Review Article

Shuaijie Lu, Chen Gong, Jiajian Yu, Junxiang Hu, Siyao Wang, and Yuan Gao*

Reinforcing mechanisms review of the graphene oxide on cement composites

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Abstract: By virtue of the abundant oxygen-functional groups, ultra-high specific surface area and superior mechanical properties, graphene oxide (GO) has been proven as one of the outstanding candidates in cement composites. Compared with the traditional cement pastes, the GO-reinforced cement composites exhibit benefits in pore structure, mechanical properties, and durability. In addition, the abundant oxygen-containing functional groups on GO can promote the hydration rate of cement and combine with hydration products to fill the pores. To further improve the performance of GO-reinforced cement composites and promote the application of composites in practical engineering, it is necessary to comprehensively understand the reinforcing mechanisms of GO on cement composites. In this work, the enhancement mechanisms of GO to improve hydration, nucleation effects, mechanical strengthening mechanisms, antiseepage mechanisms and pore-filling effects of GO are systematically revealed. The optimal dosage range of GO mixing in the current study is calculated by considering the factors of mechanical property and microscopic characterization, but the economic cost also needs to be considered in future development studies. This review will promote the application of the more cost-effective and high-performance GO-reinforced cement composites in practical construction engineering.

Keywords: GO, nano-modification, cement composites

1 Introduction

Cement-based materials have become the most widely used materials in the field of construction engineering due to their low cost and stable performance [1–3]. However, cement-based materials have long suffered from problems such as low toughness [4], poor durability [5,6], and high maintenance costs [7,8]. How to improve cement-based materials has become a hot topic [9–11]. In the past few years, many different research methods have been proposed to prepare higher-performance cement-based materials, such as nanomodification technology [12–14]. Among them, graphene oxide (GO) nanosheets, as a nanomaterial with excellent properties, have been used in various industries [1,15–19]. It is added to cement-based materials as an admixture to improve various properties of cement-based materials. With its excellent physical and mechanical properties, high specific surface area, and small dosage [20–23], it has received widespread attention and more in-depth research in the field of modified cement-based materials. Previous studies have shown that GO can effectively improve the mechanical properties of cement-based materials [24–26] and promote the hydration rate of cement [27–29]. In terms of the pore structure, GO can also bridge cracks [30,31] very well and improve the ductility of materials [32,33]. These advantages make GO have broad application prospects in the engineering field.

GO has a good enhancement effect on various aspects of the performance of cement-based materials, such as mechanical properties, durability, microstructure, impermeability, and corrosion resistance [3,26,34,35]. Abrishami *et al.* [36] believe that the compressive strength of cement-based materials mixed with GO will be improved and that the compressive strength of cement-based materials containing 0.01 wt% GO will increase by 8.5%. Gholampour *et al.* [37] before adding GO content to 0.1%, the tensile strength will steadily increase, and the compressive strength will have a similar effect. Abrishami and Zahabi [36] believe that the addition of GO will reduce the total pore volume of the material and bridge micro-cracks. Duan *et al.* [38] believe that GO will micro-reinforce cement through the crack bridging mechanism and the chemical reaction between GO and cement to form a stronger interface. Zeng *et al.* [39] found that in cement materials containing GO nanosheets, water and ion transmission are not only hindered by solid particles, but GO nanosheets also play a hindering role. Gao *et al.* [40,41] found

*** Corresponding author: Yuan Gao,** School of Transportation and Civil Engineering, Nantong University, Nantong, 226019, China; College of Civil Engineering, Tongji University, Shanghai, 200092, China,
e-mail: Y.Gao@ntu.edu.cn
Shuaijie Lu, Chen Gong, Jiajian Yu, Junxiang Hu, Siyao Wang: School of Transportation and Civil Engineering, Nantong University, Nantong, 226019, China

that GO can promote the development of cement hydration reactions and the generation of C–S–H. It can greatly optimize the capillary pores of cement paste.

However, GO exceeding the appropriate concentration will adversely affect the performance of cement-based materials [24,42,43]. When the GO content is too high, GO itself will agglomerate due to excessive van der Waals forces between molecules [44–46], which will lead to fewer nucleation sites for cement hydration [47,48], thereby hindering the development rate of cement hydration [49], increasing porosity and reducing the mechanical properties [50] of the material, and making cement-based materials loose. In addition, the enhancement effect of GO is not so prominent at higher hydration ratios [40,48,51]. This is why the use of GO to enhance cement-based materials in engineering has not been truly popular. Therefore, it is very necessary and worthy of thinking to conduct an in-depth research on the enhancement mechanism of GO-reinforced cement composites.

In recent years, many researchers have also carried out various studies on GO-reinforced cement composites [52–54], which are mainly divided into experimental research, theoretical analysis, and molecular dynamics simulation. As a scientific research activity that is closest to reality, the experiment can visually observe various macroscopic changes in the sample after GO is incorporated [55], and its microscopic changes can be observed through scanning electron microscopy methods such as scanning electron microscope (SEM) [56]. Conducting theoretical analysis can help us deeply understand the essence of things, simplify complex problems, analyze their principles, and predict future development trends based on theoretical models [57]. As an important part of scientific development, theoretical analysis can be summarized and integrated to stimulate more research and exploration and promote scientific progress. Molecular dynamics (MD) simulations provide a detailed understanding of the interactions between molecules and atoms under different operating conditions, test hypotheses and theoretical models to verify their validity [58,59]. MD simulation not only reduces experimental costs and saves valuable time for researchers, but also provides valuable information about system behavior [60].

However, there are currently relatively few studies on these mechanisms, and the research results are scattered and unsystematic. Therefore, the purpose of this review is to summarize the relevant research results in three aspects: experimental research, theoretical analysis, and MD simulation based on previous research. The hydration effect, mechanical properties, pore-filling effect, and nucleation effect of GO on cement were mainly studied, and they were discussed and summarized. In the end, the outlook for GO-reinforced cement composites is also proposed. We hope that this review can bring a more comprehensive understanding to future researchers.

2 Experimental research on GO-reinforced cement composites

2.1 Study on the mechanism of GO enhancing hydration

Since there are relatively abundant oxygen-containing functional groups on the GO nanosheets, these functional groups can attract Ca^{2+} ions in the cement and hydrate around them, promoting the overall hydration reaction of the cement-based material. As shown in Figure 1a, Babak *et al.* [61] found that due to the higher surface energy of the hydration products, the hydration products will be deposited on the GO flakes. Moreover, the hydrophilic groups on the surface of GO also act as nucleation sites, promoting and accelerating the cement hydration reaction. Chintalapudi and Pannem [62] found that flower-like polyhedral crystals can be observed after adding GO. The atomic force microscopic (AFM) image shown in Figure 1b reveals the calcium silicate hydrate (CSH) morphology of hydrated cement particles after adding an appropriate amount of GO. The different pore structures of the hydrated cement are converted into nano-based structures, forming several layers of crystals inside the cement matrix, and GO is evenly dispersed. The X-ray diffraction (XRD) pattern shown in Figure 1c shows that the peak intensity of the sample containing GO is higher than that of the control sample, indicating that chemical reactions will occur between GO and hydration products. GO has a catalytic effect on cement hydration and enhances the hydration rate of the cement system [63]. As shown in Figure 1d, when the GO concentration increased to 0.03 and 0.1%, the hydration degree at 28 days increased by 8.2 and 11.9% compared with ordinary composite cement-based materials. Among them, when the GO concentration is 0.1%, the wettability of the composite material is maximum, which is proportional to the degree of hydration [37]. There are other scholars who hold the same view. Jing *et al.* [28] found in the study that the hydration degree of hardened cement paste with an original GO content of 0.6 wt% increased by approximately 23.66%, while the hydration degree of the annealed cement increased by 4.92% accordingly. It shows that GO has a significant acceleration effect on cement hydration, and the degree of hydration gradually increases with increasing GO content. Indukuri *et al.* [64] found that after

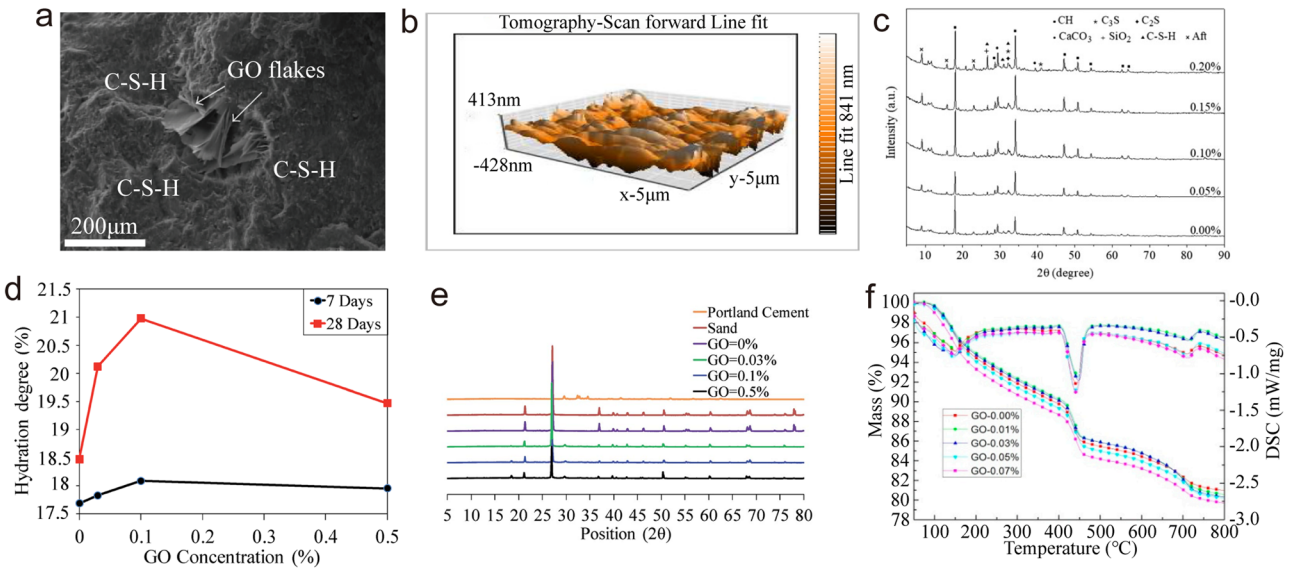

Figure 1: Various properties of composite materials incorporating GO. (a) SEM image of a composite cement-based material incorporating GO [61]. (b) Three-dimensional AFM image of GO-reinforced cement composites [62]. (c) XRD patterns of GO/CC and GO at different concentrations [63]. (d) Hydration degree of a GO-reinforced cement composite prepared with different GO concentrations after curing for 7 and 28 days [37]. (e) XRD image of a GO-reinforced cement composite [37]. (f) Thermogravimetric-differential scanning calorimetry images of cement pastes with different GO dosages [65].

incorporating GO (0.01–0.03 wt%), hydrated crystals formed interconnected, dense, flower-like crystals and were evenly distributed in cement-based composite materials.

When the GO content is too much, the van der Waals force between atoms will be too large, causing GO to agglomerate, thereby reducing the number of nucleation sites and hindering the development of hydration reactions. As shown in Figure 1e, Gholampour *et al.* [37], after conducting XRD image analysis, found that when GO concentration increased, the peak value of Ca $(OH)_2$ was also enhanced, which proved that GO could enhance the wettability and hydration of composites. However, the molecular force between GO and C–S–H will be reduced at high concentrations, and the oxygen functional group will hardly contact C–S–H, hindering the cement hydration process. As exhibited in Figure 1f, Wang *et al.* [65], according to the results of the thermogravimetric test, show that the GO in the process of cement hydration CH content had no obvious effect and also have no obvious role in promoting the process of hydration. In the weightless case of the first stage, GO had little effect on the C–S–H gel generated by the cement. The weight loss of GO-containing cement paste increased by about 0.44% in the first stage compared to the control sample, which was due to the adsorption of some water molecules on GO, preventing the complete evaporation of free water. Some other researchers have also reached the same conclusion, such as Wang *et al.* [66], who believe that the incorporation of GO improves the early hydration rate, but when the GO content increases from 0.02 to 0.03 wt%, the early hydration heat rate decreases and the cumulative hydration heat increment decreases. Gao *et al.* [67] found through experiments that excessive GO content would weaken the beneficial effect of hydration reaction, resulting in impaired efficiency of GO/multi-walled carbon nanotubes in strengthening the pore structure of hardened cement slurry.

2.2 Study on the mechanism of GO improving microstructure

As a nanosheet material, GO can adsorb the C–S–H generated nearby and play a bridge role between the surrounding C–S–H and can also fill the pores with C–S–H to make the cement matrix denser. With the increase in the GO content, the microstructure of the cement slurry becomes more denser, and the size of cracks and holes becomes smaller. As present in Figure 2a, when the GO concentration increases to 0.15 wt%, the microstructure of the cement paste becomes denser, and the crack and hole sizes become smaller. The strong interfacial bonding between GO and cement matrix also prevents the initiation and propagation of cracks [63]. As shown in Figure 2b, Qureshi and Panesar [68] argued that GO is partially filled with sheet microstructure, and the high dispersion and small plane size of GO in water are conducive to the filling of pores. As shown in Figure 2c, after the addition of 0.03 wt% GO, the structure of the hardened cement slurry

was well improved, and the C–S–H gel was more uniform and denser, which could well cover the surface of other crystals and cement particles [24]. As shown in Figure 2d, when the optimal GO concentration is reached, GO can effectively strengthen the bridge of microcracks and control their expansion from the nanoscale to the micron scale. GO is also embedded in the slurry as a separate sheet, filling pores and acting as a bridge between hydration products and composite particles [37]. Similar results have been reported by other researchers, such as Jing *et al.* [28], with the addition of GO, more hydration products are produced. The hydrated crystals overlap each other, forming a dense microstructure and reducing porosity. Duan *et al.* [38] found that the fracture surface of pure cement is relatively smooth, while the fracture surface of cement containing GO is rough, with the fracture surface length ranging from 3 to 30 mm. GO also tends to amplify hydration products and fill pores, thereby densifying the cement paste and reducing porosity.

Due to the high van der Waals forces between the atoms, the high content of GO will agglomerate, resulting in the reduction of the bridging GO sheet and the reduction of hydration products, thus increasing the porosity of the cement slurry, decreasing the workability, and the cement matrix becoming loose. As shown in Figure 2e, Suo *et al.* [63] found that with an increase in GO concentration, the fluidity of cement paste gradually decreases, and there is a significant negative correlation between concentration and fluidity. Cracks and voids also occur in the cement matrix, which aggravates the drying shrinkage of the cement paste and makes the microstructure loose. As exhibited in Figure 2f, when the GO content is too high, the GO sheet will flocculate, resulting in reduced workability, which will lead to large pores in the cement matrix and reduce the mechanical properties of the material [69]. There are other researchers with similar results, such as Abrishami and Zahabi [36], after the GO content is increased to 0.25 wt% content, the nanosheets slide against each other, and microcracks and weak bonds will form in the microstructure. GO also exhibits agglomeration, which results in a decrease in compressive strength and reduces the surface energy.

2.3 Correlation performance

Before the concentration of GO rises to the appropriate concentration, the oxygen-containing functional groups of GO will have strong interfacial bonding with cement compounds, resulting in the formation of strong covalent bonds between the matrix and GO, thus improving the mechanical properties. When the concentration of GO is excessive, the agglomeration phenomenon of GO will weaken the binding between GO and C–S–H, which will lead to the reduction of strength. As exhibited in Figure 3a [61], the tensile strength test results show that the tensile strength of the sample increases with the increase of nano-GO content before the nano-GO content reaches 1.5%. However, when the nano-GO content reaches 2%, the tensile strength of the sample

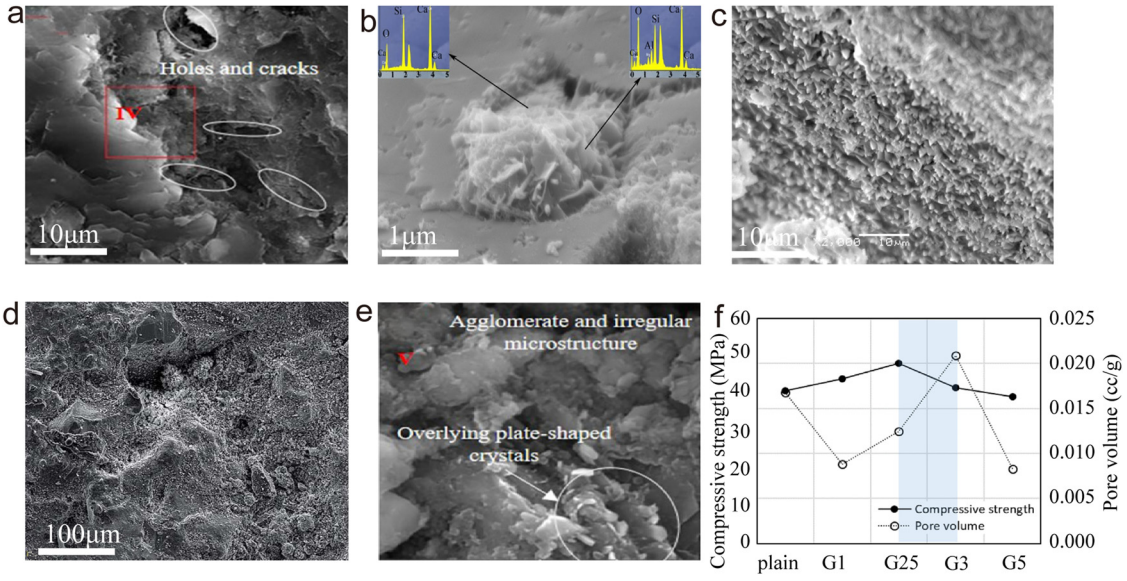

Figure 2: SEM diagram of a cement-based material mixed with GO. (a) SEM image of a cement slurry containing 0.15 wt% GO at a 0.4 water–cement ratio [63]. (b) Pore microstructure with 0.04 wt% GO [68]. (c) Microstructure of cement matrix containing GO (0.03 wt%) at 0.35 W/C [24]. (d) Low-power SEM images of cement mortar containing 0.03 wt% GO [37]. (e) SEM image of 0.15 wt% GO cement paste [63]. (f) Correlation between compressive strength and pore volume [69].

decreases and is lower than that of the sample without GO. As shown in Figure 3b, the tensile strength increases steadily when the GO content reaches 0.1% and then begins to decline when the GO content exceeds 0.1%. The strength of 7 days increased by 44.4%, and the strength of 28 days increased by 37.5%. Compressive strength has a similar effect [37]. As demonstrated in Figure 3c, with an increase in GO content, the strength of the sample first increases and then decreases. Among them, 0.10% is the most suitable GO content, which can best improve the compressive strength of the cement paste [63]. As shown in Figure 3d, Lu *et al.* [70] found in the study that the addition of 0.08 wt% GO could increase the compressive strength and tensile strength of the material by 24.8 and 37.7%, respectively, but the compressive strength decreased with the further increase of GO content. Other researchers have similar results, such as Naseem *et al.* [71], where GO nanosheets act as antifoaming agents in GO polymer-modified composites, reducing the pore volume by 60.1% compared to polymer-modified cement materials, and improving the 28 days tensile and compressive strength by 59 and 33%, respectively. Duan *et al.* [38] argued that Young's modulus increases with the increase of GO volume fraction, and the increase shows a roughly linear relationship.

Under the lower water–cement ratio, GO flakes are easier to be evenly distributed, which improves the stability of GO in cement-based materials, so that the GO lifting effect is more obvious. As shown in Figure 3e, the water–cement ratios from top to bottom are 0.2, 0.3, and 0.4, respectively. When the water–cement ratio is 0.4, the maximum compressive strength and bending strength of 28 days are increased by 10.97 and 25.45%, respectively, while the compressive strength and bending strength of 0.2 water–cement ratio are increased by 21.37 and 39.62%, respectively. When the content of GO reaches 0.05%, the flexural strength and compressive strength both decrease. This indicates that the optimal GO content is 0.03% at a lower water–cement ratio, and the effect on bending strength is the best [24]. As shown in Figure 3f, when the GO content is 0.03 wt%, the bending strength reaches the maximum value, which is increased by 21.86%. The compressive strength reaches the maximum value when the GO content is 0.01 wt %, and the growth rate is 5.16%. Then, the flexural strength and compressive strength decreased at 0.05 wt% GO content. When W/C rises from 0.3 to 0.5, compressive strength and bending strength decrease significantly, indicating that the higher the W/C, the lower the strength [65]. Other researchers have similar results, such as Cong *et al.* [72], and when the content of GO is 0.1 wt% and the water–cement ratio is 0.5, GO has the best strengthening effect on cement-based materials.

GO also affects some other properties such as cement's alkali-silica reaction (ASR) expansion, microhardness, *etc.* GO nanomaterials effectively reshape and refine the gel

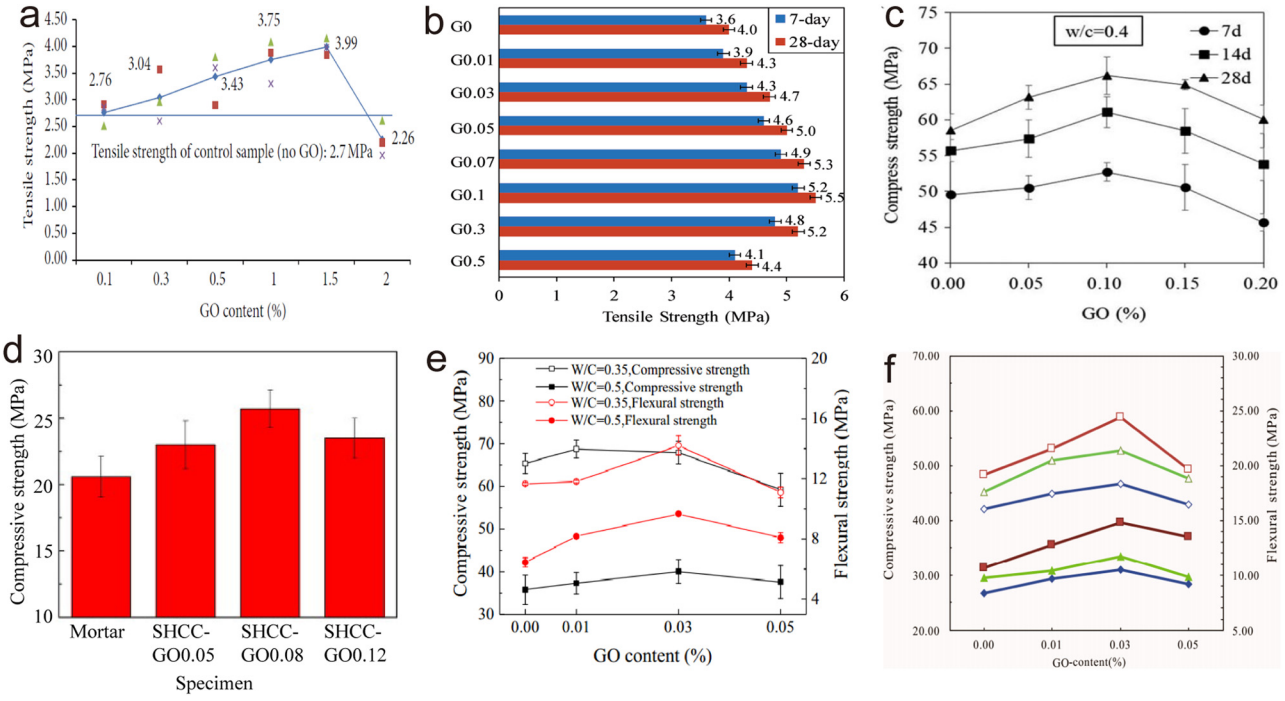

Figure 3: Related properties of cement-based materials after incorporation of GO. Tensile properties (a) and (b) and compressive properties [37,61] (c) at different GO contents [63]. (d) Compressive strength results of the GO reinforced strain hardening cementitious composites [70]. (e and f) Compressive strength and flexural strength with different GO contents under different water–cement ratio [24,65].

around the interfacial transition zone through their excellent nano nucleation and interlocking effects, which is beneficial to control the ASR expansion of cement mortar. Luo *et al.* [73] found that the sample containing 0.04% GO expanded less than the sample containing 0.02% GO and expanded less than the sample with baseline. Which means that a small amount of GO loading has a stabilizing effect on controlling ASR expansion through the nano nucleation effect. Samimi *et al.* [74] found that graphene can reduce the generation of ASR gel by preventing the transformation of tobermorite to polymeric C–S–H phase. By generating a dense structure, graphene can form boundaries around aggregates, preventing OH species from penetrating and mitigating the formation of ASR gels.

GO as a nanomaterial is beneficial to the enhancement of the micro-region mechanical properties of cement paste. Zhao *et al.* [43] found that when the GO content was 0.06 wt%, the microhardness was optically enhanced by 8.6%. When an appropriate amount of GO is mixed into cement, GO is evenly dispersed in the cement matrix and enhances the microhardness by filling the internal pores of the cement-based material. However, when the content is too high, GO agglomerates and forms stress concentration points in the cement-based material, which may form more pores in the cement-based material and thereby reduce the microhardness of the cement-based material. Du *et al.* [75] believe that as the GO content increases, the microhardness, scratch surface roughness, and scratch hardness properties of high-content fly ash concrete first increase and then deteriorate. Adding 0.05 wt% GO showed the highest microhardness value, the lowest scratch surface roughness, and the highest scratch hardness value.

GO (0.03–0.1 wt%) can effectively enhance the mechanical properties and durability of the cement composites. Nevertheless, excessive GO concentration will make the intermolecular van der Waals force too large among the nanosheets, resulting in agglomeration and weakening the reinforcing efficiency of the GO. The agglomerated GO can cause stress concentration in hardened cement-based materials. Therefore, the dispersion of GO is the key to playing its cement composites' strengthening role.

3 Theoretical research on GO-reinforced cement composites

3.1 Mechanism analysis of nucleation effect

The GO surface will provide a growth platform for hydration products, and oxygen-containing functional groups can attract nearby Ca^{2+} ions and promote the growth of surrounding hydration products. The addition of GO makes the chemical reaction more intense and promotes the growth and crystallization of the hydration products. Among them, the wrinkled GO (Figure 4a) can be regarded as the nucleation site of early cement hydration. After GO incorporation, the dissolution rate and hydration of cement can be accelerated, and the hydration products become larger and more mature, forming a dense microscopic mechanism [32]. As shown in Figure 4b, CH and C–S–H increase with GO concentration, indicating that GO acts as a nucleation site to trigger C3S hydration, which affects cement hydration during the nucleation phase and growth phase. The oxygen-containing functional groups on GO react to promote the formation of hydration products, which form a chemical linkage with the folded plane of GO [76]. de Souza *et al.* [77] found that C–S–H gels formed at the GO interface showed a growth mechanism similar to that of the SK mode (Figure 4c). GO acts as a two-dimensional platform, so that the C–S–H foil is stacked regularly, rather than randomly arranged. It acts as a structure-oriented platform in the ordinary portland cement (OPC) hydration process, enabling the foils to effectively stack each other. C–S–H begins to grow outward from the surface of the microplate, marking the beginning of the island growth pattern. de Souza *et al.* also constructed a model for the evolution of the gel nanostructure of GO–OPC composites (Figure 4d), in which GO nanosheets are arranged in random positions to form 3D networks with or without interconnection. The GO surface interacts with Ca^{2+} ions to provide multiple nucleation sites for the precipitation of the C–S–H gel. Gao *et al.* [48,67] believe that the volume fraction and hydration degree of hydration products are related to the volume fraction of C–S–H, which conform to the following formula [48,67]:

$$\alpha = \frac{(1-\phi)\left(\frac{W}{C}\right) - 0.32\phi}{0.36}, \tag{1}$$

$$V_{\text{hyd}} = \frac{0.68\alpha}{\left(\frac{W}{C}\right) + 0.32}, \tag{2}$$

$$V_{\text{unhyd}} = \frac{0.32(1-\alpha)}{\left(\frac{W}{C}\right) + 0.32}, \tag{3}$$

$$\phi_{\text{C-S-H}} = \frac{V_{\text{C-S-H}}}{V_{\text{hyd}} + V_{\text{CH}} + V_{\text{C-S-H}}}, \tag{4}$$

where ϕ is the total intrusive volume of the specimen obtained by the mercury intrusion porosimetry test, V_{hyd} is the hydration product volume fraction, and α is the degree of hydration. There are other scholars with similar findings. Zhao *et al.* [78] analyzed the hydration heat curve

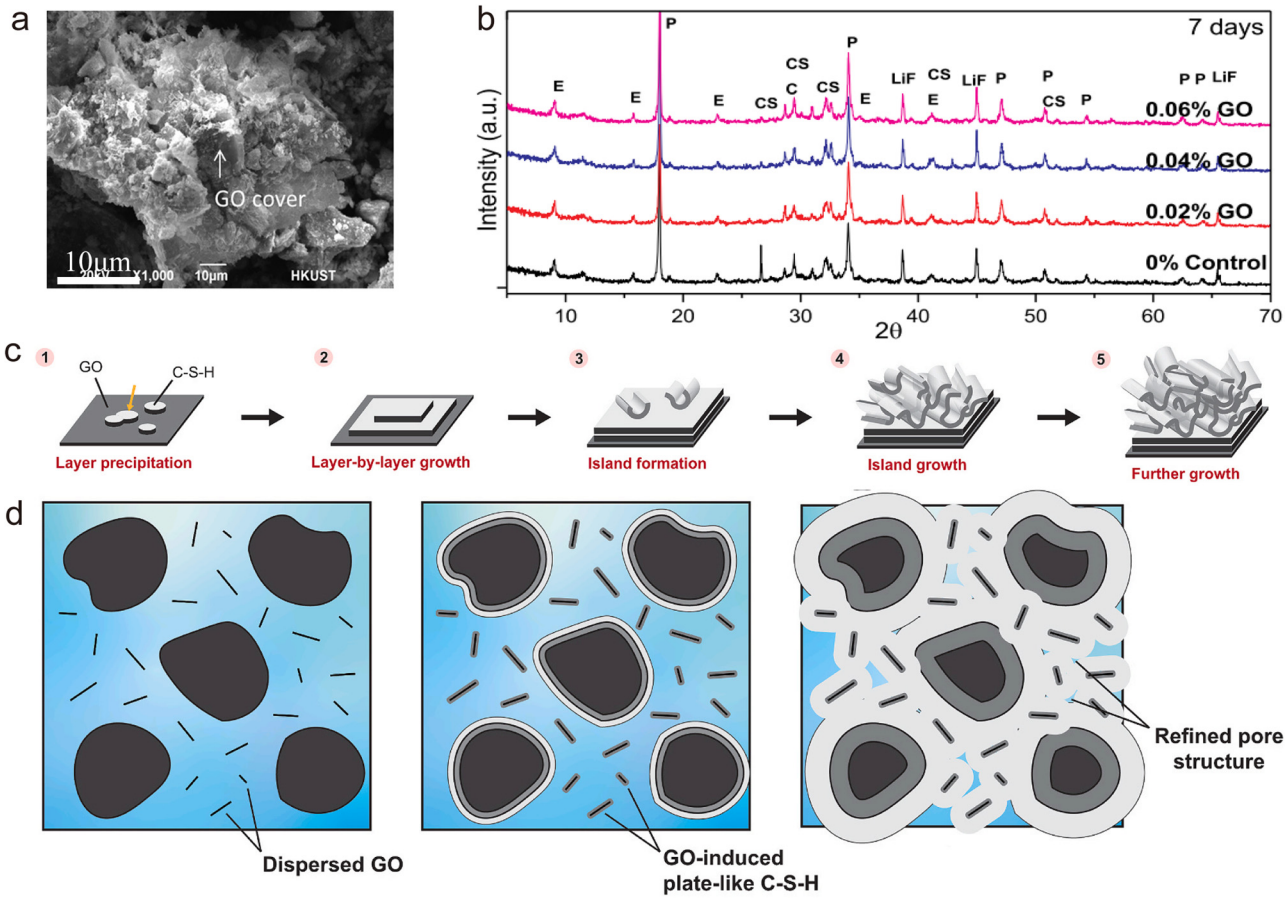

Figure 4: SEM image and theoretical model of the GO–cement matrix. (a) High-power SEM images of the microstructure of cement particles and hydration products containing GO [32]. (b) XRD curve of the composite after 7 days of hydration [76]. (c) Growth patterns of nucleating materials on two-dimensional surfaces [77]. (d) Structural evolution of C–S–H in cement slurry containing GO nanosheets [77].

and found that due to the delayed effect of polycarboxylate superplasticizer, the time of hydration entering the accelerated stage was delayed to about 2.5 h. However, the peak heat flow of GO containing 0.05 wt% was significantly increased by 16.78%, which verified that the remaining functional groups of GO could affect the nucleation site of hydration products. Liu *et al.* [79] believed that the oxygen-containing functional groups on GO sheets improved their dispersion in water, and the carboxyl groups and hydroxyl groups existing in the well-dispersed GO lattice structure would combine with hydration products to form potential nucleation sites. Suo *et al.* [63] found that when GO interacts with Ca^{2+}, making GO is a platform for the growth of hydration products, thus promoting the formation of CH and C–S–H in the hydration process and providing nucleation sites.

GO will agglomerate due to large van der Waals forces, reducing the platform used as nucleation sites and hindering the hydration of the cement mortar. Babak *et al.* [61] found that under the condition of a constant water–cement ratio, increasing the content of GO will be difficult to improve the workability of the cement paste, and GO is difficult to disperse in the matrix, reducing its use as a nucleation agent site platform. Due to the hydrophilic groups on the surface of GO, GO nanosheets will also absorb a non-negligible amount of water, hindering the hydration of cement mortar. Suo *et al.* [63] believe that GO's unique two-dimensional structure and large surface area containing rich oxygen-containing functional groups require more water to wet the surface and reduce free water in the freshly mixed mixture. GO has opposite charges in water, and the negatively charged oxygen functional groups can physically adsorb metal cations generated during cement hydration, resulting in loss of fluidity. Therefore, as the GO content increases, the higher the concentration, the slower the cement hydration reaction rate, and the fluidity of the cement slurry also decreases.

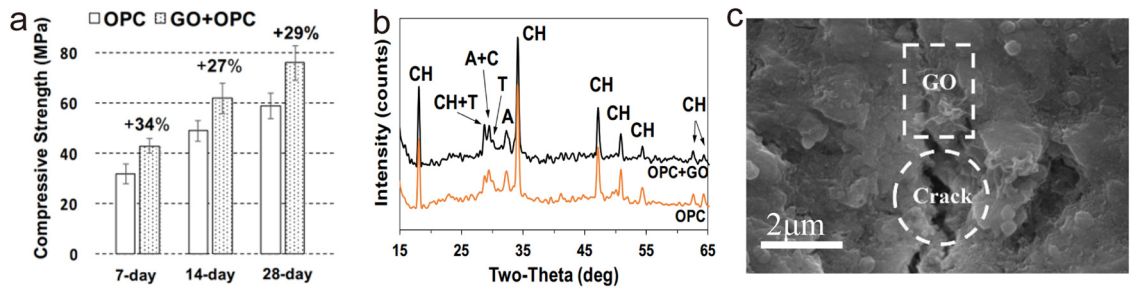

Figure 5: GO-reinforced cement-based materials under 28 days. (a) Compressive strength test results [80]. (b) XRD images of the hardened paste at 28 days [80]. (c) SEM images of GO-containing cement slurry [50].

3.2 Mechanism analysis of pore-filling effect

3.2.1 Bridging effect

The functional groups at both ends of the GO nanosheet will react with the C–S–H gel to form a strong chemical bond and form a bridge to connect the two ends of the crack when it occurs. As shown in Figure 5a, Xu *et al.* [80] found that the addition of 0.02 wt% GO could increase the compressive strength of 7, 14 and 28 days by 34, 27 and 29%, respectively. This is due to the excellent mechanical properties of GO itself. Another factor is the blocking effect of GO on crack propagation due to its lamellar structure. The incorporated GO also connects the hydration products together, thereby reducing matrix loss during loading and increasing compressive strength. In Figure 5b, the XRD pattern indicates that the peak value of CH is slightly reduced after incorporation of GO into cement mortar, which is attributed to the attraction of GO to Ca^{2+}. This further leads to the formation of a local calcium-rich environment near the GO sheet, which promotes the formation of hydration products and bonding pores [80]. As shown in Figure 5c, Long *et al.* [50] argued that GO exhibits a unique two-dimensional structure, which can enable GO to effectively deflect tilt or distort the surrounding crack, thereby hindering crack growth and increasing peak load. The doped GO also creates an entangled network of thin non-uniform platelets and rod-like crystals at various locations, bridging the cracks.

Gao *et al.* [40] summarized the strengthening mechanism model of nanomaterial reinforced cementing composites and estimated the crack bridging force of GO nanosheets in the cement matrix, as shown in Figure 6. There is a frictional interaction between GO nanosheets and the cement matrix. When cracks form and expand under load, the GO nanosheets will be pulled out of the cement-based material. The whole pull-out will go through two stages, the debonding stage and the debonded stage. The first stage will be partially detached, and the second stage will be completely detached. The relationship between crack opening displacement (δ) and drawing force (P) can be expressed by the following formula [40]:

$$P(\delta)_{\text{debonding}} = A_f E_f \in (\delta) = A_f E_f \sqrt{2c\delta}, \delta \le \delta_0, \tag{5}$$

$$P(\delta)_{\text{debonded}} = C_f \tau l \left(1 - \frac{\delta - \delta_0}{l}\right), \delta_0 < \delta < l, \tag{6}$$

$$P_{\text{peak}} = P(\delta_0) = C_f \tau l, \tag{7}$$

where A_f is the cross-section area of GO, C_f is the perimeter of the GO nanoparticle, τ is the interfacial shear strength between the GO nanoparticle and cement matrix, and E is the Young's modulus of GO.

There are some other researchers with similar results, such as the study Chen *et al.* [81], GO pulling out process

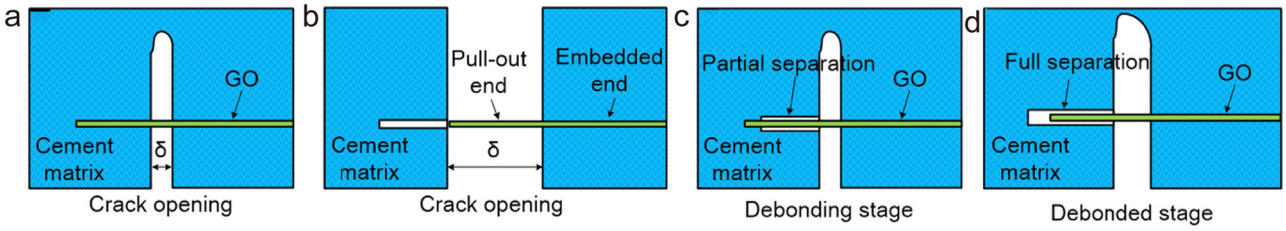

Figure 6: Enhancement effect of 2D geometric nanomaterials in cement matrix [40]. (a) Before pulling out, the GO nanosheets and cement matrix interact with each other *via* friction. (b) When cracks form and open wider under loading, the GO nanosheets will eventually be pulled out. Two stages of GO pull-out process (c) debonding stage and (d) debonded stage.

can be divided into two stages: debonding and debonded, Gd (chemical bond energy) has a dominant influence on the maximum σ_B (stress that helps to close the crack during crack propagation) and maximum stress σ_{max} of GO before debonding. As the size of GO nanosheets and tortuosity τ increase, friction begins to make a greater contribution and gradually becomes the dominant force. Hou *et al.* [82] found that chemical and hydrogen bonds between Ca atoms and oxygen functional groups play a crucial bridging role between GO sheets and C–S–H, while the restricted environment of C–S–H gel affects the stability of functional group grafted GO.

3.2.2 Pore filling

As a two-dimensional nanomaterial, GO usually enters pores, dividing large pores into smaller ones, or it adsorbs on a nearby C–S–H gel, filling the pores with hydration products and reducing the porosity. GO nanosheets easily fill the pores between the cement matrices, increasing the density of the matrix and thus enhancing the strength of the composite. As shown in Figure 7a, the incorporation of GO nanosheets resulted in more regular hydrated crystals inside the cement paste, which continuously filled the pores of the hardened cement paste. The GO nanosheets are dispersed in the cement matrix, some of which fill the pores, while the rest of the GO is embedded in the cement matrix and acts as a bridge [50]. As shown in Figure 7b, GO nanosheets in the cement matrix increase the contact area of their internal surface area. Therefore, when the sample receives an external force, the damping ability of the cement paste can be improved by increasing the degree of internal friction. There are other scholars who have similar research conclusions, such as Suo *et al.* [63], GO can fill the pores between hydration products and accelerate hydration reaction. Wang *et al.* [65] found that as a two-dimensional material with a relatively large number of layers, GO can fill the pores and divide the large pores into small pores, thereby reducing the porosity.

Due to the small size of GO nanosheets, part of the pores will be filled with GO nanosheets, while the remaining GO nanosheets are embedded in the cement matrix. GO nanosheets in the cement matrix increase the contact area of their inner surface. When the sample is subjected to external force, GO can promote the internal friction of the cement paste [50]. In addition, Zou *et al.* [83] and Chuang [84] found that increasing the degree of internal friction can improve the damping capacity of cement paste, and Liu *et al.* [85] believed that appropriate pore size has a positive impact on its damping capacity. As shown in Figure 8, since Young's modulus of GO is higher than that of the cement paste, it is expected that the stress distribution will be uneven when a load is applied to the modified cement paste. The uneven distribution of stress will cause relative motion of GO nanosheets at the interface, which will lead to energy dissipation [50].

However, the improvement effect of the high content of GO on porosity is not so good, and the high concentration of GO does not actively participate in filling the pores of the composite [36]. Long *et al.* [50] believed that too much GO incorporation would produce more regular hydrated crystals inside the cement slurry and continuously fill the pores of the hardened cement slurry. However, too much GO would increase water consumption and agglomerate the nanosheets, which would have a negative impact on the porosity and static mechanical properties of the sample.

3.3 Impermeability mechanism

The high specific surface area of the GO sheet will form a barrier-like structure in the material, which hinders the penetration rate of the permeable material. Zeng *et al.* [39], through research, found that in cement materials

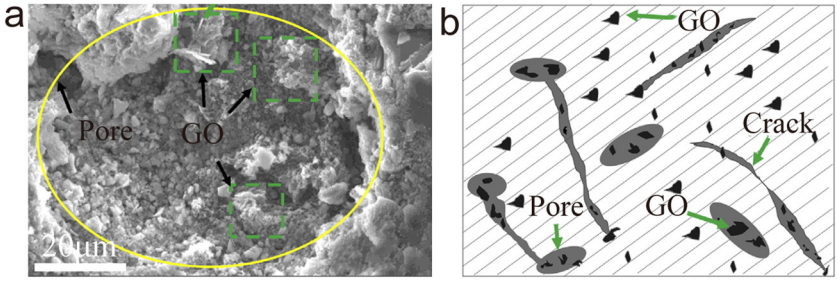

Figure 7: The increased interface of cement matrix [50]. (a) Pore interface of the cement matrix. (b) Simulated image of the GO nanosheet increasing the contact area of its inner surface.

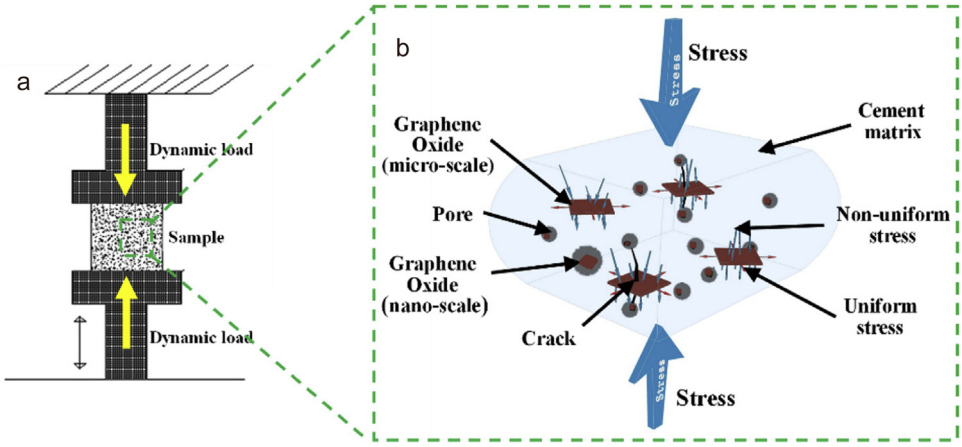

Figure 8: Mechanism analysis of nonuniform stress distribution [50]. (a) Schematic diagram of force loading direction. (b) Simulation image during the force loading process.

containing GO nanosheets, water and ion transport was not only hindered by solid particles but also by GO nanosheets, as demonstrated in Figure 9a. The diffusion of water molecules will bypass the nanosheet to form a very tortuous path, and the tortuosity τ can be expressed as a function of the size, concentration, arrangement, and orientation of the nanosheet [39]:

$$\tau = \sqrt{\frac{\delta}{A\phi_0^{n-1}}} + \frac{\lambda}{3}\gamma_s\left(\frac{2}{3}\right)\left(S + \frac{1}{2}\right). \tag{8}$$

ϕ_0 is the capillary porosity of the cement slurry, δ is the shrinkage coefficient of the cement material, A and n are the parameters related to deflection, λ is the aspect ratio of the nanosheet, γ_s is the volume fraction of the nanosheet relative to the cement material, and S is the parameter related to the direction of the nanosheet. After taking into account the influence of GO nanosheet concentration, arrangement, and other factors, the researchers established a simple theoretical model of permeability curvature [39]:

$$K_r = \frac{1-\gamma_s}{\tau} = \frac{1-\gamma_s}{\sqrt{\frac{\delta}{A\phi_0^{n-1}}} + \frac{\lambda}{3}\gamma_s\left(\frac{2}{3}\right)\left(S + \frac{1}{2}\right)}. \tag{9}$$

Although the permeability-enhancing effect of GO nanosheets is currently limited by the existing technology, the permeability-tortuosity [39] model proposed by the researchers can predict the permeability of mortars containing nanosheets. According to this model, the relative permeability changes with changes in GO content and aspect ratio. As shown in Figure 9b, the relative permeability decreases with the increase of aspect ratio and GO content, and the change range is large, reaching more than 50%. It can be inferred that the permeability is very sensitive to the GO content and the aspect ratio of GO nanosheets. Theoretically, high dosage and high aspect ratio of GO can improve the impermeability [39]. Other researchers have had similar results. Mohammed *et al.* [86] found that GO can form a barrier in cement-based materials, reduce the movement of aggressive substances, reduce the penetration of chloride ions, and effectively enhance the impermeability of cement-based materials. Guo *et al.* [34] found that when the content of GO exceeds 0.06 wt%, the ability of GO to improve the permeability of recycled concrete will be reduced. Berry [87] found that graphene is the most impermeable material because graphene repels all polymers due to its high electron density, the enclosed spaces of carbon atoms in graphene, and its high strength. But artificial pores in graphene can increase its permeability and permeation selectivity.

GO can not only promote the hydration reaction of cement through nucleation effects to improve the hydration degree of the matrix after hardening but also connect the generated C–S–H with GO nanosheets through covalent bonding. In the hardened cementitious matrix, GO will attach to C–S–H to further reinforce the pore structure of the composites and significantly enhance the impermeability and durability of the cement composites. When the cement cracks under load, some GO bridges in the ends of the cracks, limiting the development of cracks and improving the mechanical properties of cement composites.

4 Molecular dynamics simulation

Molecular dynamics (MD) simulation is a powerful computational method that can model the physical motions of atoms and molecules, followed by computer numerical

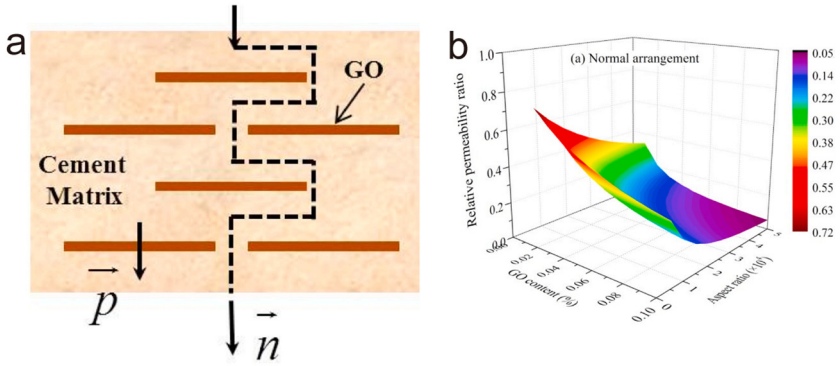

Figure 9: The effect mechanism of GO on osmosis. (a) Water transport in a cement matrix containing nanosheets. (b) In the nano normal case, GO content and aspect ratio are the influences on permeability [39].

simulations of atomic/molecular forces based on interatomic potential energy and Newtonian classical mechanics [88,89]. As the third scientific research method to study the structure and properties of molecular systems, MD simulation has been widely used in many technical fields such as chemistry, materials science [90–92], biomedicine, and so on. This technique not only expands the research methods in the atomic/molecular field but also complements the experimental and theoretical research.

Nowadays, MD simulation has been widely used in the field of cement-based composites to study the properties of C–S–H and other applications, such as carbon nano-modified cement-based materials, polymer-modified cement-based materials, *etc.* [93–95]. GO nanomaterials have attracted more and more attention in the construction industry due to their excellent mechanical properties, good dispersibility, and ultra-high specific surface area, and stand out among various modified materials [2,96–98]. Studies have shown that GO can enhance the mechanical properties, pore structure, and durability of cement-based composites [22,69,99,100] and also reduce the amount of cement used, thereby reducing costs and reducing environmental damage. Therefore, it is necessary to understand the interaction between GO and C–S–H gelling materials at the atomic/

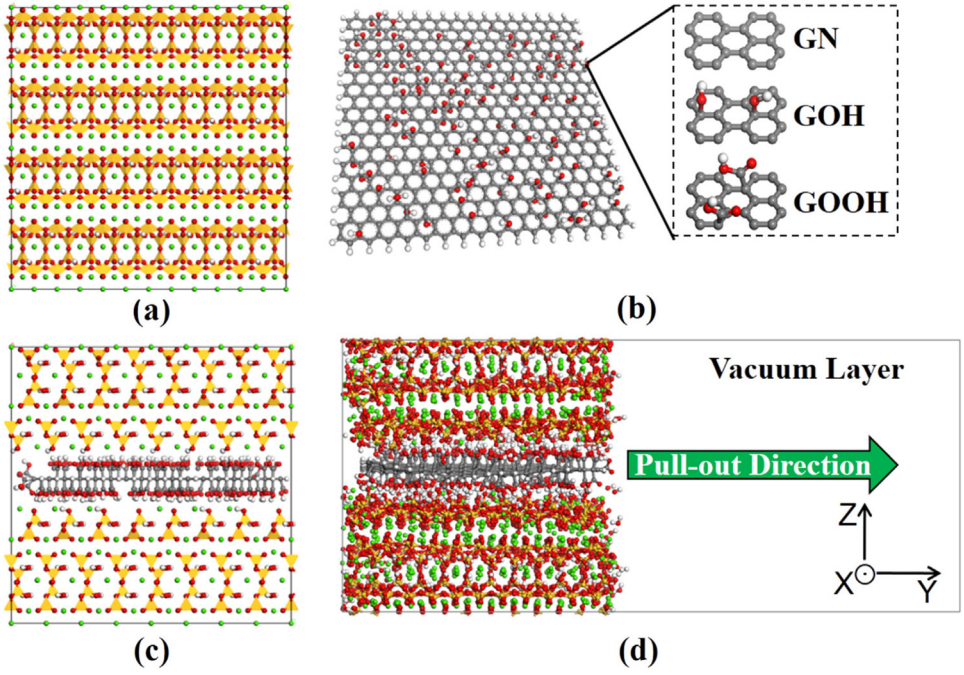

Figure 10: Simulation model of GO extraction from CSH [101]. (a) C–S–H model constructed by tobermorite. (b) GO nanosheet and oxygen-containing functional groups. (c) Initial model of GO/C–S–H. (d) The pull-out process model of GO.

molecular level. However, the current research on the use of MD is extensive and disorganized, so this section summarizes the MD research on GO/C–S–H, hoping to be helpful for readers' future research (Figure 10).

4.1 GO–CSH extraction simulation

The rich oxygen-containing functional groups of GO will generate strong chemical bonds with the surrounding C–S–H, which will enhance the interface strength, so as to generate strong friction when GO is extracted from C–S–H. As shown in Figure 11a, Fan *et al.* [102] show that GO continues to be pulled out after the first cycle of interfacial shear load. When the force drops to a lower level during the second cycle, GO has been pulled out by half and the interaction between GO and C–S–H will become less and less, and the interface energy will decrease. As present in Figure 11b, when the GO nanosheets with carboxyl groups is pulled out of C–S–H matrix, the pulling force and interface bonding performance fluctuate greatly. The chemical bond between GO and C–S–H is repeatedly broken and joined, and the drawing force is also affected

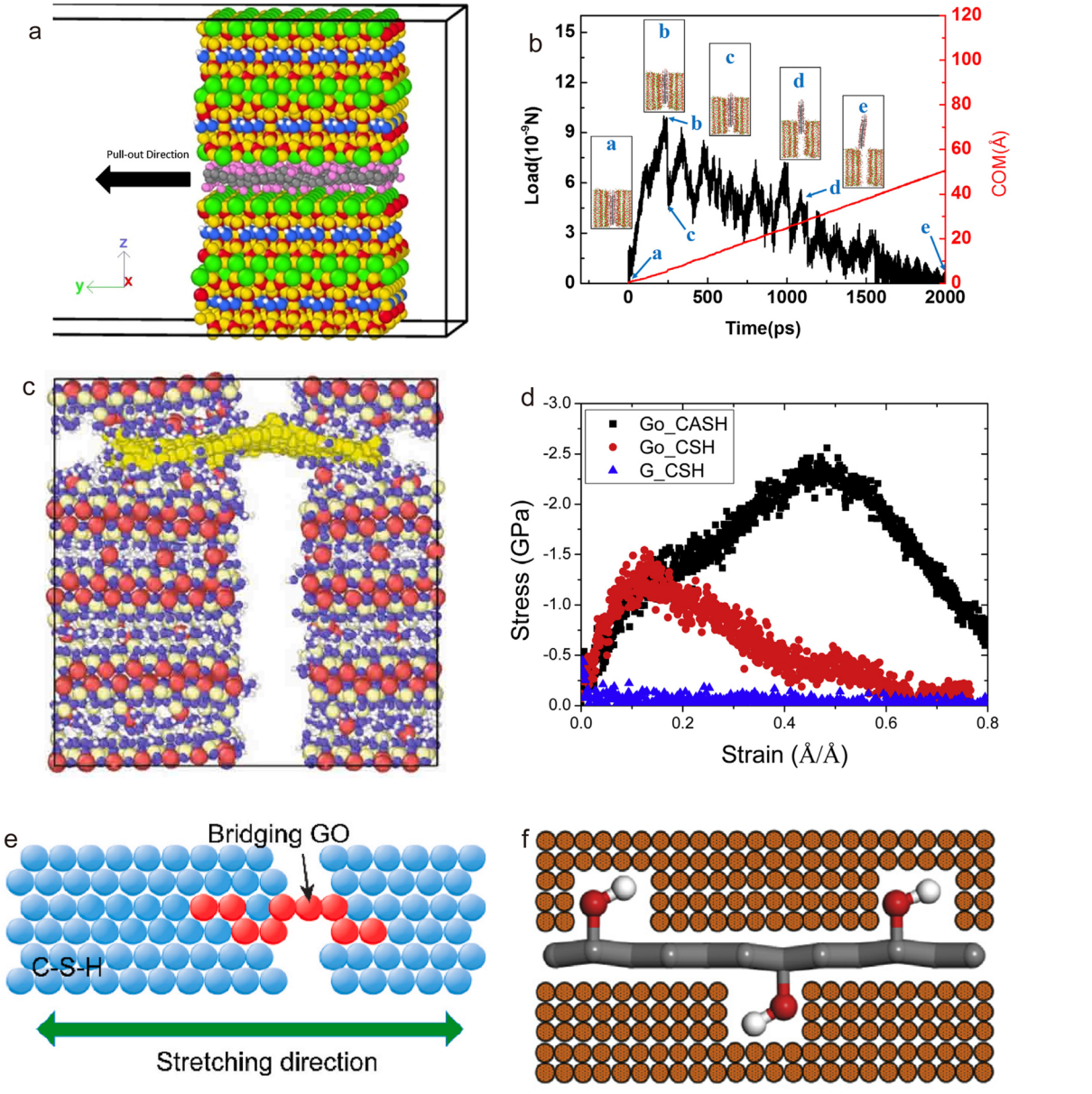

Figure 11: Molecular dynamics simulation of GO/C–S–H. (a) MD simulation cell for GO cement [102]. (b) GO dynamic pull-out process from C–S–H [101]. (c) Unilateral debonding during GO tensile simulation [103]. (d) Stress–strain curve for stretching along the *z*-axis [104]. (e) Schematic diagram of GO bridging in the C–S–H gel [42]. (f) The structural interlocking effect between GO and C–S–H [105].

by mechanical interlocking caused by the roughness of the GO sheet surface [101]. A s shown in Figure 11c, Fan *et al.* [103] found that the improvement in the performance of the composite was attributed to the strong chemical bond between GO and C–S–H. The C–C bonds in GO are generally much stronger than the chemical bonds in C–S–H gels, and they are transferred to C–S–H when GO is incorporated, resulting in a stronger composite material. In the draw test, GO withstood a draw force of about 0.58 GPa through the chemical bond between them and inhibited the damage of silica through the bridging action, thus preventing the cracking of C–S–H and even partially restoring the integrity of the damaged C–S–H gel. As shown in Figure 11d, Hou *et al.* [104] found that the functional groups C–OH and –C–O bridge the C–S–H matrix and GO together to resist mechanical loads. At the strain of 0.4 A, some functional groups will pull out from C–S–H, but if some chemical bonds are rooted in C–S–H, a large ladder stress drop can be observed, indicating that the brittleness of C–S–H gel is greatly improved along the interlayer direction. Similar results have been reported by other researchers, such as Wan *et al.* [101] found that GO is stretched and gradually separated from the C–S–H surface during Z-stretching, indicating that the C–S–H/GO interface is the weakest area. During the stretching process, both ends of the GO sheet are attached to C–S–H, and the COO-groups on the GO edge form a strong Ca–O ionic bond connecting GO and C–S–H. During the stretching process, the interfacial water is attached to the GO, constantly deforming with the structure, and the hydrogen bond is constantly rebuilt.

The oxygen-containing functional groups at both ends of GO that play a bridging role will generate strong chemical bonds with C–S–H. When stretched, GO will transfer part of the externally loaded stress and slow down the crack propagation, thereby improving the ductility of the material. As shown in Figure 11e, when GO plays a bridging role, the ductility of the structure continues to increase with the increase of GO content in C–S–H, resulting in

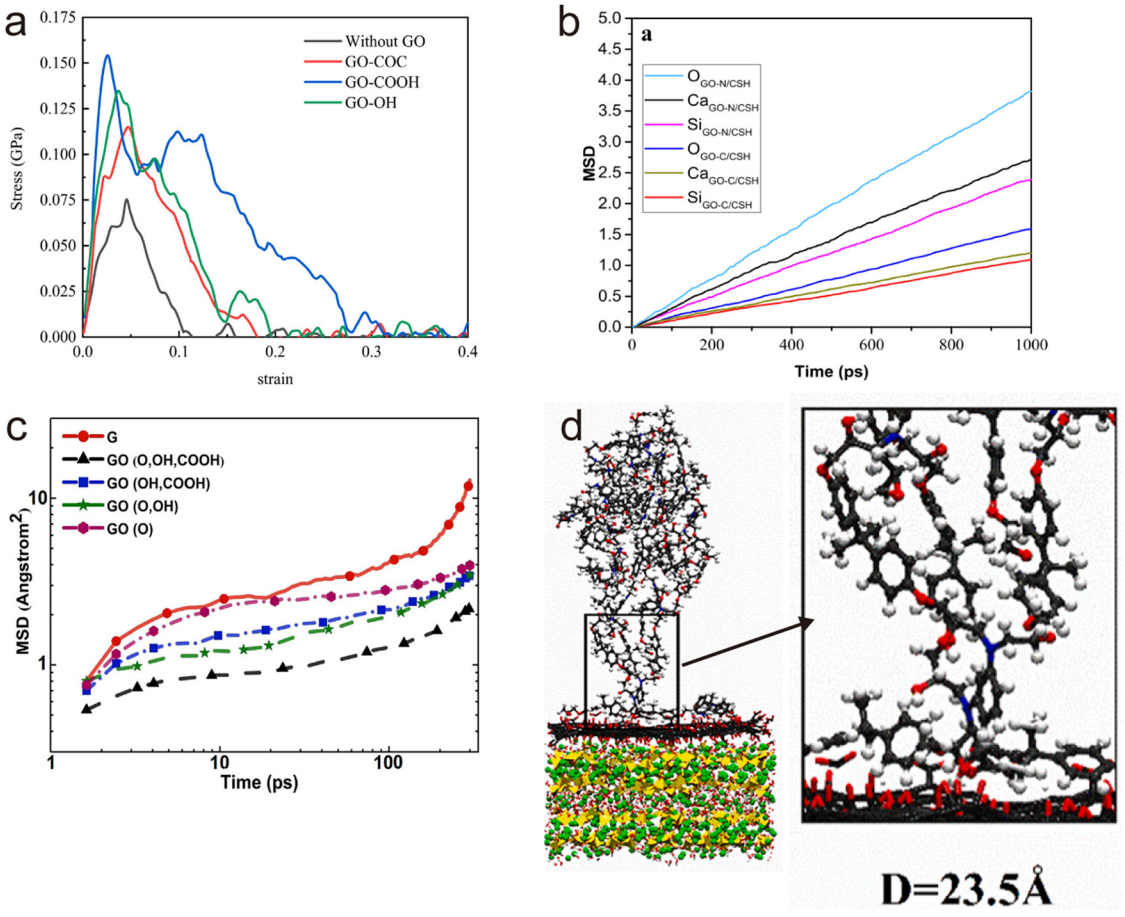

Figure 12: Interface reaction of GO/C–S–H. (a) Stress–strain curve of C–S–H/GO composites under uniaxial tensile load [107]. (b) MSD results of adsorbed interface atoms [108]. (c) MSD values of the GO plane covered by different functional groups in C–S–H [109]. (d) Filamentary failure phase snapshot of GO/C–S–H [110].

greater structural deformation. When GO is two-layer, the ductility is increased by about 33% compared with pure C–S–H. However, once GO has no bridging effect, it will damage the integrity of the structure and reduce the ductility of the material [42]. As shown in Figure 11f, the good interlocking phenomenon between GO and C–S–H atoms can effectively transfer the load from the matrix to the GO nanosheets, and reduce the crack growth inside the C–S–H composite during the crack growth stage [105]. While, as the number of GO layers increases, the self-diffusion coefficient of the silicate chain increases slightly, indicating that increasing the number of embedded GO layers weakens the structure to a certain extent. The reduction of reaction barriers under the thermal effect promotes the frequent exchange of oxygen between GO and C–S–H, resulting in the introduction of a small amount of silicon species into GO [106].

4.2 Interface property study

The oxygen functional group on GO will form a strong hydrogen bond with C–S–H, making the interface between GO/C–S–H firmer, which will greatly restrict the movement of atoms. As shown in Figure 12a, Min *et al.* [107] concluded that GO sheet can significantly improve the plastic deformation ability of the C–S–H/GO quartz interface, and its interfacial binding energy is 62.97–109.44% higher than that without GO. Especially when the functional group is –COOH, the interface binding energy is the highest, which indicates that GO with high carboxyl content and hydration of quartz surface can improve the plastic deformation ability of the interface system. As shown in Figure 12b, Fan *et al.* [108] found that different functional groups on GO can affect the interfacial adsorption capacity and affect the formation of hydrogen bonds. The researchers pointed out that the chemical bond at GO-C/C–S–H is stronger than that at GO-N, and the atoms are more tightly bound. After the reaction occurs, the GO-C sheet is tightly adsorbed, which greatly limits the atomic movement. As shown in Figure 12c, the mean square displacement of graphene and epoxy functional fossil graphene is about twice that of other GO, indicating that carboxyl and hydroxyl groups on GO can react quickly with C–S–H matrix. By optimizing the coverage of functional groups on GO, a stronger chemical bond can be formed between GO and C–S–H [109]. Hou *et al.* [110] held that the insertion of GO significantly enhanced the mechanical properties of the interface between epoxy resin and C–S–H, which led to a significant delay in the interface bonding failure of GO/C–S–H systems. As shown in Figure 12d, after the addition of GO, due to the larger contact area between GO and epoxy molecules, an obvious filamentous phenomenon was observed, and epoxy molecules had excellent deformation ability. There are other researchers who have similar results, such as Fan *et al.* [103], the addition of GO significantly improves the compression resistance of C–S–H gel and forms a stronger hydrogen bond between C–S–H and GO. Lu *et al.* [106] found that the GO sheet not only fills the nanopore and enhances the integrity between the gelling particles, but also improves the safety of cement-based materials and the stability of C–S–H at high temperatures.

4.3 Water permeability simulation

GO nano high specific surface area and oxygen atoms attract water molecules to form hydrogen bonds effectively limiting the transmission of the NaCl solution. As shown in

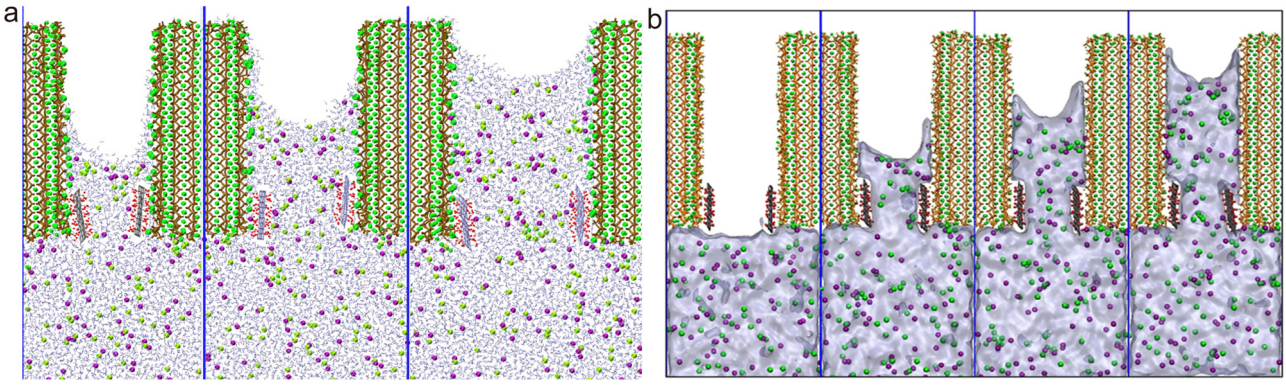

Figure 13: (a) Transport of water and ions in C–S–H gel pores incorporated with GO [93]. (b) Schematic diagram of the molecular structure of water transport in C–S–H gel at 0, 1, 2, and 3 ns [111].

Figure 13a, the addition of GO will significantly reduce the pore area, and the transmission of water and ions will be significantly hindered. Zhao *et al.* [93] suggested that GO nanosheets hindered the transmission channel of NaCl solution and reduced the connectivity of gel pores, reducing their pore size from 3.5 nm to 2.5 nm. The oxygen atoms in the groups can combine GO atoms with water, combined with ions and water, thereby limiting their displacement. As shown in Figure 13b, the pinning effect at the edge of GO limits the movement of the contact line of the NaCl solution, slowing down its transport rate significantly, and the NaCl solution is only transported forward by 2–5 nm [111]. Other researchers have similar results, such as Chen *et al.* [112], a small amount of GO can significantly improve the resistance of cement-based materials to chloride ion erosion, and GO can effectively limit the penetration of water molecules and chloride ions.

5 Conclusions and outlooks

The vast potential of GO to enhance the properties of cement composites has attracted significant attention in the construction materials fields. In recent years, thousands of researchers devoted themselves to study on the effects and reinforcing mechanisms of the GO on cement composites. Studies revealed that GO nanosheets can effectively reinforce the cement composites, mainly through two reinforcing mechanisms, namely the nucleation effects and pore-infilling effects. By virtue of the abundant oxygen-functional groups and ultra-high surface area ratio of the GO nanosheets, they can generate nucleation effects, which provide a platform for cement hydration, the oxygen functional groups will also attract Ca^{2+} ions to promote the cement hydration reaction. As a two-dimensional nanomaterial, GO is usually adsorbed on nearby C–S–H in the hardened cement matrix, filling pores with hydration products or acting as bridges to connect cracks in cement-based materials.

The experiment tests further verify that an appropriate amount of GO (0.03–0.1 wt%) can effectively enhance the mechanical properties and durability of the cement composites. Nevertheless, excessive GO concentration will make the intermolecular van der Waals force too large among the nanosheets, resulting in agglomeration and weakening the reinforcing efficiency of the GO. The agglomerated GO can cause stress concentration in hardened cement-based materials. The dispersion of GO is the key to playing its cement composites' strengthening role.

Theoretical analysis shows that GO can not only promote the hydration reaction of cement through nucleation effects to improve the hydration degree of the matrix after hardening, but also connect the generated C–S–H with GO nanosheets through covalent bonding. When the cement cracks under load, some GO bridges in the ends of the cracks, limiting the development of cracks and improving the mechanical properties of cement composites.

Molecular dynamics simulations further revealed the enhancement mechanisms of GO acting as the "crack-bridging" role in the C–S–H gel of the cement composites. In addition to bridging cracks, the interfacial strength, ductility and plastic deformation capacity of GO-reinforced C–S–H gel are enhanced. Besides, the permeability-related properties of the GO-reinforced C–S–H gel were also investigated *via* molecular dynamics simulations. The simulations revealed that GO-reinforced C–S–H gel can significantly reinforce the impermeability of the cement composites, particularly limiting the transmission of NaCl solution, thus improving the durability of the hardened cement matrix.

Overall, as a candidate of superior nanomaterials with outstanding performance, GO has application prospects and research value in reinforcing cement composites. However, at present, the research on GO-reinforced cement composites is more concentrated in the laboratory and theoretical research stage, and the promotion and application of GO-reinforced cement composites have not been widely carried out. And there are still some critical problems, such as high cost, dispersion difficulty and complicated preparation process in GO-reinforced cement composites. Some recent work reported several innovative dispersion methods to assist GO-reinforced cement composites for practical application, such as covalent functionalization, coating treatment and nano-silica hydrating *et al.* Their dispersion mechanisms should be systematically investigated and reported in the future. Moreover, based on the proposed reinforced mechanism of the GO on cement composites, more cost-effective and high-performance GO-reinforced cement composites are expected to be fabricated.

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