvement efficiency. Systematic research on performance improvement is still worth extensive exploration. It is necessary to conduct necessary analysis and research from the aspects of material selection, test method, measuring index, statistical method, and so on.

5 Mechanical properties of nanomaterials-modified GPC

By adding various nanomaterials to modify the concrete matrix, concrete with good mechanical properties can be obtained, which is one of the most promising research fields of nanomaterials in concrete. More and more studies have shown that nanomaterials can be used to improve the mechanical properties of GPC. The mechanism of this improvement can be summarized as filling effect, bridging effect, and hydration regulation effect of nanomaterials, *etc*., which will be discussed in the following chapters.

5.1 Study on compressive strength

The compressive strength of concrete is one of the most basic and important mechanical properties. Alomayri [13] made GPC from low-calcium fly ash (FA) and studied it with NA. It was found that the compressive strength can be increased by 12% when the optimum NA content is 2% mass fraction, but the strength will decrease when the content of NA exceeds this amount. Due to the increase of the concentration of NA, the amount of aluminum available for reaction also increases, the reaction speed increases, and active aluminum promotes gel formation. Due to the influence of dispersion mode, excessive NA will increase the porosity of GPC and decrease the strength, when the concentration of NA exceeds the optimum concentration. On this basis, Phoo-ngernkham *et al.* [7] added the same 2 wt% NS and NA composite nanomaterials, and the strength of GPC is further increased by 26%. Singh *et al.* [61] used 5% of NS; after 24 h of curing, the compressive strength increased by more than 60%. Deb *et al.* [62] also blended NS with a mass fraction of 2% and increased the 28-day compressive strength of GPC by 129%.

The modification mechanism of NS is different from that of NA. NS improves the compressive strength not only because of the additional hydration reaction of nanomaterials, but also because NS promotes further volcanic ash reaction. The modification effect of NS is naturally better than that of NA [63].

Similarly, the improvement of compressive strength of concrete by NT is only related to its pore filling effect. Compared with NS, NT has no pozzolanic reaction. The research shows that the optimum content of NT is 3% [64]. When the optimum content is exceeded, NT may aggregate and form a weak area in GPC [65]. At the same time, Duan *et al.* [66] demonstrated that after NT addition, the micro-cracks and micropores were refined due to bridging and nano-filling effects of NT. They also described the microstructure differences of NT at different ages in a simulation model, as shown in Figure 5 [26].

Some scholars have studied the influence of nanomaterial modification on the properties of fiber GPC and analyzed the data through experiments. Amin and Abu el-Hassan [67] have studied the influence of NS content from 0 to 1.8% and different content of basalt fibers on compressive and tensile strength. The research shows that with the increase of NS content, hydration reaction will produce a large amount of C–S–H gel and alumina, iron oxide, and trisulfide crystals. When the content is 1.2%, the content of C–S–H gel is the highest, which makes the concrete more compact. These inferences are also demonstrated from the compressive strength observed in the tests. However, Li *et al.* [22] did similar studies and found that 2% is the best amount to improve concrete performance.

In order to summarize and consider the influence laws of various materials on GPC, it is necessary to find a model to describe the modification effect. Considering the large amount of data distribution of various studies, it is difficult to integrate these intensity enhancement mechanisms with a common formula. Instead, using a box plot makes it easier to see and summarize the strength enhancement levels of different nanomaterials, as shown in Figure 6 [26]. The majority of nanoscale enhancements occur in the 28-day compressive strength of GPC, ranging from 7 to 49%, with median and average values of about

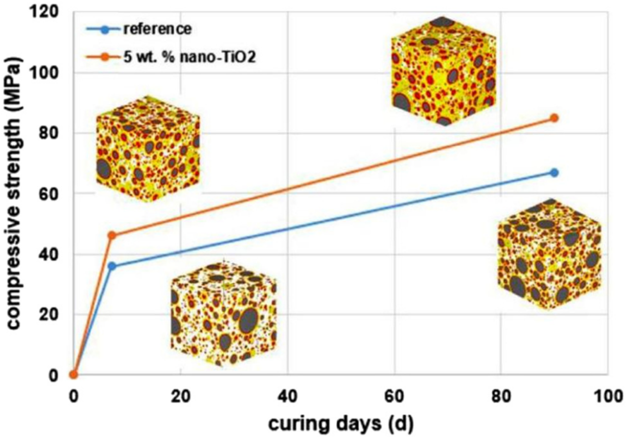

Figure 5: Simulated microstructure of NT-modified GPC at different maintenance ages [26].

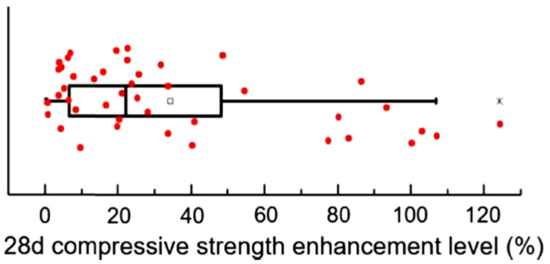

Figure 6: Distribution of GPC strength enhancement levels by different nanomaterials [26].

22 and 34%, respectively. These data provide a good predictor of strength improvement. The research shows that the dispersion level of nanomaterials has a great influence on the engineering properties of GPC. Therefore, good dispersion and high-quality nanomaterials can make the modification effect of GPC reach the ideal data shown in the diagram, that is, the strength enhancement effect is higher than 60%.

From the above analysis, it is not difficult to find that the effect of modification of GPC compressive strength by nanomaterials is directly affected by material type, dispersion mode, reaction mechanism, *etc*. Existing research has accumulated valuable exploration results, but there are still uncertainties in many issues, and there is still a great potential research value in this aspect.

5.2 Study on tensile strength

It is well-known that concrete has a low tensile strength of only 1/10–1/20 of its compressive strength. For the tensile strength of GPC, due to the different physical and chemical properties of different nanomaterials, there is often a significant difference in the modification effect.

Du *et al.* [68] and others used FA to prepare high-performance GPC with GO. Unlike the traditional method of directly incorporating nanomaterials into GPC, they have explored a more targeted method; nanomaterials are used to improve the interface between coarse aggregate and mortar. The key point is to coat the coarse aggregate with a layer of cementitious material mortar containing GO, as shown in Figure 7 [68]. Research shows that the tensile strength of GPC made by this method can be increased by 20%. Mokhtar *et al.* [69] directly filled GO into GPC; the tensile strength only increased by 9.2%. Through the comparison of the strength improvement of the two, it can be seen that the new method of modification and application of nanomaterials has great use value.

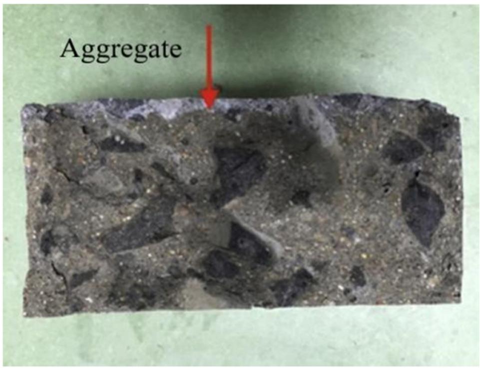

Figure 7: Aggregate diagram [68].

Some scholars used 8% nano-clay instead of slag, and the tensile strength increased by about 50% [70]. This increased tensile strength can be attributed to the filling ability and high volcanic ash activity of nano-clay, which also acts as an activator in the pores, thus increasing and accelerating the formation of hydration products. On the other hand, Chiranjeevi *et al.* [71] modified rice hull ash GPC with NT; the tensile strength only increased by about 9%, because NT only had bridging and nano-filling effects and did not have volcanic ash activity; the reaction mechanism was similar to that of modified compressive strength.

From the above discussion, because NS has high pozzolanic activity, it is helpful to improve the strength of concrete. However, Seifan *et al.* [72] found that the content of geopolymer also had a great influence on the strength of GPC modified by nanomaterials, and excessive addition would have a negative impact. They prepared GPC specimens with NS-modified FA. With the increase of fly ash content, the splitting tensile strength decreased. At low FA content (10%), the splitting strength of the specimens was 22% lower than that of the best specimens (only a small amount of fly ash), but not significantly lower than that of the control specimens (without nanoparticles). The splitting tensile strength of the sample decreases by 0.19 MPa when the fly ash content increases from 10 to 20%. This value is lower than the strength decreases of 0.529 MPa from 20 to 30% FA. The splitting tensile strength decreases the most, when the maximum FA content is 30%, as shown in Figure 8 [72].

At this stage, due to its low price and the combination of chemical function, nucleation function, and filling function, NC has attracted more and more attention [73]. According to literature, it is found that when the content of NC exceeds the optimum content, it is not advantageous to improve the properties of the material. The main reason is that the VDW of NC is larger than that of

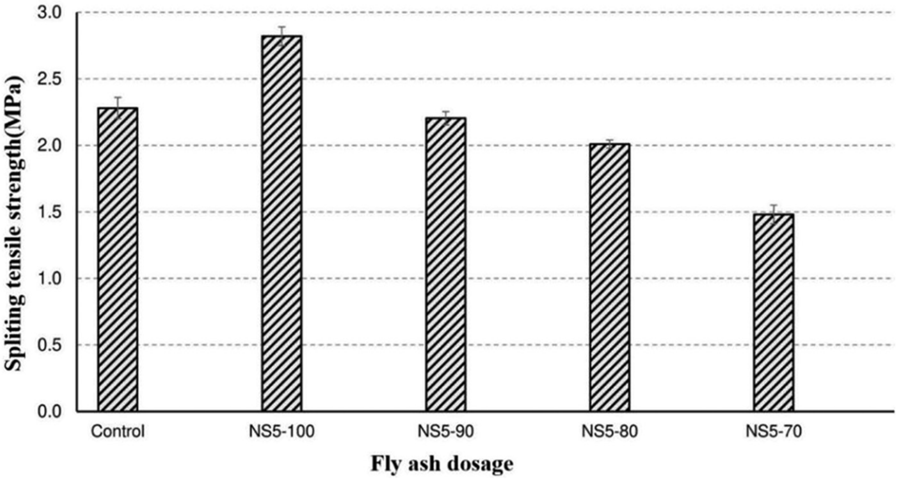

Figure 8: Tensile strength [72].

cementitious materials, and NC with fine particles is easily produced in the mixture. The optimum content of NC is 2.2% when FA content is 29.0%. The tensile strength of GPC was 27.3% higher than that of the control group with this addition [74]. But the strength decreases when this optimum content is exceeded.

At present, it is generally believed that nanomaterial modification can obviously improve the tensile properties of polymer concrete, and some experimental results have been accumulated. Considering the influence of multiple factors such as cost, method, principle, technology, and so on, the current work is still in its infancy, and a large number of scholars are conducting extensive exploration from the aspects of material selection, microscopic mechanism, application conditions, and so on and will make further progress in the future.

5.3 Study on flexural strength

Just like the tensile strength, the flexural strength of concrete is relatively low. However, unlike the compressive strength, the main reason for the improvement of the flexural strength of GPC modified by nanomaterials is the bridging effect of nanomaterials [75].

Zhang *et al.* [76] considered the serious concrete disease of tunnel structure, took FA as basic material, and combined pre-suspended NS with superfine admixture to improve the flexural strength of GPC. The test found that when the NS content is 5%, this method can steadily increase the flexural strength of GPC by more than 17%, and more importantly, it can improve the crack resistance of GPC very well. Zhang *et al.* [77] used fly ash and metakaolin to make reinforcing bar GPC, modified with NS, and added PVA fiber to enhance flexural strength of GPC. It was found that the bonding properties of GPC were optimized when the PVA fiber content was between 0.6 and 0.8% and NS content was between 1.5 and 2%. And the relationship between steel slip and stress is obtained, as shown in Figure 9 [77].

Nanomaterials have a great influence on the improvement of GPC by the amount of doping, and there is often an optimum amount of doping. If this limit is exceeded, the strength will decrease instead. Studies by Lucas *et al.* [78] have shown that the high content of nanomaterials (*i.e.*, more than 2.5%) in concrete leads to a decrease in flexural strength, which is observed to be about 30% when

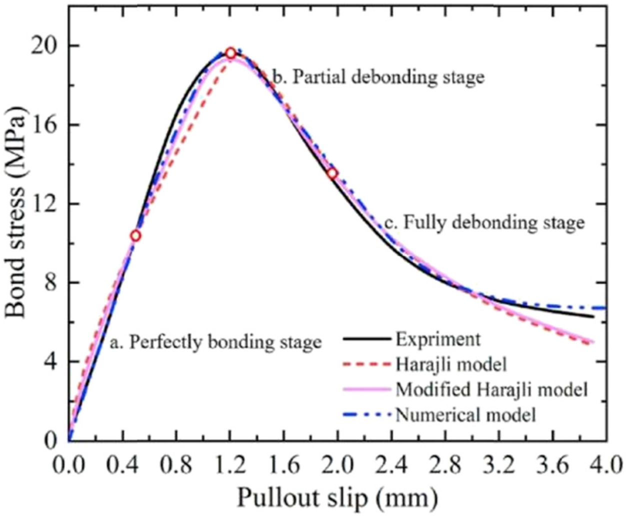

Figure 9: Relationship between slip and stress of reinforcement [77].

NA is used as a substitute for Geopolymer in the range of 2.5–5%. At the same time, Wang *et al.* [79] analyzed that the reason for the decrease in strength might be the short curing age. He added 0.75% NS and 3% nano-clay into the concrete. After 90 days of curing, the bending strength could be increased by 9%. No reduction in bending strength was found. Adding 3% nanoparticles (containing 25% NS and 75% nano-clay) had a great effect on improving mechanical properties.

Many scholars are very interested in the optimal mixing amount of nanomaterials. Studies by Morsy *et al.* [25] and Li *et al.* [80] have shown that aggregation of nanomaterials in cemented composites will lead to micropore and corresponding weak areas in the composites. Li *et al.* [80] also concluded that NS and NA could only increase the flexural strength of concrete at a maximum dosage of 1%, and that it was observed that the flexural strength would decrease at higher nano-content. Konsta *et al.* [81] also showed that the flexural strength of high-strength concrete can be improved by adding 4.8% NC, while the flexural strength of common GPC can be improved by adding low NS content (*i.e.*, 0.5%). Changes in the optimum quantities of different types of nanomaterials indicate that the optimum quantities of these types of nanomaterials should be evaluated preliminarily before they can be used on a large scale.

The flexural strength is greatly affected by the crack of concrete, and the inhibition of crack is the research focus of nanometer-modified materials to improve the performance of concrete. The internal structure will be rapidly polluted by water and pollutants, when cracks occur on the surface of concrete. Some studies have shown that porous and honeycomb structures of alkali-activated blast furnace slag particles can be used as ideal carriers for photocatalytic removal of atmospheric and water pollutants [82]. Based on this, Zhu *et al.* [83] and others added NT through impregnation method to join photocatalytic-activated slag particles. The physicochemical properties and NO removal properties of activated slag particles/NT photocatalyst were studied by X-ray diffraction, SEM, and photocatalytic performance test. Research shows that the GPC has 31% more ability to absorb pollutants and 40% higher flexural strength when NT is added.

Nanomaterial-modified geopolymer self-compacting concrete also has high engineering application value [84,85]. Langaroudi and Mohammadi [86] found that the flexural strength of geopolymer self-compacting concrete was significantly improved when the NC content was 3% compared with 1 and 2% NC, and 3% is the optimum NC content for geopolymer self-compacting concrete. Hamed *et al.* [87] studied the influence of different NC contents (5, 7.5, and 10%) on the performance of concrete and found that the performance of concrete treated with NC particles by ultrasonic treatment was significantly improved compared with that of NC concrete directly added, and that the optimum content of NC substitute geopolymer was 7.5%.

In addition to the above discussion studies, other studies are listed in Table 3 [88–90]. In a word, the influence factors of nanomaterials on the mechanical properties of GPC are complex, involving material properties, curing age, material combination, and so on [91–93]. Therefore, a lot of research is needed to support breakthrough progress.

6 Summary and prospect

Nanomaterials have a good effect on improving the performance of GPC and expand the engineering application field of GPC. Modification of GPC with nanomaterials is still in the primary stage, and some valuable research results have been achieved. At the same time, it proves that there is great research value potential in this field. In order to further improve the application value of nanomaterial-modified GPC and make the research in this field more mature, some key bottlenecks need to be solved and

Table 3: Optimum doping amount of nanomaterials (%)

Nanomaterials	Compressive strength content	Tensile strength content	Flexural strength content	References
NS	4.8	4.8	3.0	[88]
NS	1	0.5	0.5	[21]
NS	2	2	2	[1]
NC	2	—	1	[1]
NA	3	—	—	[89]
NMK	9	—	—	[90]
NS	2.5	2.5	3	[88]

some key technologies need to be explored. The main conclusions and prospects of this paper are summarized as follows:

(1) Due to its excellent physical and chemical mechanism, nanomaterials can improve the properties of GPC, which is a hot research topic in recent years. There are many kinds of nanomaterials; NS is the most common choice to modify Geopolymer Materials. Although the modification effect of NS is remarkable, the high cost of NS greatly limits the development of this field. Therefore, it is very important to optimize the production process of NS or develop other feasible nanomaterials.

(2) There is a lack of systematic research and unified understanding of the dispersion methods and characterization methods of nanomaterials. Different dispersion methods have a significant impact on the performance of concrete. There is a certain conflict between the convenience of operation mode and the uniformity of dispersion, and the two cannot be perfectly coordinated, which is worthy of further exploration. On the other hand, the way of characterizing the dispersion of nanomaterial in concrete is not uniform and clear enough. At present, it can only be inferred from the macroscopic physical and mechanical properties of concrete. These two aspects are the primary influencing factors of the performance of GPC modified by nanomaterials, and scholars need to increase research efforts in this aspect.

(3) Nanomaterials have a significant effect on the performance of GPC. Some studies have found that nanomaterials will significantly reduce the fluidity of GPC, which is detrimental to the pouring and transportation of GPC. Although superplasticizer can be added to improve the flow performance of concrete, it will increase the difficulty of preparing GPC. Therefore, efforts need to be made to develop more admixtures in material selection to improve the working performance of GPC.

(4) The mechanical properties of GPC modified by nanomaterial are significant, but the results are different with the kinds and contents of nanomaterials. Nanomaterials have no uniform effect on the compressive strength, tensile strength, flexural strength, and other strength indexes of GPC; it often has different dosage and modification mechanisms for different strength indexes of concrete. For example, the improvement of compressive strength is mainly due to the hydration reaction, pozzolanic effect, and other chemical properties of nanomaterial, but the tensile and flexural strength index are due to its bridging effect at the micro level. Complex mechanism and many influencing factors hinder the development of this field. How to systematically study the modified mechanical properties of nanomaterials and establish a unified theory has become the focus of current exploration.

(5) Most of the researches on GPC modified by nanomaterial are in the initial stage of exploration, and few studies pay attention to the application value in this field, mainly because the price of nanomaterial and the research results in this field are not unified. Therefore, more basic research is needed to make up for the research gap in nanomaterial, dispersion effect, and performance, to promote the field of nanomaterial-modified GPC, and to develop its application value rapidly.

Acknowledgments: The writing of this paper has been supported by many projects, which can be seen in funding information. At the same time, the project team members and all authors have supported this paper. A note of thanks to them.

Funding information: This study was supported by the Open Project of Chongqing groundwater Resources Utilization and Environmental Protection Laboratory (DXS20191029), Sichuan Science and Technology Program (2020JDR0266), Sichuan Mingyang Construction Engineering Management Co., Ltd. Specialized Project (MY2021-001).

Author contributions: All authors have accepted responsibility for the entire content of this manuscript and approved its submission.

Conflict of interest: David Hui, who is the co-author of this article, is a current Editorial Board member of *Nanotechnology Reviews*. This fact did not affect the peer-review process. The authors declare no other conflict of interest.

References

[1] Diab AM, Elyamany HE, Abd elmoaty AEM, Sreh MM. Effect of nanomaterials additives on performance of concrete resistance against magnesium sulfate and acids. Constr Build Mater. 2019;210:210–31.

[2] Arel H, Thomas B, Arel HS, Thomas BS. The effects of nano- and micro-particle additives on the durability and mechanical properties of mortars exposed to internal and external sulfate attacks. Results Phys. 2017;7:843–51.

[3] Khater HM. Effect of calcium on geopolymerization of aluminosilicate wastes. J Mater Civil Eng. 2012;24(1):92–101.

[4] Ranjbar N, Zhang M. Fiber-reinforced geopolymer composites: a review. Cement Concrete Comp. 2020;107:103498.

[5] Scrivener KL, John VM, Gartner EM. Eco-efficient cements: potential economically viable solutions for a low-CO_2 cement-based materials industry. Cement Concrete Res. 2018;114:2–26.

[6] Sumesh M, Alengaram UJ, Jumaat MZ, Mo KH, Alnahhal MF. Incorporation of nano-materials in cement composite and geopolymer based paste and mortar – a review. Constr Build Mater. 2017;148:62–84.

[7] Phoo-ngernkham T, Chindaprasirt P, Sata V, Hanjitsuwan S, Hatanaka S. The effect of adding nano-SiO_2 and nano-Al_2O_3 on properties of high calcium fly ash geopolymer cured at ambient temperature. Mater Design. 2014;55:58–65.

[8] Khater HM, El gawaad HAA. Characterization of alkali activated geopolymer mortar doped with Mwcnt. Constr Build Mater. 2016;102:329–37.

[9] Cioffi R, Maffucci L, Santoro L. Optimization of geopolymer synthesis by calcination and polycondensation of a kaolinitic residue. Resour Conserv Recy. 2003;40(1):27–38.

[10] Liu Y, Shi C, Zhang Z, Li N. An overview on the reuse of waste glasses in alkali-activated materials. Resour Conserv Recy. 2019;144:297–309.

[11] Xu Z, Huang Z, Liu C, Deng X, Hui D, Deng S. Research progress on mechanical properties of geopolymer recycled aggregate concrete. Rev Adv Mater Sci. 2021;60(1):158–72.

[12] He J, Zhang J, Yu Y, Zhang G. The strength and microstructure of two geopolymers derived from metakaolin and red mud-fly ash admixture: a comparative study. Constr Build Mater. 2012;30:80–91.

[13] Alomayri T. Experimental study of the microstructural and mechanical properties of geopolymer paste with nano material (Al_2O_3). J Build Eng. 2019;25:100788.

[14] Wang L, Jin M, Wu Y, Zhou Y, Tang S. Hydration, shrinkage, pore structure and fractal dimension of silica fume modified low heat portland cement-based materials. Constr Build Mater. 2021;272:121952.

[15] Sobolev K, Gutierrez M. How nanotechnology can change the concrete world. Am Ceram Soc Bull. 2005;84(11):16–9.

[16] Hosseini P, Booshehrian A, Farshchi S. Influence of nano-SiO_2 addition on microstructure and mechanical properties of cement mortars for ferrocement. Transport Res Rec. 2010;2141:15–20.

[17] Senff L, Hotza D, Repette WL, Ferreira VM, Labrincha JA. Mortars with nano-SiO_2 and micro-SiO_2 investigated by experimental design. Constr Build Mater. 2010;24(8):1432–37.

[18] Szczepanik B. Photocatalytic degradation of organic contaminants over clay-TiO_2 nanocomposites: a review. Appl Clay Sci. 2017;141:227–39.

[19] Ismael R, Silva JV, Carmo RNF, Soldado E, Lourenco C, Costa H, et al. Influence of nano-SiO_2 and nano-Al_2O_3 additions on steel-to-concrete bonding. Constr Build Mater. 2016;125:1080–92.

[20] Braganca MOGP, Portella KF, Bonato MM, Alberti E, Marino CEB. Performance of portland cement concretes with 1% nano-Fe_3O_4 addition: electrochemical stability under chloride and sulfate environments. Constr Build Mater. 2016;117:152–62.

[21] Khaloo A, Mobini MH, Hosseini P. Influence of different types of nano-SiO_2 particles on properties of high-performance concrete. Constr Build Mater. 2016;113:188–201.

[22] Li W, Huang Z, Cao F, Sun Z, Shah SP. Effects of nano-silica and nano-limestone on flowability and mechanical properties of ultra-high-performance concrete matrix. Constr Build Mater. 2015;95:366–74.

[23] Vazinram F, Jalal M, Foroushani MY. Effect of nano ZnO_2 and lime water curing on strength and water absorption of concrete. Int J Mater Prod Tec. 2015;50(3):356–65.

[24] Supit SWM, Shaikh FUA. Effect of nano-$CaCO_3$ on compressive strength development of high volume fly ash mortars and concretes. J Adv Concr Technol. 2014;12(6):178–86.

[25] Morsy MS, Alsayed SH, Aqel M. Hybrid effect of carbon nanotube and nano-clay on physico-mechanical properties of cement mortar. Constr Build Mater. 2011;25(1):145–9.

[26] Li Z, Fei M, Huyan C, Shi X. Nano-engineered, fly ash-based geopolymer composites: an overview. Resour Conserv Recy. 2021;168:105334.

[27] Ranjbar N, Mehrali M, Mehrali M, Alengaram UJ, Jumaat MZ. Graphene nanoplatelet-fly ash based geopolymer composites. Cement Concrete Res. 2015;76:222–31.

[28] Brzicova T, Sikorova J, Milcova A, Vrbova K, Klema J, Pikal P, et al. Nano-TiO_2 stability in medium and size as important factors of toxicity in macrophage-like cells. Toxicol In Vitro. 2019;54:178–88.

[29] Zhang H, Banfield JF. Structural characteristics and mechanical and thermodynamic properties of nanocrystalline TiO_2. Chem Rev. 2014;114(19):9613–44.

[30] Cheung W, Pontoriero F, Taratula O, Chen AM, He H. DNA and carbon nanotubes as medicine. Adv Drug Deliver Rev. 2010;62(6):633–49.

[31] Shi T, Li Z, Guo J, Gong H, Gu C. Research progress on CNTS/CNFS-modified cement-based composites. Constr Build Mater. 2019;202:290–307.

[32] Li D, Mueller MB, Gilje S, Kaner RB, Wallace GG. Processable aqueous dispersions of graphene nanosheets. Nat Nanotechnol. 2008;3(2):101–5.

[33] Sato T, Diallo F. Seeding effect of nano-$CaCO_3$ on the hydration of tricalcium silicate. Transport Res Rec. 2010;2141:61–7.

[34] Deweerdt K, Benhaha M, Lesaout G, Kjellsen KO, Justnes H, Lothenbach B. Hydration mechanisms of ternary portland cements containing limestone powder and fly ash. Cement Concrete Res. 2011;41(3):279–91.

[35] Lim S, Mondal P. Effects of incorporating nanosilica on carbonation of cement paste. J Mater Sci. 2015;50(10):3531–40.

[36] Chuah S, Li W, Chen SJ, Sanjayan JG, Duan WH. Investigation on dispersion of graphene oxide in cement composite using different surfactant treatments. Constr Build Mater. 2018;161:519–27.

[37] Suzuki T, Sakka Y, Nakano K, Hiraga K. Effect of ultrasonication on the microstructure and tensile elongation of zirconia-dispersed alumina ceramics prepared by colloidal processing. J Am Ceram Soc. 2001;84(9):2132–4.

[38] Saafi M, Andrew K, Tang PL, Mcghon D, Taylor S, Rahman M, et al. Multifunctional properties of carbon nanotube/fly ash geopolymeric nanocomposites. Constr Build Mater. 2013;49:46–55.

[39] Abbasi SM, Ahmadi H, Khalaj G, Ghasemi B. Microstructure and mechanical properties of a metakaolinite-based

geopolymer nanocomposite reinforced with carbon nanotubes. Ceram Int. 2016;42(14):15171–6.
[40] Xu G, Zhong J, Shi X. Influence of graphene oxide in a chemically activated fly ash. Fuel. 2018;226:644–57.
[41] Kashif ur rehman S, Kumarova S, Ali memon S, Javed MF, Jameel M. A review of microscale, rheological, mechanical, thermoelectrical and piezoresistive properties of graphene based cement composite. Nanomaterials-Basel. 2020;10(10):2076.
[42] Zhao L, Guo X, Liu Y, Zhao Y, Chen Z, Zhang Y, et al. Hydration kinetics, pore structure, 3d network calcium silicate hydrate, and mechanical behavior of graphene oxide reinforced cement composites. Constr Build Mater. 2018;190:150–63.
[43] Lu Z, Hanif A, Ning C, Shao H, Yin R, Li Z. Steric stabilization of graphene oxide in alkaline cementitious solutions: mechanical enhancement of cement composite. Mater Design. 2017;127:154–61.
[44] Li Y, Umer R, Samad YA, Zheng L, Liao K. The effect of the ultrasonication pre-treatment of graphene oxide (GO) on the mechanical properties of go/polyvinyl alcohol composites. Carbon. 2013;55:321–7.
[45] Liu H, Yu Y, Liu H, Jin J, Liu S. Hybrid effects of nano-silica and graphene oxide on mechanical properties and hydration products of oil well cement. Constr Build Mater. 2018;191:311–9.
[46] Jandt KD, Watts DC. Nanotechnology in dentistry: present and future perspectives on dental nanomaterials. Dent Mater. 2020;36(11):1365–78.
[47] Park J, Hwang JC, Kim GG, Park JU. Flexible electronics based on one-dimensional and two-dimensional hybrid nanomaterials. Infomat. 2020;2(1):35–6.
[48] Forbot N, Bolibok P, Wisniewski M, Roszek K. Carbonaceous nanomaterials-mediated defense against oxidative stress. Mini-Rev Med Chem. 2020;20(4):294–307.
[49] Du S, Wu J, Alshareedah O, Shi X. Nanotechnology in cement-based materials: a review of durability, modeling, and advanced characterization. Nanomaterials-Basel. 2019;9(9):1213.
[50] Li Z, Shi X. Graphene oxide modified, clinker-free cementitious paste with principally alkali-activated fly ash. Fuel. 2020;269:117418.
[51] Prozeller D, Morsbach S, Landfester K. Isothermal titration calorimetry as a complementary method for investigating nanoparticle-protein interactions. Nanoscale. 2019;11(41):19265–73.
[52] Zhou S, Wu L, Xiong M, He Q, Chen G. Dispersion and UV-vis properties of nanoparticles in coatings. J Disper Sci Technol. 2004;25(4):417–33.
[53] Jadhav UU, Lahoti M, Chen Z, Qiu J, Cao B, Yang E. Viability of bacterial spores and crack healing in bacteria-containing geopolymer. Constr Build Mater. 2018;169:716–23.
[54] Wu Z, Khayat KH, Shi C, Tutikian BF, Chen Q. Mechanisms underlying the strength enhancement of uhpc modified with nano-SiO_2 and nano-$CaCO_3$. Cement Concrete Comp. 2021;119:103992.
[55] Tao M, Kuangliang Q, Xiaoqian Q, Shutin Z. Effect of composite nano-addition on mechanics strength and microstructure of cement paste. Rare Metal Mat Eng. 2008;37:631–3.
[56] Hani N, Nawawy O, Ragab KS, Kohail M. The effect of different water/binder ratio and nano-silica dosage on the fresh and hardened properties of self-compacting concrete. Constr Build Mater. 2018;165:504–13.
[57] Adesina A. Overview of workability and mechanical performance of cement-based composites incorporating nanomaterials. Silicon. 2020;146:154–63.
[58] Sun X, Wang Q, Wang H, Chen L. Influence of multi-walled nanotubes on the fresh and hardened properties of a 3d printing Pva mortar ink. Constr Build Mater. 2020;247:118590.
[59] Lei L, Chan H. Investigation into the molecular design and plasticizing effectiveness of HPEG-based polycarboxylate superplasticizers in alkali-activated slag. Cement Concrete Res. 2020;136:106150.
[60] Sikora P, Horszczaruk E, Cendrowski K, Mijowska E. The influence of nano-Fe_3O_4 on the microstructure and mechanical properties of cementitious composites. Nanoscale Res Lett. 2016;11:182.
[61] Singh LP, Agarwal SK, Bhattacharyya SK, Sharma U, Ahalawat S. Preparation of silica nanoparticles and its beneficial role in cementitious materials regular paper. Nanomater Nanotechno. 2011;1(1):44–51.
[62] Deb PS, Sarker PK, Barbhuiya S. Effects of nano-silica on the strength development of geopolymer cured at room temperature. Constr Build Mater. 2015;101:675–83.
[63] Stynoski P, Mondal P, Marsh C. Effects of silica additives on fracture properties of carbon nanotube and carbon fiber reinforced portland cement mortar. Cement Concrete Comp. 2015;55:232–40.
[64] Chen J, Kou S, Poon C. Hydration and properties of nano-TiO_2 blended cement composites. Cement Concrete Comp. 2012;34(5):642–9.
[65] Akono A. Effect of nano-TiO(2)on C–S–H phase distribution within portland cement paste. J Mater Sci. 2020;55(25):11106–19.
[66] Duan P, Yan C, Luo W, Zhou W. Effects of adding nano-TiO_2 on compressive strength, drying shrinkage, carbonation and microstructure of fluidized bed fly ash based geopolymer paste. Constr Build Mater. 2016;106:115–25.
[67] Amin M, Abuel-hassan K. Effect of using different types of nano materials on mechanical properties of high strength concrete. Constr Build Mater. 2015;80:116–24.
[68] Du S, Ge Y, Shi X. A targeted approach of employing nanomaterials in high-volume fly ash concrete. Cement Concrete Comp. 2019;104:103390.
[69] Mokhtar MM, Abo-el-enein SA, Hassaan MY, Morsy MS, Khalil MH. Mechanical performance, pore structure and microstructural characteristics of graphene oxide nano platelets reinforced cement. Constr Build Mater. 2017;138:333–9.
[70] Allalou S, Kheribet R, Benmounah A. Effects of calcined halloysite nano-clay on the mechanical properties and microstructure of low-clinker cement mortar. Case Stud Constr Mat. 2019;10:2214.
[71] Chiranjeevi K, Vijayalakshmi MM, Praveenkumar TR. Investigation of fly ash and rice husk ash-based geopolymer concrete using nano particles. Appl Nanosci. 2021;15:113–45.
[72] Seifan M, Mendoza S, Berenjian A. Mechanical properties and durability performance of fly ash based mortar containing nano- and micro-silica additives. Constr Build Mater. 2020;252:119121.
[73] Liu C, Huang X, Wu Y, Deng X, Zheng Z, Xu Z, et al. Advance on the dispersion treatment of graphene oxide and the graphene oxide modified cement-based materials. Nanotechnol Rev. 2021;10(1):34–49.

[74] Meng T, Qian KL, Qian XQ, Zhan ST. Effect of composite nano-addition on mechanics strength and microstructure of cement paste. Rare Metal Mat Eng. 2008;37:631–3.

[75] Riahi S, Nazari A. Compressive strength and abrasion resistance of concrete containing SiO_2 and Cuo nanoparticles in different curing media. Sci China Technol Sci. 2011;54(9):2349–57.

[76] Zhang JW, Peng HJ, Mei ZR. Microscopic reinforcement mechanism of shotcrete performance regulated by nanomaterial admixtures. J Mater Res Technol. 2020;9(3):4578–92.

[77] Zhang P, Gao Z, Wang J, Wang K, Zhang P, Gao Z, et al. Numerical Modeling of rebar-matrix bond behaviors of nano-SiO_2 and Pva fiber reinforced geopolymer composites. Ceram Int. 2021;47(8):11727–37.

[78] Lucas SS, Ferreira VM, Barroso de aguiar JL. Incorporation of titanium dioxide nanoparticles in mortars – influence of microstructure in the hardened state properties and photocatalytic activity. Cement Concrete Res. 2013;43:112–20.

[79] Wang D, Zheng Q, Jian OY, Yu X, Han B. Influences of curing period on mechanical properties of reactive powder concrete incorporating nanoparticles. Mater Res Express. 2019;6(2):025023.

[80] Li H, Xiao H, Yuan J, Ou J. Microstructure of cement mortar with nano-particles. Compos Part B-Eng. 2004;35(2):185–9.

[81] Konsta GMS, Metaxa ZS, Shah SP. Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites. Cement Concrete Comp. 2010;32(2):110–5.

[82] Song H, Kwon S. Evaluation of chloride penetration in high performance concrete using neural network algorithm and micro pore structure. Cement Concrete Res. 2009;39(9):814–24.

[83] Zhu LD, Chen J, Si HY, Fang YL, Wang XY, Wang ZS, et al. The Preparation of porous activated slag granules/TiO_2 photocatalyst and its de-nox performance. J Wuhan Univ Technol. 2021;36(3):347–52.

[84] Shu J, Tang DP. Recent advances in photoelectrochemical sensing: from engineered photoactive materials to sensing devices and detection modes. Anal Chem. 2020;92(1):363–77.

[85] Qiu ZL, Tang DP. Nanostructure-based photoelectrochemical sensing platforms for biomedical applications. J Mater Chem B. 2020;8(13):2541–61.

[86] Langaroudi MAM, Mohammadi Y. Effect of nano-clay on workability, mechanical, and durability properties of self-consolidating concrete containing mineral admixtures. Constr Build Mater. 2018;191:619–34.

[87] Hamed N, El-feky MS, Kohail M, Nasr EAR. Effect of nano-clay de-agglomeration on mechanical properties of concrete. Constr Build Mater. 2019;205:245–56.

[88] Sbia LA, Peyvandi A, Soroushian P, Balachandra AM, Sobolev K. Evaluation of modified-graphite nanomaterials in concrete nanocomposite based on packing density principles. Constr Build Mater. 2015;76:413–22.

[89] Behfarnia K, Salemi N. The effects of nano-silica and nano-alumina on frost resistance of normal concrete. Constr Build Mater. 2013;48:580–4.

[90] Adak D, Sarkar M, Mandal S. Structural performance of nano-silica modified fly-ash based geopolymer concrete. Constr Build Mater. 2017;135:430–9.

[91] Lv SZ, Zhang KY, Zhu L, Tang DP. ZIF-8-assisted $NaYF_4$: Yb, Tm@ZnO converter with exonuclease III-powered DNA walker for near-infrared light responsive biosensor. Anal Chem. 2020;92(1):1470–6.

[92] Cai GN, Yu ZZ, Tong P, Tang DP. Ti_3C_2 MXene quantum dot-encapsulated liposomes for photothermal immunoassays using a portable near-infrared imaging camera on a smartphone. Nanoscale. 2019;11(33):15659–67.

[93] Liu C, Deng X, Liu J, Hui D. Mechanical properties and microstructures of hypergolic and calcined coal gangue based geopolymer recycled concrete. Constr Build Mater. 2019;221:691–708.