

Back to basics: Nanomodulating calcium silicate hydrate gels to mitigate CO₂ footprint of concrete industry

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Abstract: To realize the sustainable development of concrete, it is vital to mitigate its consumption and environmental footprint (especially the CO₂ footprint) from prolonging the service life through upgrading mechanical and durable performances of concrete. Incorporating nanofillers can effectively tailor the microstructures and performances of concrete. The hydrated calcium silicate (C-S-H) gels account for half of the volume of hardened Portland cement pastes, and they are the fundamental source of the overall properties of concrete. However, the underlying mechanisms of nanofillers on C-S-H gels remains unclear. Herein, this paper underpinned the role of 5 types of representative nanofillers in tailoring the nanostructure of C-S-H gels in cement composites. The research results demonstrated that through the nano-core effect; nanofillers induce the formation of two new C-S-H gels in outer hydration products, namely nano-core-shell element doped low-density C-S-H (NEDLD C-S-H) and nano-core-shell element doped high-density C-S-H (NEDHD C-S-H). The indentation modulus/hardness of NEDLD and NEDHD C-S-H reaches 25.4/0.80 GPa and 46.7/2.72 GPa, respectively. Such superior performances of NEDLD and NEDHD C-S-H derive from the existence of nano-core-shell elements in C-S-H gels rather than the increase in C-S-H packing density. In a short-range, nanofillers form nano-core-shell elements by adsorbing silica tetrahedrons during the hydration process, improving the mechanical properties of C-S-H basic building blocks. In the long-range, the nano-core-shell elements modify the nano-scale performances of C-S-H gels in outer hydration products due to the increase of C-S-H gels' integrality.

Keywords: Nanomodulation; Hydrated calcium silicate (C-S-H); Concrete; CO₂ footprint

1 Introduction

Carbon emission reduction has become a critical survival problem that humans must face and solve. As the most used construction material, concrete is vital to the development of human society but produces a considerable amount of carbon emission [1]. Over 90% of the concrete carbon emissions come from using raw materials, mainly cement. In 2020, China produced 2.476 billion tons of cement and emitted about 1.48 billion tons of carbon dioxide. China's total carbon emission

35 was 10 billion tons in 2020, and cement carbon emission accounts for about 15% of the total [2-5]. According to the
36 composition of carbon emissions in concrete industry, the technical route of carbon emission reduction of concrete includes
37 three aspects [6, 7]: one is to decrease the amount of cement in concrete to directly achieve carbon emission reduction, for
38 example, the utilization of supplement cementitious materials and industrial wastes [8-10], as well as alternative
39 cementitious materials with low carbon emissions [11]; the other is to prolong the concrete service life through upgrading
40 its performance, for instance, the carbon emissions can be halved if the service life is doubled [4, 5].

41 The performance of concrete lie on the nanoscale organizational structure of hydration products that make up concrete,
42 rather than on the material itself [12]. So it is conceivable to tailor concrete performance through regulating the nanoscale
43 structures of hydration products of cement. This move modifies the concrete's mechanical properties and durability without
44 the increase of cement content, in other words, decreases the demand of cement under the promise of required performance,
45 demonstrating the enormous potential for achieving the carbon footprint reduction in the concrete industry.

46 Calcium-silicate-hydrate (C-S-H) gels account for over 50 vol.% of hardened Portland cement, and they are fundamental
47 source of the overall properties of concrete. Former studies [13, 14] demonstrated that the mechanical behavior of C-S-H
48 gels shows nanogranular nature, namely, the C-S-H gels present an accumulation of some C-S-H building blocks with a
49 characteristic particle size of 5 nm, and the packing form and particle-to-particle contact dominate its mechanical responses.
50 According to the C-S-H building blocks' packing densities, classic studies [13–15] classified C-S-H gels into low-density
51 calcium-silicate-hydrate (LD C-S-H) with a packing density of 0.64 and high-density calcium-silicate-hydrate (HD C-S-
52 H) with a packing density of 0.74. Generally, LD and HD C-S-H gels are associated with outer and inner hydration products
53 of hardened cement paste in concrete, respectively [15]. Vandamme et al. [16] identified a new type of C-S-H gels with a
54 packing density of 0.87 in low water-to-binder concrete, known as ultra-high-density calcium-silicate-hydrate (UHD C-S-
55 H). These various sorts of C-S-H gels provide cohesive force in concrete, which is the origin of mechanical performance
56 of concrete [17]. Hence, following the bottom-up theory, it is unsurprisingly conceived to modify the structures and
57 properties of C-S-H gels at the nanoscale for improving the performance of concrete at the macroscale. However, many
58 studies have confirmed that the nanogranular nature and nanomechanical behaviors possessed by C-S-H gels are the
59 Portland cement concrete's intrinsic characteristics, not dependent on types of cement, mix proportions, curing conditions,
60 etc. [18, 19]. Moreover, traditional approaches for reinforcing concrete, such as adding macro or micro fillers, are also
61 helpless to modify C-S-H gels' structures or enhance their mechanical properties [20–22].

62 As a new technological revolution, nanoscience infiltrates and impetus for the development of new generation concrete.
63 The breakthroughs in nanotechnology have been beneficial in essentially upgrading the concrete performance, offering
64 practical approaches to tailor C-S-H gels structures from the nanoscale [23–27]. Such improvement may even break

65 through the concrete intrinsic limitations in conventional concepts [28–32]. In general, C-S-H gels in nano-engineered
 66 concrete show the characteristics of increased polymerization degree [33], refined pore structures [34], as well as optimized
 67 chemical compositions [35] in comparative terms with C-S-H gels in traditional concrete. However, existing studies have
 68 only demonstrated the overall changes of C-S-H gels in nano-engineered concrete. Little attention is conducted to effect
 69 and modification mechanisms of C-S-H gels on the nanoscale mechanical properties and nanogranular nature of C-S-H
 70 gels. Understanding the effect of nanofillers on C-S-H gels is undeniably critical to comprehending the intricate phenomena
 71 in nano-engineered concrete and further controlling and designing the performances of concrete for mitigating CO₂
 72 footprint.

73 Therefore, this study investigates how nanofillers affect the nanoscale performances and nanogranular nature of C-S-H
 74 gels in hydration products of cement paste in concrete. It then explores the mechanical performance improvement of
 75 concrete tailored by incorporating nanofillers from a bottom-up approach. For these purposes, cement paste samples
 76 without/with nanofillers were characterized using a nanoindentation technique together with SEM and EDS tests to allow
 77 a determination of nanoscale performances and microstructures of C-S-H gels. Moreover, micromechanical analysis and
 78 molecular dynamics (MD) together with discrete element method (DEM) simulations, were employed for revealing the
 79 modification mechanisms for nanofillers to the performances of C-S-H gels and the link between C-S-H gel properties and
 80 macroscale mechanical performances of nano-engineered concrete.

81 2 Experimental, theoretical, and numerical methods

82 2.1 Experimental programs

83 2.1.1 Mix proportions

84 In this study, P·O 42.5 R Portland cement, grade II fly ash, silica fume, water reducer with a water reduction capacity of
 85 30%, and nanofillers were used as raw materials to fabricate cement paste samples. Existing studies have exhibit that
 86 various nanofillers, such as nano-silica [36], nano-titania [37], carbon nanotubes [38], graphene [39], and nano boron
 87 nitride [40] are effective in modifying cement-based materials performance; Their morphologies are shown in Fig. 1(a).
 88 Herein, this study employed these 5 representative nanofillers to analyze the effect of nanofillers on C-S-H gels. The
 89 properties of raw materials used are listed in Tables 1–3.

90 Table 1. Chemical composition of cement

Chemical composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O
Mass fraction (%)	61.13	21.45	5.24	2.89	2.08	2.05	0.77

91 Table 2. Chemical composition of fly ash

Chemical composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO
Mass fraction (%)	2.27	53.36	29.09	3.87	0.81

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Table 3. Properties of nanofillers

Types	Morphology	Purity (%)	Diameter (nm)	Length (μm)	Thickness (nm)	Specific surface area (m^2/g)	Surface treatment
Nano-silica	Powder	≥ 99	20	-	-	≥ 600	-
Nano-titania	Powder	≥ 96	20	-	-	-	Silica-coated
Carbon nanotubes	Tube	-	20-30	10-30	-	70	Nickel-coated
Multi-layer graphene	Sheet	-	<2000	-	1-5	500	-
Nano boron nitride	Sheet	-	<1000	-	5-100	19	-

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Table 4 exhibits the mix proportions of cement pastes in this study. They are determined by reference to previous studies

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[41] for achieving good mechanical performance and workability of cement pastes modified with different nanofillers.

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Table 4. Mix proportions of cement pastes

Nanofiller	Code	Mix proportions (mass ratio)					
		Cement	Fly ash	Silica fume	Water	Superplasticizer	Nanofiller
-	Blank	1	0.25	0.313	0.375	0.015	-
Nano-silica	S	0.970	0.25	0.313	0.375	0.020	0.030
Nano-titania	T	0.980	0.25	0.313	0.375	0.015	0.020
Carbon nanotubes	C	0.997	0.25	0.313	0.375	0.015	0.003
Multi-layer graphene	G	0.995	0.25	0.313	0.375	0.015	0.005
Nano boron nitride	B	0.997	0.25	0.313	0.375	0.015	0.003

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2.1.2 Sample preparation

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Sample preparation aims to flatten the surface as possible for maximizing the validity of nanoindentation results.

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Therefore, after fabricating cement paste samples (the detailed procedure may be found in [41]), the samples were

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pretreated using the following steps [42]: 1) The cement paste samples were cut into prismatic pieces measuring 5 mm×10

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mm×10 mm; 2) Cylindrical phenolic resin were filled with the cut samples after drying at 50 °C for 24 h; 3) The surfaces

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of samples were ground with sandpapers from coarse to fine; 4) The ground samples were successively polished with 0.5

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μm and 0.04 μm polishing agents on a velvet cloth; 5) The samples were cleaned using an ultrasonic device for cleaning

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the surfaces; 6) The samples were dried at 50 °C for 24 h prior nanoindentation tests. It is noted that ethanol was selected

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as the washing medium and cooling agent to avoid changes in hydration products during sample pretreatment process.

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2.1.3 Measurements

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This study employed nanoindentation technology together with SEM and EDS tests to identify the nanomechanical

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properties and microstructures of C-S-H gels and provide references for further analyzing nanofillers' modification

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mechanisms on C-S-H gels. For these purposes, on the one hand, the indentation depth should satisfy the 1/10 rule of thumb

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and scale separability condition to ensure the nanoindentation results can reflect the intrinsic characteristics of the phases

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in concrete [43]. On the other hand, the loading program should be carefully selected to eliminate the discreteness derived

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from the C-S-H gels' time-dependent characteristics. Therefore, a trapezoidal loading program was selected in the

112 nanoindentation test. The load increased linearly from the initial contact between Berkovich indenter and sample to 4 mN
 113 at a constant loading speed of 1 mN/s; then, the load of 4 mN sustained for 30 s; finally, the load decreased at a constant
 114 loading speed of 1 mN/s. The representative indentation load-depth curves for various phases in cement pastes are depicted
 115 in Fig. 1 (b). The nanoindentation results are considered valid because the curve shapes are consistent with that in previous
 116 studies [18, 44, 45]. The indentation modulus M and hardness H are obtained by combining the continuum scale model
 117 and load-depth curves through the following equations [46]:

$$M \stackrel{\text{def}}{=} \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_c}} \quad (1)$$

$$H \stackrel{\text{def}}{=} \frac{P_{\max}}{A_c} \quad (2)$$

118 where S equaling $(dP/dh)_{h=h_{\max}}$ represents the contact stiffness, β equaling 1.034 is a correction coefficient for
 119 Berkovich indenter, and A_c represents the indenter-sample contact area under the peak load.

120 To obtain nanoscale mechanical behaviors of different nanoscale phases in cement pastes, statistical methods were
 121 employed for quantitative analysis of nanoindentation results. As a prerequisite for using statistical methods, each
 122 nanoindentation should be independent, which can be regarded as an event in statistical analysis. Hence, referring to
 123 previous studies [47, 48], a 10×10 grid nanoindentation test was conducted on a randomly selected region for every sample
 124 with a 10- μm spacing. The M and H of different types of C-S-H gels were analyzed by using the deconvolution method
 125 based on a probability density function (PDF), as given in Formula (3) [16].

$$\text{Find } (\mu_J, s_J, f_J) \text{ from } \min \frac{1}{m} \sum_{i=1}^m (P_i - P(x_i))^2, \text{ s.t. } \sum_{J=1}^n f_J = 1 \quad (3)$$

126 where μ_J , s_J and f_J are the mean value, standard deviation, and volume fraction of phase J ($J = 1, 2, \dots, n$),
 127 respectively. P_i and $P(x_i)$ represent the frequency density of nanoindentation results and probability distribution
 128 function at x_i , respectively. Note that the nanomechanical property of each phase was considered to satisfy Gaussian
 129 distribution in this study, as expressed in Formula (4).

$$P(x_i) = \sum_{J=1}^n \frac{f_J}{\sqrt{2\pi s_J^2}} \exp \left[-\frac{(x_i - \mu_J)^2}{2s_J^2} \right] \quad (4)$$

130 In addition, this study introduced some constraints for ensuring the accuracy and repeatability of statistical analysis [49].
 131 First, the synchronous minimization of indentation modulus and hardness frequency distribution analysis was carried out.
 132 Second, the bin number m and the unknown phase number n satisfied $m > 5n - 1$. Third, the μ and s of adjacent phases
 133 should satisfy Formula 5 to ensure the validity of deconvolution.

$$\mu_j + s_j < \mu_{j+1} - s_{j+1} \quad (5)$$

134 After the nanoindentation test, SEM and EDS were performed for characterizing the microstructures at the
 135 nanoindentation point. Note that before SEM/EDS characterization, the sample surfaces were covered by a platinum film
 136 to ensure the sample's conductivity.

137 2.2 Theoretical analysis method

138 C-S-H gels present nanogranular nature, and their mechanical responses can be calculated by micromechanics. The M
 139 of C-S-H gels is given by Equations (6)–(8) [16].

$$M = m_s \times \Pi_M(v_s, \eta, \eta_0) \quad (6)$$

$$m_s = \frac{E_s}{1 - v_s^2} \quad (7)$$

$$\Pi_M(v_s = 0.2, \eta, \eta_0 = 0.5) = 2\eta - 1 \geq 0 \quad (8)$$

140 where m_s is the indentation modulus assuming the packing density $\eta = 1$ determined by the C-S-H basic building
 141 block's modulus E_s and Poisson's ratio v_s . The values of $E_s = 59$ GPa [50] and $v_s = 0.2$ [16] are assumed in the
 142 current study. Moreover, M of C-S-H gels is influenced by the minimum packing density of solids capable of withstanding
 143 external forces η_0 ($= 0.5$ [12]) and packing density η of C-S-H building blocks. Meanwhile, the H can be expressed
 144 as Formulas (9) to (13) [12, 16, 51].

$$H_i = h_s \times \Pi_H(\alpha_s, \eta_i, \eta_0) \quad (9)$$

$$h_s = c_s \times A(1 + B\alpha_s + (C\alpha_s)^3 + (D\alpha_s)^{10}) \quad (10)$$

$$\Pi_H(\alpha_s, \eta_i, \eta_0 = 0.5) = \Pi_1(\eta_i, \eta_0) + \alpha_s \times (1 - \eta) \times \Pi_2(\alpha_s, \eta_i, \eta_0) \quad (11)$$

$$\Pi_1(\eta_i, \eta_0) = \frac{\sqrt{2(2\eta - 1)} - (2\eta - 1)}{\sqrt{2} - 1} \times (1 + a(1 - \eta) + b(1 - \eta)^2 + c(1 - \eta)^3) \quad (12)$$

$$\Pi_2(\alpha_s, \eta_i, \eta_0) = \frac{2\eta - 1}{2} (d + e(1 - \eta) + f(1 - \eta)\alpha_s + g\alpha_s^3) \quad (13)$$

145 where h_s is the hardness assuming the packing density $\eta = 1$ related to cohesion c_s and friction coefficient α_s
 146 between neighboring C-S-H basic building blocks. The cohesion c_s and friction coefficient α_s equal to 0.44 GPa and
 147 0.181, respectively [16]. Moreover, the coefficients in Formula (11) to (13) are all constants when nanoindentation test
 148 uses Berkovich indenter. The coefficients $A, B, C, D, a, b, c, d, e, f,$ and g equal to 4.7644, 2.5934, 2.1860, 1.6777, $-5.3678,$
 149 $12.1933, -10.3071, 6.7374, -39.5893, 34.3216,$ and $-21.2053,$ respectively [12, 51]. By applying micromechanics, the C-
 150 S-H gels' nanogranular nature of in nano-engineered concrete can be revealed based on nanoindentation results.

151 2.3 Numerical simulation strategy

152 2.3.1 Molecular dynamics (MD) simulation

153 Under the action of nanofillers, the nanoscale microstructures and chemical composition of hydration products of cement

154 paste may vary significantly. Unfortunately, because of the limitation of experimental technique, monitoring the hydration
155 process is still challenging at the nanoscale. Therefore, MD method is recently employed to explore the effect of nanofillers
156 on the hydration process of cement [52, 53]. Considering the complex composition of cement-based systems, C-S-H gels,
157 the uppermost production in cement pastes were selected in this study as the research object. The MD model [54, 55] was
158 established according to the following steps: 1) Construction: where a CaO-SiO₂-H₂O system was constructed by putting
159 125 Si(OH)₄, 125 Ca(OH)₂, and 375 H₂O molecules into a periodic cubic lattice, as depicted in Fig. 1 (c), the Ca/Si ratio is
160 selected based on experimental results; 2) Relaxation: where the system was relaxed for 100 ps under a canonical ensemble
161 of 300 K, and further for 500 ps under an isothermal-isobaric ensemble of 300 K and 0 Pa; 3) Reaction: where the system
162 was subjected to the dynamic calculation by using a reaction force field ReaxFF for 1000 ps under a canonical ensemble
163 of 2000 K; 4) Annealing: where the system was cooled to 300 K under the condition of a canonical ensemble to obtain the
164 final structures, as depicted in Fig. 1 (d). Fig. 1 (d) demonstrates that some Si(OH)₄ molecules were polymerized to form
165 a chain structure composed of a series of silica tetrahedrons. Moreover, the velocity Verlet algorithm was used throughout
166 for solving equations of the above process. The detailed information about ensemble, reaction force field ReaxFF, and other
167 related knowledge of molecular dynamics can refer to in the literature [56-58].

168 Additionally, because the size of nanofillers is much larger than that of the simulation area, the size of nanofillers in MD
169 model was reduced to approximately 300 atoms, as shown in Fig. 1 (e). On the basis of the above MD model, the influence
170 of nanofillers on cementitious composites' hydration products was discussed by analyzing the reaction evolution and
171 product distribution.

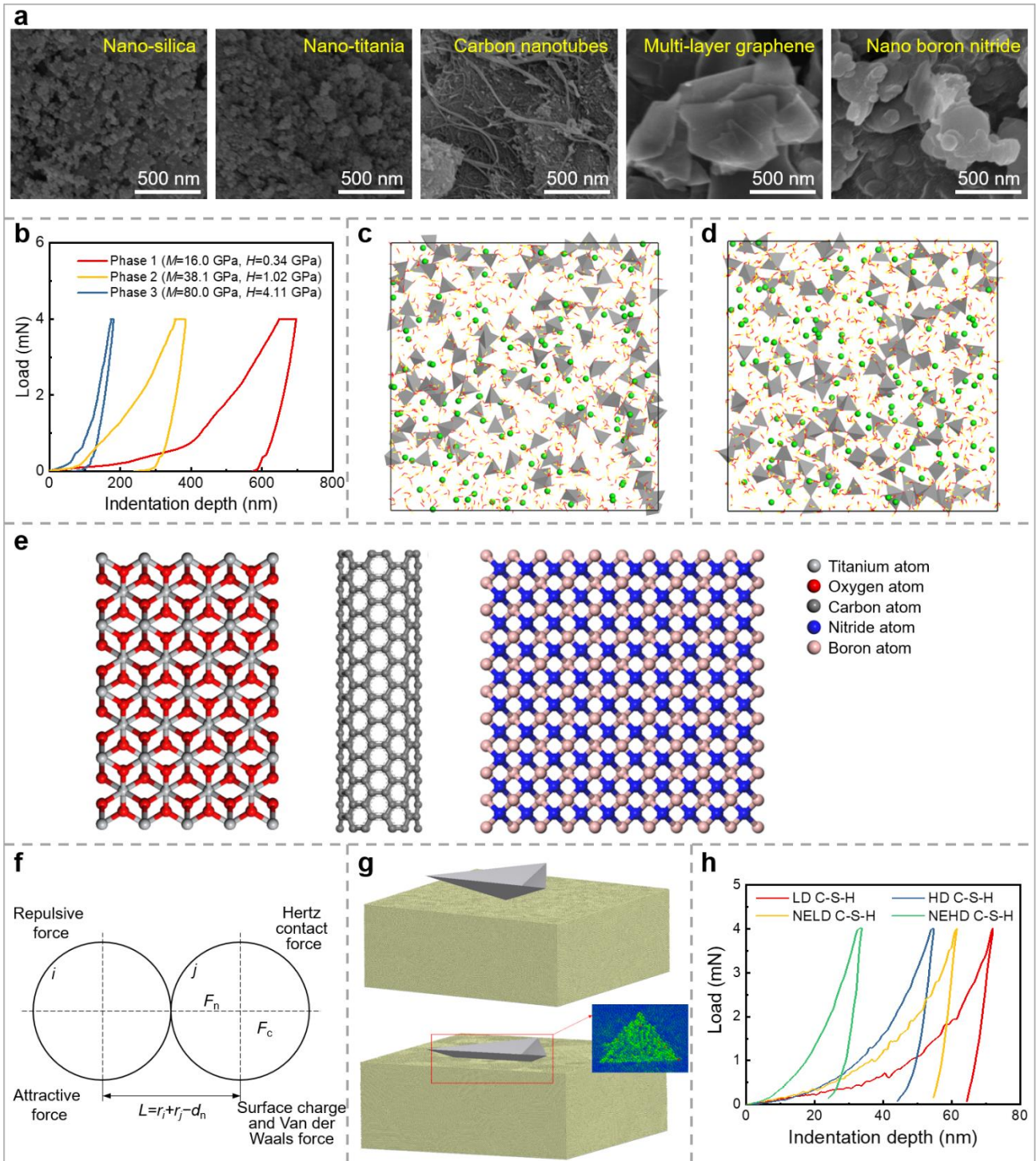


Fig. 1 Experimental, theoretical, and numerical methods and typical results. (a) Morphology of nanofillers; (b) Characteristic indentation load-depth curves of nanoindentation tests; (c) and (d) Configurations of CaO-SiO₂-H₂O system in initial and after-reaction MD model, respectively (in which gray tetrahedrons and green spheres represent silica tetrahedrons and Ca atoms, respectively); (e) Construction of nanofillers (namely nano-titania, carbon nanotube, graphene, nano boron nitride) in MD model; (f) Normal contact model between adjacent C-S-H basic building blocks in DEM model; (g) Schematic diagram of DEM model before Loading and Loaded to peak force; (h) Nanoindentation load-depth curve obtained from DEM simulation

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173 2.3.2 Discrete element method (DEM) simulation

174 Micromechanics, assuming the C-S-H gels only consist of the C-S-H basic building blocks, can accurately analyze the

175 packing density of traditional C-S-H gels. Nonetheless, the micromechanics may be no longer valid after adding nanofillers,
 176 because new nanofiller particles/tubes/sheets appear in the system. Hence, DEM was employed to further investigate
 177 nanofillers' effect on the gels' nano-scale mechanical properties. Jennings [15] demonstrated that, C-S-H gels can be
 178 modelled as an accumulation of some spherical building blocks with a 5-nm characteristic particle size. In general, there
 179 are repulse forces caused by normal contact, friction forces caused by tangential sliding, charge force, and van der Waals
 180 force between adjacent C-S-H building blocks. The normal repulse force F_n can be described by the Hertz contact model
 181 [59], as expressed in Formula (14).

$$F_n = \frac{4}{3} E^* \sqrt{R^*} \delta_n^{3/2} \quad (14)$$

182 where E^* and R^* represent the equivalent Young's modulus and particle radius, respectively, as given in Formula (15)
 183 and (16) [60]; δ_n is the normal overlap.

$$\frac{1}{E^*} = \frac{(1 - \nu_i^2)}{E_i} + \frac{(1 - \nu_j^2)}{E_j} \quad (15)$$

$$\frac{1}{R^*} = \frac{1}{R_i} + \frac{1}{R_j} \quad (16)$$

184 where E_i/E_j , ν_i/ν_j , R_i/R_j respectively represent Young's modulus, Poisson's ratio, and radius of particle i/j . The values
 185 of Young's modulus, Poisson's ratio, and radius of C-S-H spherical building blocks are taken as 70 GPa, 0.2, and 2.5 nm,
 186 respectively [61]. Moreover, the charge attraction force and van der Waals forces are the C-S-H gel strength's primary
 187 sources. The Johnson-Kendall-Roberts model [62] was used to describe the normal cohesion between particles, as given in
 188 Formula (17).

$$F_c = -4\sqrt{\pi\gamma E^*} a^{3/2} + \frac{4E^*}{3R^*} a^3 \quad (17)$$

189 where γ represents the surface energy, a is the interaction parameter that back-analyzed from Formula (18).

$$\delta_n = \frac{a^2}{R^*} - \sqrt{\frac{4\pi\gamma a}{E^*}} \quad (18)$$

190 Moreover, this study takes $r = 1.1d$ as the cut-off radius of normal cohesion and $F_{c,max} = 1.5$ nN as the maximum
 191 normal cohesive force to reduce computational cost [61]. Combined with Formulas (14) to (18), the normal contact model
 192 of C-S-H building blocks is established as depicted in Fig. 1 (f). The tangential friction force obeys Coulomb's law. The
 193 sliding friction coefficient μ_s and rolling friction coefficients μ_r between adjacent basic building globules in C-S-H gels
 194 equal to 0.65 and 5 [61], respectively.

195 Based on the above constitutive relationships, the DEM model of various sorts of C-S-H gels was established by the
 196 following steps: 1) Construction: where C-S-H building globules with a diameter of 5 nm were put into a box with a

197 dimension of 800 nm × 800 nm × 300 nm, as shown in Fig. 1 (g), and the packing densities assigned 0.64 and 0.74 to LD
198 and HD C-S-H [12]; 2) Property assignation: where the mechanical properties are assigned to C-S-H basic building
199 globules; 3) Interaction assignation: where the interactions, such as cohesion and friction, are established between C-S-H
200 basic building globules; 4) Loading: where the accumulation was loaded to 4 nm by a Berkovich indenter at a constant
201 loading speed of 75 nm/s, as depicted in Fig. 1 (g), and unloaded at the same rate after holding 0.1 s; 5) Calculation: where
202 the M and H of different types of C-S-H gels are calculated combined the indentation load-depth curves obtained from step
203 4 and Formulas (1) and (2). Fig. 1 (h) depicted the simulated load-indentation depth curves of various C-S-H gels.

204 By the above method, nano-titania, carbon nanotube, and nano boron nitride were included into the system to explore
205 the effect of nanofillers on C-S-H gels' mechanical properties. Based on the nano-core theory [41, 49], nanofillers will be
206 coated by C-S-H gels during hydration process. Therefore, this paper assumes that the surface of nanofillers is evenly
207 covered with a 2.5 nm layer of C-S-H and forms nano-core-shell elements, and the contact between nano-core-shell
208 elements and C-S-H building blocks is the same as that among C-S-H basic particles. In addition, because of the large size
209 of carbon nanotubes and nano boron nitride, their length/area were reduced so that a single nanofiller can be placed in a
210 800 nm × 800 nm × 300 nm box at any angle.

211 3 Results and discussion

212 3.1 Nanomechanical characteristics of C-S-H gels

213 According to previous studies [18, 19], the nanoscale mechanical characteristics are the intrinsic characteristics of C-S-
214 H gels, independent on types of cement, mix proportions, curing conditions, etc. Because the purpose of this work is to
215 explore the effect of nanofillers on hydration products (especially C-S-H gels), the unhydrated binders were excluded from
216 the deconvolution analysis. As demonstrated in the literature [18, 19], the phases were identified as unhydrated binder in
217 cement pastes if their indentation modulus were higher than 50 GPa. The deconvolution results of M and H are illustrated
218 in Fig. 2, Fig. 3, and Table 5.

219 The deconvolution results identified four phases existing in cement pastes without/with nanofillers. However, the C-S-
220 H gels' types and contents, even the nanoscale mechanical properties, are quite different in nano-engineered cement pastes
221 and plain cement paste.

222 1) Phase 1, with an indentation modulus $M = \mu_{M1} \pm s_{M1} = 8.1 \pm 1.9$ GPa and a hardness $H = \mu_{H1} \pm s_{H1} = 0.20 \pm$
223 0.15 GPa, identified as micro pore (MP) [18, 19, 22], occupied 9.3 vol.% of hydration products in plain cement paste.
224 Moreover, no MP was observed in cement paste with nanofillers. Noteworthy, both M and H of MP itself are actually 0
225 GPa. The obtained M and H from deconvolution analysis reflect the nanomechanical properties of solid phases with

226 micropores. The MP is analyzed as an independent phase due to its reference value in multiscale numerical analysis [12].

227 2) Phase 2, with an indentation modulus $M = \mu_{M2} \pm s_{M2} = 19.7 \pm 3.8$ GPa and a hardness $H = \mu_{H2} \pm s_{H2} = 0.68 \pm$
228 0.08 GPa, identified as LD C-S-H [18, 19, 22], accounted for 8.0 vol.% of hydration products in plain cement paste. After
229 adding nanofillers (except for nano-silica), the M and H of LD C-S-H, respectively, increases to 22.0–25.4 GPa and 0.74–
230 0.90 GPa; the LD C-S-H content alters to 6.5–23.0 vol.%.

231 3) Phase 3, with an indentation modulus $M = \mu_{M3} \pm s_{M3} = 30.8 \pm 3.0$ GPa and a hardness $H = \mu_{H3} \pm s_{H3} = 1.05 \pm$
232 0.16 GPa, identified as HD C-S-H [18, 19, 22], occupied 61.0 vol.% of hydration products in plain cement paste. The
233 addition of nanofillers showed no significant effect on the HD C-S-H's nanomechanical properties. Meanwhile, the
234 incorporation of 3 wt.% nano-silica, 2 wt.% nano-titania, 0.3 wt.% carbon nanotubes, 0.5 wt.% multi-layer graphene, and
235 0.3 wt.% nano boron nitride decreases HD C-S-H content to 28.9%, 38.0%, 27.0%, 46.0%, and 37.5%, respectively.

236 4) Phase 4, with an indentation modulus $M = \mu_{M4} \pm s_{M4} = 37.5 \pm 1.9$ GPa and a hardness $H = \mu_{H4} \pm s_{H4} = 1.51 \pm$
237 0.16 GPa, identified as UHD C-S-H [18, 19, 22], accounted for 21.8 vol.% of hydration products in plain cement paste.
238 After adding nanofillers, the nanomechanical properties of UHD showed no obvious changes, and the content increased to
239 28.4–43.1 vol.%. Note that UHD C-S-H possesses similar nanomechanical properties with calcium hydroxide (CH),
240 indicating these two phases cannot be made a distinction through nanoindentation tests [16]. Considering the low water-
241 binder ratio and large amounts of pozzolanic fillers in binder, it can be inferred that the CH content is low in samples [63,
242 64]. Hence, CH was ignored in deconvolution analysis.

243 5) Phase 5, with an indentation modulus $M = 44.4–46.7$ GPa and a hardness $H = 1.70–2.72$ GPa, occupied 5.7–24.7 vol.%
244 of hydration products in cement paste with different types of nanofillers. This phase is considered as a new nano-induced
245 hydration product for the following reasons. First, the nanomechanical properties of a given phase in cement-based
246 composites are its intrinsic characteristics [18, 19], and the nanomechanical properties of the new phase differ from that of
247 all raw materials and known hydration products in cement-based composites. Second, the new phase occupied 5.7–24.7
248 vol.% of hydration products in cement pastes with nanofillers, demonstrating the identified new phase is a major component
249 of cement paste in nano-engineered concrete. Third, the new phase is only identified in samples with nanofillers.

250 To sum up, the nanofillers optimize the component of hydration products in cement pastes, as well as forms new
251 hydration products. These phenomena may be attributed to the influences of nanofillers on the microstructures of LD and
252 HD C-S-H through the nano-core effect [65], which is discussed in greater detail by using micromechanics analysis and
253 MD/DEM simulations in sections 3.3 to 3.5.

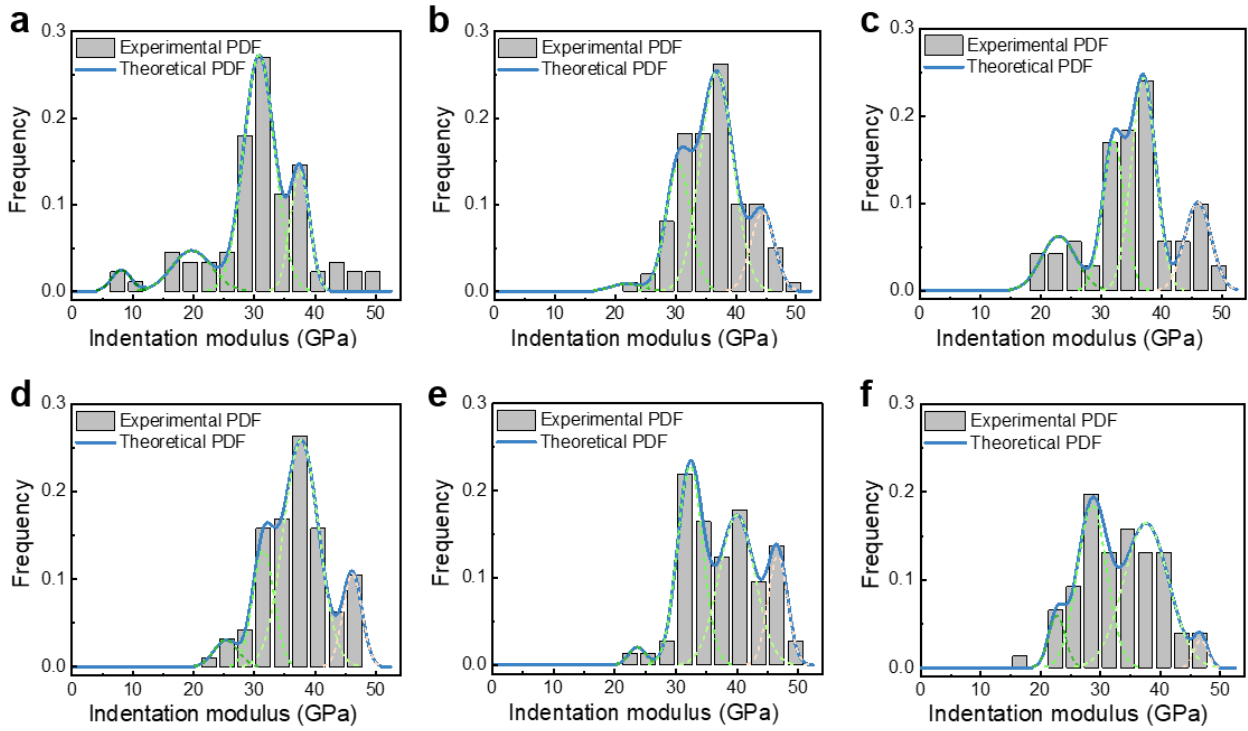


Fig. 2. Deconvolution results of the indentation modulus results. (a) Without nanofillers; (b) With nano-silica; (c) With nano-titania; (d) With carbon nanotubes; (e) With multi-layer graphene; (f) With nano boron nitride

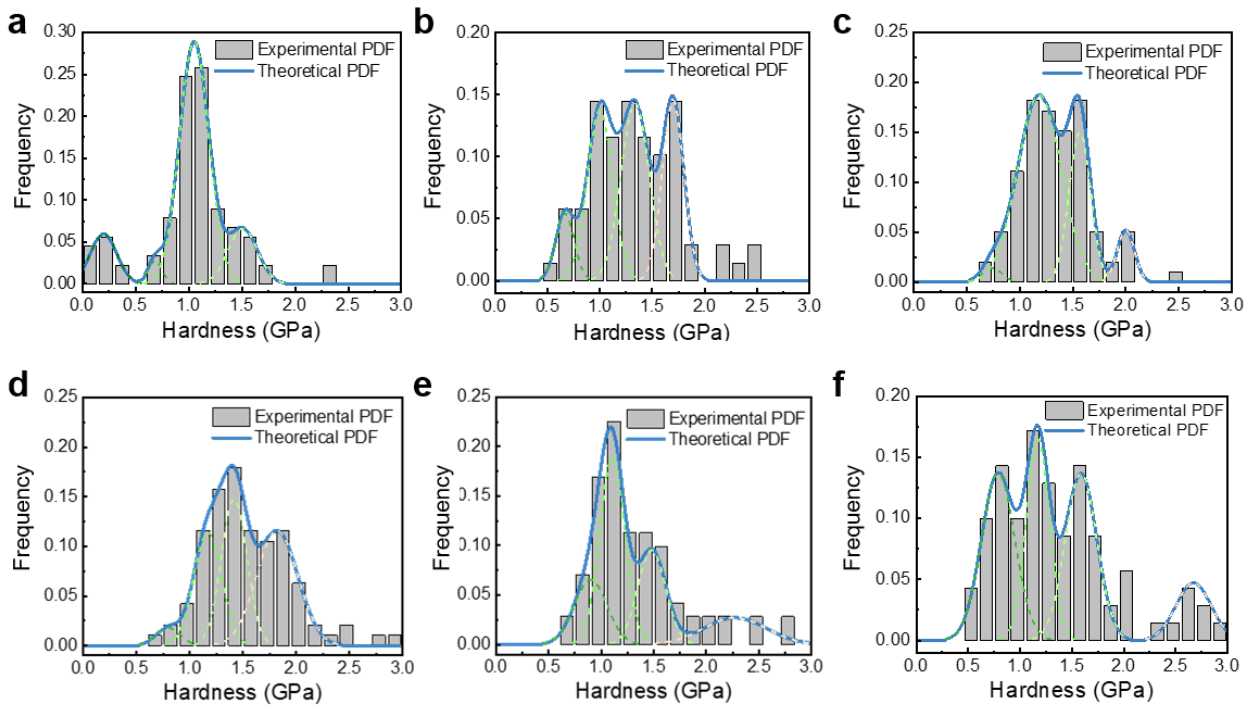


Fig. 3. Deconvolution results of the hardness results. (a) Without nanofillers; (b) With nano-silica; (c) With nano-titania; (d) With carbon nanotubes; (e) With multi-layer graphene; (f) With nano boron nitride

Table 4. Deconvolution results of M and H

Group	Phase 1			Phase 2			Phase 3			Phase 4			Phase 5		
	M (GPa)	H (GPa)	f (%)	M (GPa)	H (GPa)	f (%)	M (GPa)	H (GPa)	f (%)	M (GPa)	H (GPa)	f (%)	M (GPa)	H (GPa)	f (%)
Blank	8.1 ±	0.20 ±	9.3	19.7 ±	0.68 ±	8.0	30.8 ±	1.05 ±	61.0	37.5 ±	1.51 ±	21.8	-	-	-

	1.9	0.15		3.8	0.08		3.0	0.16		1.9	0.16				
				22.0	0.67		30.5	1.00		36.8	1.34		44.4	1.70	
S	–	–	–	±	±	6.5	±	±	28.9	±	±	40.2	±	±	24.3
				3.1	0.10		2.4	0.14		3.2	0.16		2.3	0.12	
				23.0	0.74		32.1	1.18		37.0	1.57		46.0	2.00	
T	–	–	–	±	±	7.1	±	±	38.0	±	±	39.7	±	±	15.2
				3.4	0.11		2.1	0.24		2.4	0.12		2.6	0.10	
				25.4	0.80		31.5	1.17		37.7	1.42		46.2	1.82	
C	–	–	–	±	±	5.2	±	±	27.0	±	±	43.1	±	±	24.7
				2.3	0.13		2.1	0.15		3.4	0.14		1.8	0.23	
				23.7	0.90		32.3	1.11		40.0	1.48		46.6	2.27	
M	–	–	–	±	±	10.6	±	±	46.0	±	±	28.4	±	±	15.0
				1.7	0.18		2.4	0.14		3.4	0.16		1.9	0.35	
				22.7	0.78		28.6	1.18		37.6	1.59		46.7	2.72	
B	–	–	–	±	±	23.0	±	±	37.5	±	±	33.9	±	±	5.7
				1.6	0.18		2.9	0.14		4.4	0.18		1.3	0.27	

255 3.2 Morphology and chemical composition of C-S-H gels

256 Figs. 4 show the morphology and chemical composition at the indentation point. As depicted in Fig. 4 (a), several
257 nanoscale cracks appear at the indentation point, and the Ca/Si ratio equals 0.97. After adding nanofillers, the defects reduce
258 at the indentation point in Fig. 4 (b)–(e). Noteworthy, the nanofillers with unique morphology (namely carbon nanotubes,
259 multi-layer graphene, and nano boron nitride) are observed at the indentation point, as shown in Fig. 4 (c)–(e). The
260 protrusions with the same shape as the nanofillers confirmed the presence of nanofillers at the indentation point, which
261 may lead to C-S-H gels' superior nanomechanical properties due the high modulus and hardness of nanofillers. Meanwhile,
262 the nanofillers are covered by hydration products as their morphologies in Fig. 4 (c) are quite different from their original
263 morphologies in Fig. 1 (a). For example, the diameter of carbon nanotubes in Fig. 4 (c) is obvious larger than that of carbon
264 nanotubes in Fig. 1 (a), indicating the carbon nanotubes are covered by hydration products. EDS results indicated that the
265 protrusions at the indentation point in Fig. 4 (e) contained nano boron nitride sheets because of their high content of element
266 nitride. Moreover, some nanoscale substances, which the indenter cannot flatten, appear near the edge of nano boron nitride
267 in the indentation point, meaning that the substances are a kind of hard crystal. Owing to their hexagonal plate shape, the
268 substances may be nanoscale CH crystals rather than C-S-H gels formed by the accumulation of C-S-H basic building
269 blocks. As for the Ca/Si ratio, the ratio ranges are 0.09-1.63 after adding nanofillers, showing no obvious regularity.
270 SEM/EDS results demonstrate that the presence of nanofillers may enhance the nano-scale mechanical properties of
271 hydration products. The mechanisms and influences of these phenomena are investigated and discussed in detail in section
272 3.5.

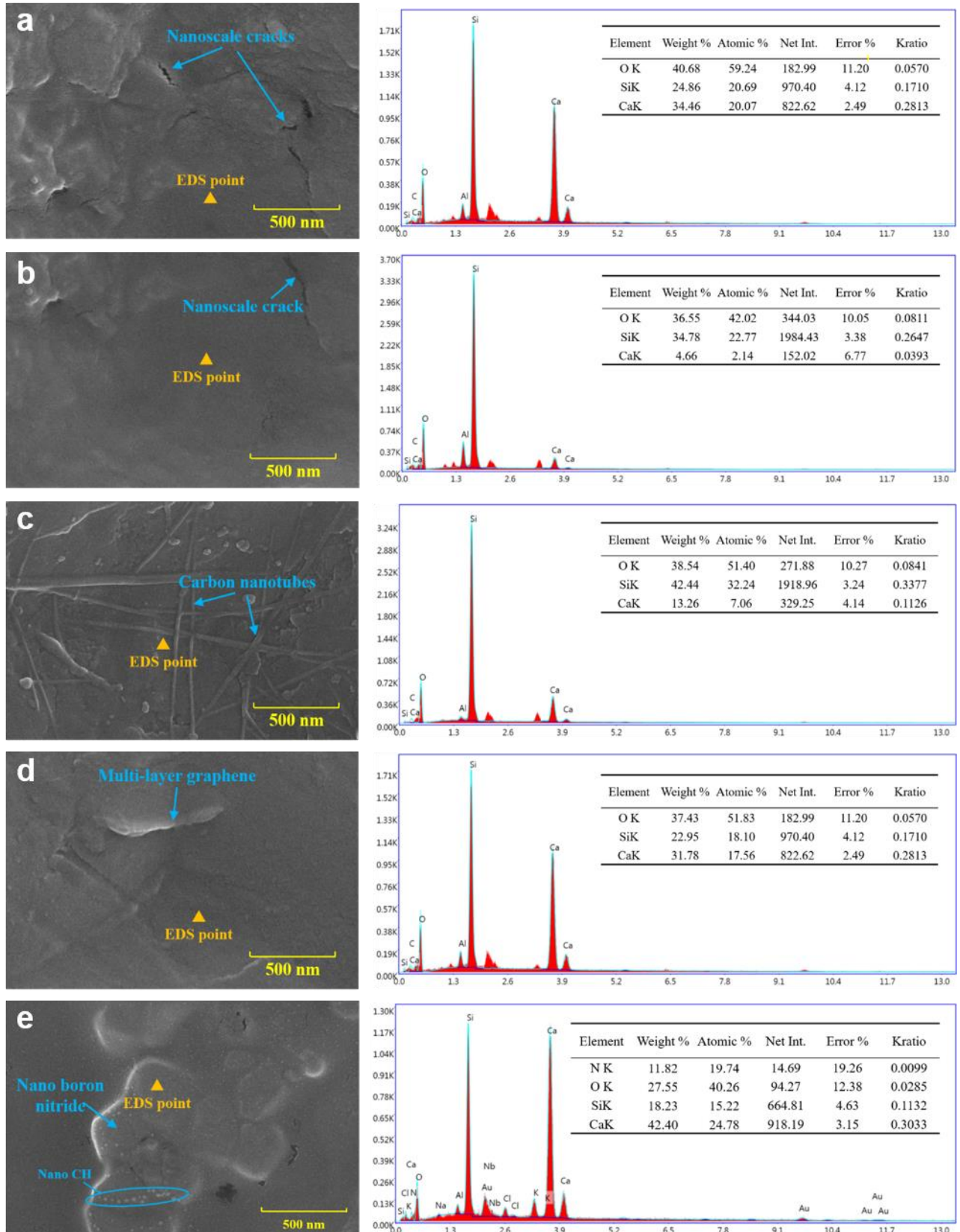


Fig. 4. Morphology and chemical composition at indentation point of sample without/with nanofillers. (a) Without nanofillers; (b) With nano-silica; (c) With carbon nanotube; (d) With multi-layer graphene; (e) With nano boron nitride

273 3.3 Packing density analysis

274 Combining nanoindentation deconvolution results with micromechanics, the packing densities of different C-S-H gels
275 were obtained, as depicted in Fig. 5 and 6. The LD C-S-H's calculated packing density is 0.67, that approximates the
276 random limit packing of spheres. The HD C-S-H's calculated packing density is 0.75, similar to the densest packing of
277 spheres. As for UHD C-S-H, its packing density is 0.81, showing a packing characteristic of the two-scale random limit
278 packing of 0.87. The packing densities of various C-S-H gels are consistent with those in former studies [16, 66],
279 demonstrating that the nanogranular nature is the C-S-H gel inherent feature.

280 According to micromechanics, the nanofillers hardly affect the nanoscale mechanical properties of HD and UHD C-S-
281 H. As demonstrated in former studies [12], the HD and UHD C-S-H mainly appear in inner hydration products that form
282 in situ from binder particles. The nanofillers cannot enter the binder particles due to the steric hindrance effect [67].
283 Therefore, nanofillers cannot affect the mechanical properties of the HD and UHD C-S-H in inner products.

284 In contrast, LD C-S-H's M and H increase after adding nanofillers. Based on the micromechanics, the LD C-S-H's
285 packing density in cement pastes containing nanofillers increases to 0.69–0.72. Moreover, a new phase with an indentation
286 modulus of 44.4–46.7 GPa and a hardness of 1.70–2.72 GPa is identified in this study. The packing density of the new
287 phase is 0.85–0.90, calculated according to micromechanics. These two phases occupy 22.3–30.8 vol.% in cement paste
288 with nanofillers, which is close to the volume proportion of outer hydration products (28.1 vol.%, calculated from the water
289 volume ratio to total volume during casting). These phenomena may be benefits to the improvement of outer hydration
290 products owing to the availability of numerous nanofiller particles. According to the literature [68], nanofillers can adsorb
291 hydration products owing to their high surface energy, forming nano-core-shell elements, i.e., nanofillers act as the nano
292 cores, and the adsorbed hydration products serve as the shell. The nano-core-shell elements serve as a new type of C-S-H
293 building blocks with superior mechanical properties, enhancing the nanomechanical behaviors of C-S-H gels in outer
294 hydration products. Noteworthy, to distinguish the C-S-H gels in outer products in cement pastes with nanofillers from
295 that without nanofillers, phases 2 and 5 (in Table 5) are identified as nano-core-shell element doped low-density (NEDLD)
296 C-S-H and nano-core-shell element doped high-density (NEDHD) C-S-H, respectively.

297 After adding nanofillers into cement paste, the packing density of C-S-H gels obtained from indentation modulus is
298 significantly different from that calculated from hardness. Because of the introduction of new nanofiller particles, the
299 equations in mechanics cannot accurately describe the nanomechanical properties of C-S-H with nanofillers. The
300 nanomechanical behaviors and granular nature of NEDLD and NEDHD C-S-H are therefore investigated by DEM
301 simulation in section 3.5.

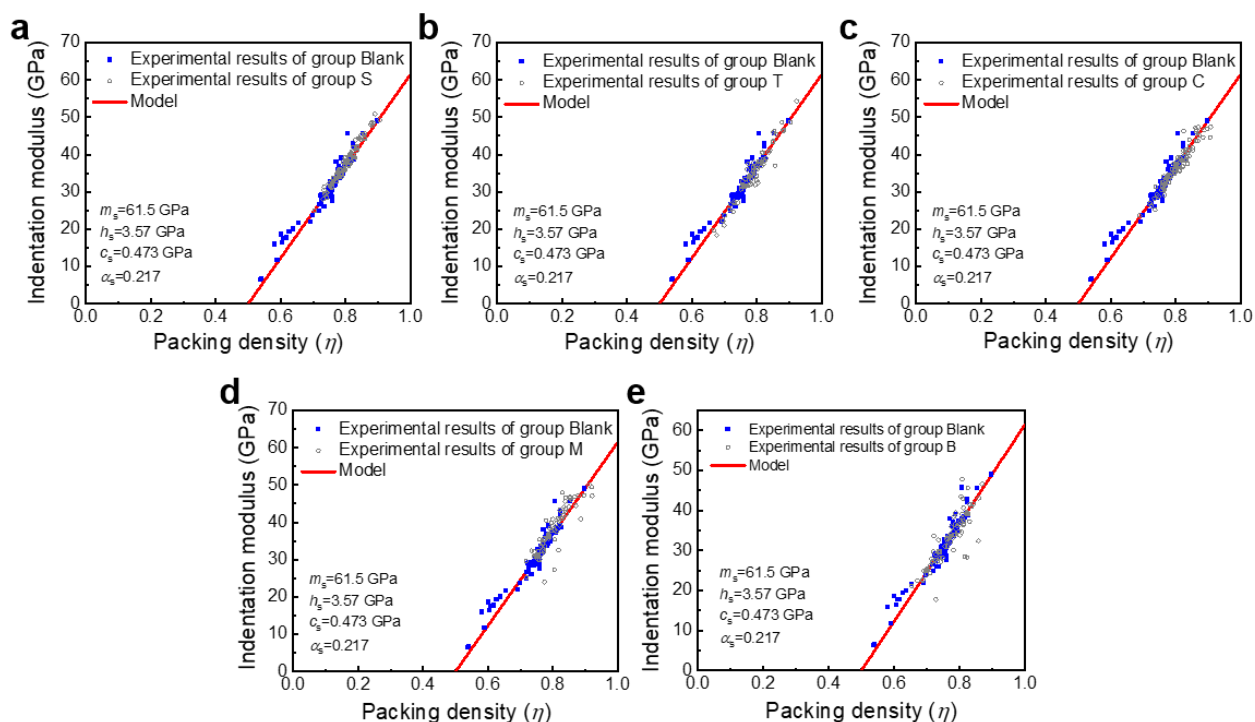


Fig. 5 Indentation modulus-packing density. (a) Without/with nano-silica; (b) Without/with nano-titania; (c) Without/with carbon nanotubes; (d) Without/with multi-layer graphene; (e) Without/with nano boron nitride

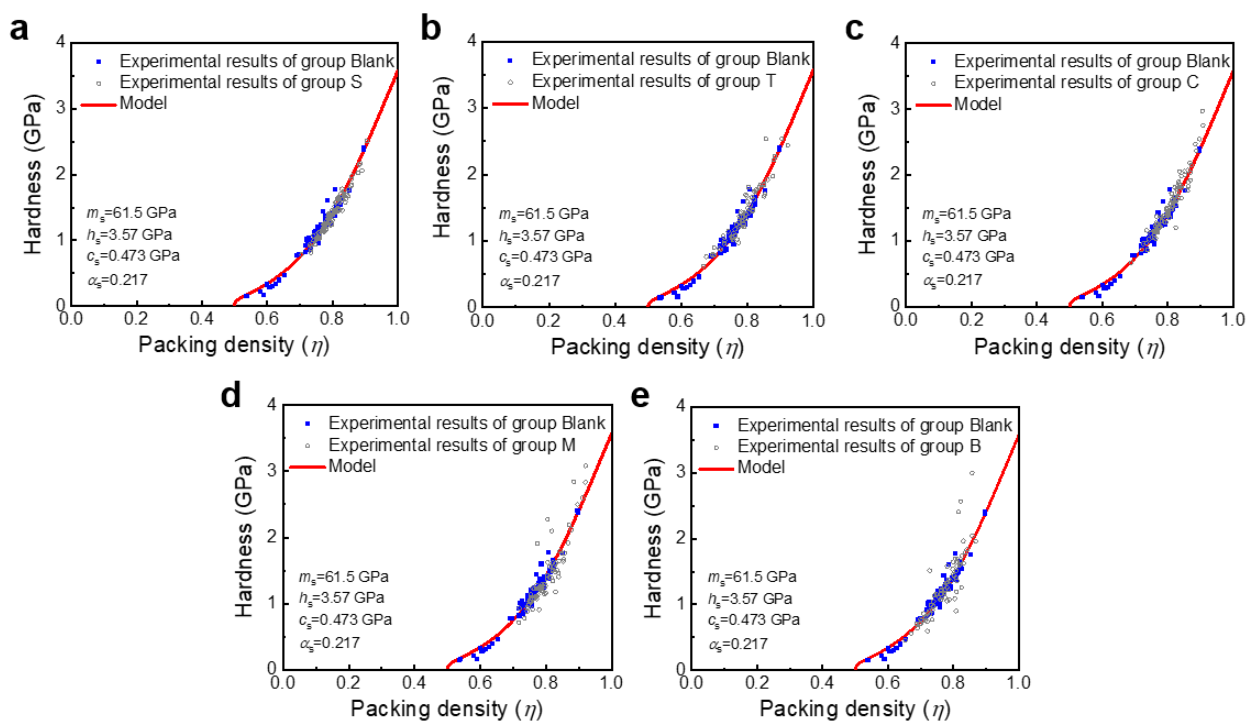


Fig. 6 Hardness-packing density. (a) Without/with nano-silica; (b) Without/with nano-titania; (c) Without/with carbon nanotubes; (d) Without/with multi-layer graphene; (e) Without/with nano boron nitride

302 3.4 Effect of nanofillers on C-S-H gels during hydration process

303 To reveal the effect of nanofillers on the hydration products, the structural evolution and product distribution were
 304 investigated based on the MD model.

305 1) Structural evolution

306 The formation of C-S-H gels is essentially the process of silica tetrahedron polymerization, i.e., forming Si-O-Si bond.
307 Therefore, the structural evolution of the system can be inferred from the variation of Si-O-Si bond number with reaction
308 time [69]. As demonstrated in Fig. 7 (a), the presence of carbon nanotube, multi-layer graphene, nano boron nitride has no
309 noticeable effect on the formation of Si-O-Si bond number, indicating these nanofillers hardly affect forming C-S-H gels.
310 Differently, adding nano-titania reduces the number of Si-O-Si bond. According to the model, the Ti atoms at the nano-
311 titania surface can polymerize with silica tetrahedron and form Ti-O-Si bond, thus reducing the number of Si-O-Si bond.

312 2) Product distribution

313 The product distribution can be quantitatively analyzed and qualitatively observed by radial distribution function (RDF)
314 and product distribution image, respectively. The RDF reflects the density of particles on the sphere with given particles
315 as the center and r as the radius, as shown in Formula (19) [58].

$$g(r) = \frac{n(r)}{\rho_0 V} \approx \frac{n(r)}{4\pi r \rho_0 \delta_r} \quad (19)$$

316 where $n(r)$ is the number of particles in the spherical shell, ρ_0 is the ideal crystal density, δ_r is the thickness of the
317 spherical shell. The RDF distributions of oxygen element in the CaO-SiO₂-H₂O post-reaction systems without/with
318 nanofillers are shown in Fig. 7 (b). Fig. 7 (b) depicted that the RDF curve of oxygen element the CaO-SiO₂-H₂O post-
319 reaction systems without nanofillers contains three peaks. The peaks appear near 0.97 Å, 1.64 Å, 2.05 Å, and 2.69 Å,
320 corresponding to the H-O, Si-O, Ti-O and Ca-O bonds, respectively. Note that the interference function between RDF
321 results and small-angle X-ray scattering test is the Fourier transform, which provides the link between experiment and MD
322 model [58]. According to previous studies [70, 71], the position of peaks obtained from MD simulation is in a good
323 agreement with that obtained from experiments, indicating that the MD simulation results in this study are valid. After
324 adding nanofillers, the positions of the peaks may slightly shift, which is attributed to the interaction between particles
325 changing the bond length between local atoms near nanofiller surface. However, the interaction does not change the type
326 of the bond, that is, nanofiller hardly affects the process of hydration.

327 In addition to RDF analysis, the product distributions are also observed by images. The product distribution images
328 display only the calcium, silicon, and nitrogen elements as well as nanofiller particles, but hide the oxygen and hydrogen
329 elements, as depicted in Figs. 7 (c)-(g). The calcium and silicon elements in the system without nanofillers, as shown in
330 Fig. 7 (c), are evenly distributed in lattice without obvious aggregation. In contrast, Figs. 7 (d)-(g) demonstrates that the
331 presence of nanofillers can adsorb silica tetrahedrons and calcium ions, leading to the aggregation of calcium and silicon
332 elements near the nanofillers. Moreover, the silica tetrahedrons tend to accumulate on the surface of nano boron nitride,
333 while the calcium ions are easier to be adsorbed on the edge of nano boron nitride. These phenomena are consistent with

334 the SEM results that indicate CH crystals tend to form and grow near the edge of nano boron nitride, as depicted in Fig. 4
 335 (e). Such a phenomenon may derive from the van der Waals force and charge force. The charge on the edge of nano boron
 336 nitride is higher than that on the surface [72]. The particles near the edge of nano boron nitride are subjected to strong
 337 charge force, so the calcium ions with opposite charges are adsorbed on the edge. The calcium ions with opposite charge
 338 near the surface are subjected to a small charge force that is not strong enough to break through the steric hindrance effect.
 339 Hence, the surface of nano boron nitride mainly adsorbs silica tetrahedrons rather than calcium ions. In actual fresh cement
 340 pastes, the solubility and diffusion rates of calcium ions are much higher than silica tetrahedrons. The adsorbed calcium
 341 ions may be more than the simulation results at the early hydration process.

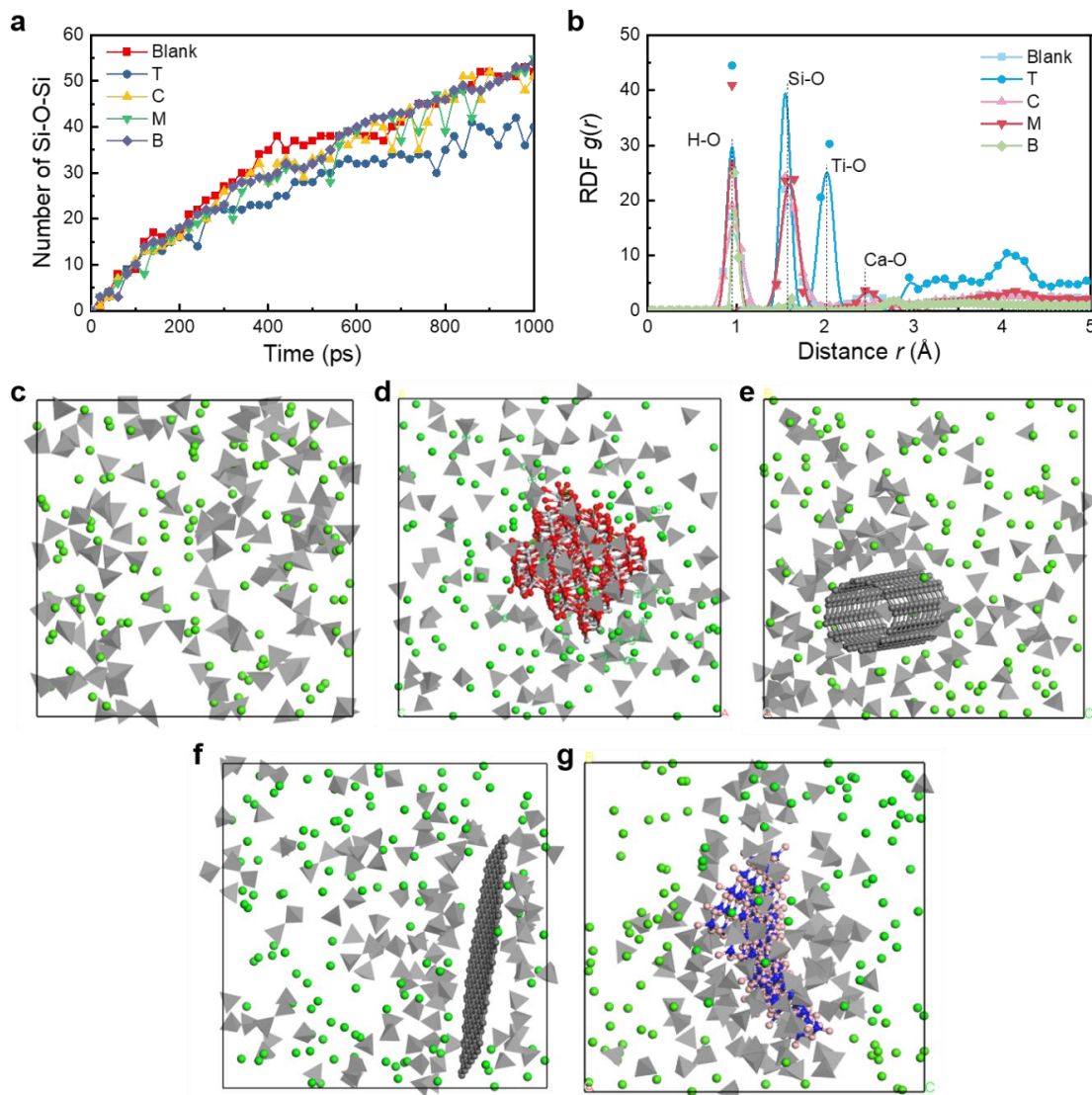


Fig. 7 Results of MD simulation. (a) Variation of Si-O-Si bond number vusus reaction time; (b) RDF distribution of oxygen element; Image of the post reaction system (c) without nanofillers, (d) With nano-titania, (e) With carbon nanotubes, (f) With multi-layer graphene and (g) With nano boron nitride

342 After early hydration of cement pastes, nanofillers together with the adsorbed calcium ions and silica tetrahedrons form
 343 numerous nano-core-shell elements, that is, nanofillers act as a nano core, and the adsorbed calcium ions and silica

344 tetrahedrons form a shell. The nano-core-shell elements can be speculated to possess superior mechanical properties due
 345 to the existence of the nano core. The influences of these phenomena on the nanoscale mechanical properties of C-S-H gels
 346 are discussed in detail in the following sections.

347 **3.5 Modification mechanisms of nanofillers on nanomechanical characteristics of C-S-H gels**

348 Combining the load-indentation depth curves with Formulas (1) and (2), the calculated M and H were listed in Table 6,
 349 in which the M and H of LD and HD C-S-H derived from micromechanics analysis are in good agreement with
 350 experimental results, confirming the validity of established DEM model.

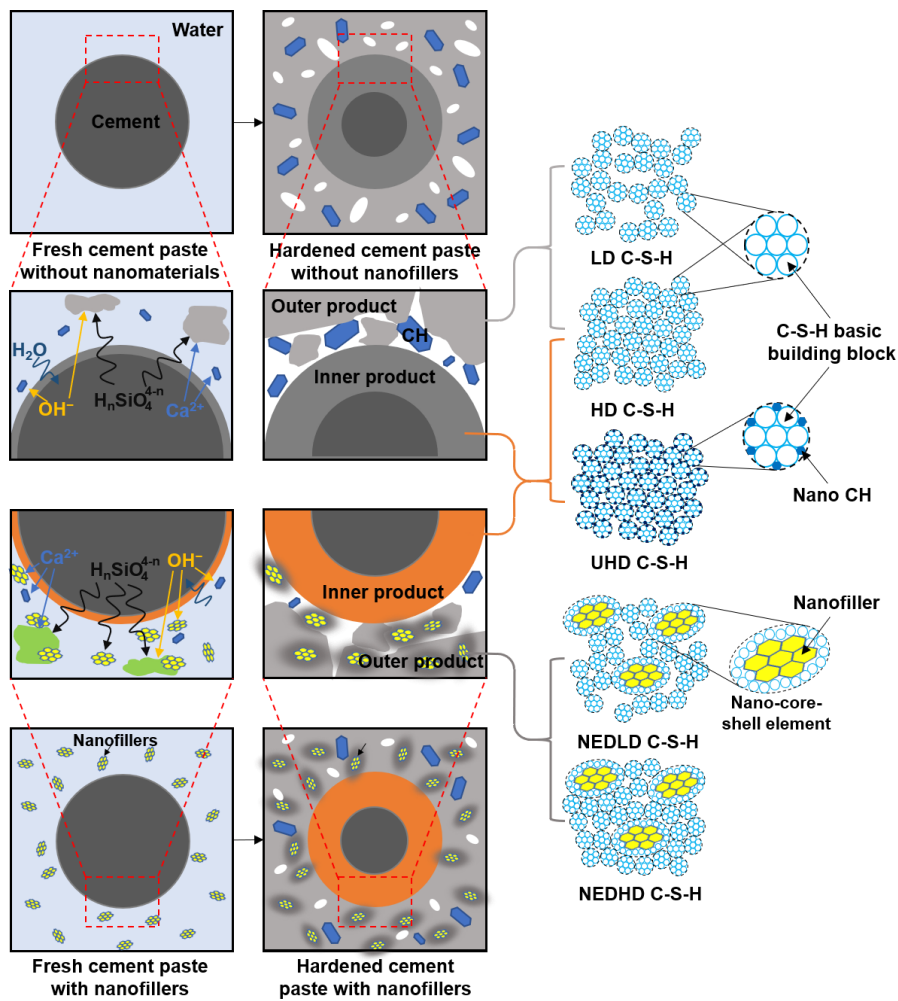
351 Unlike micromechanics analysis results, the DEM results demonstrate the packing densities of NEDLD and NEDHD C-
 352 S-H are slightly lower than those of LD and HD C-S-H. This finding indicates the improved the nanoscale mechanical
 353 properties of NEDLD and NEDHD C-S-H derives from the presence of nano-core-shell elements rather than the increase
 354 in C-S-H gels' packing density. The nano-core-shell elements replace some C-S-H building blocks, thus modifying the
 355 indentation modulus of C-S-H gels owing to their high modulus. Meanwhile, the nano-core-shell elements, together with
 356 the surrounding particles increase the C-S-H gels' integrality through the interaction between the particles, so as to increase
 357 the C-S-H gels' hardness.

358 Table 6. Comparison between simulation results and experimental/micromechanics results

Phase	Indentation modulus (GPa)		Hardness (GPa)		Packing density	
	Experimental results	DEM results	Experimental results	DEM results	Micromechanics analysis results	DEM results
LD C-S-H	19.7	21.3	0.68	0.69	0.67	0.64
LD C-S-H with nano-titania	23.0	24.4	0.74	0.80	0.69	0.64
LD C-S-H with carbon nanotubes	25.4	22.3	0.80	0.85	0.71	0.64
LD C-S-H with multi-layer graphene	23.7	18.8	0.90	0.60	0.71	0.64
LD C-S-H with nano boron nitride	22.7	29.2	0.78	0.81	0.70	0.64
HD C-S-H	30.8	29.1	1.05	1.07	0.75	0.74
HD C-S-H with nano-titania	44.4	34.9	2.00	2.18	0.86	0.74
HD C-S-H with carbon nanotubes	46.0	34.8	1.82	1.54	0.86	0.74
HD C-S-H with multi-layer graphene	46.2	36.6	2.27	2.78	0.88	0.74
HD C-S-H with nano boron nitride	46.7	52.6	2.72	3.18	0.90	0.74

359 According to the above results, Fig. 8 summarizes the underlying mechanisms of nanofillers on C-S-H gels. As
 360 demonstrated in Fig. 8, the nanofillers mainly affect the nanoscale mechanical characteristics of C-S-H gels in outer
 361 hydration products. The nanofiller particles, as demonstrated in MD simulation results, act as core sites to adsorb calcium

362 ions and silica tetrahedrons, forming numerous nano-core-shell elements during the hydration process. Such formed
 363 elements help to reduce the calcium concentration in the early hydration solution, to reduce the nucleation of CH and
 364 further limit the growth of micron CH crystals. Meanwhile, the polymerization process of silica tetrahedron is not affected.
 365 Under this condition, most of the space of outer hydration products is occupied by nanofiller particles and surrounding
 366 adsorbed C-S-H building blocks, restricting the growth space of micron CH crystals in subsequent hydration process.
 367 Therefore, the nanofillers significantly refine the C-S-H gels and turns micron CH into nano CH in outer hydration products
 368 at the late stage of hydration.



369
 370

Fig. 8 The underlying mechanisms of nanofillers on C-S-H gels

371 Moreover, NEDLD and NEDHD C-S-H possess better nanoscale mechanical properties at lower packing densities than
 372 LD and HD C-S-H as demonstrated by micromechanics analysis and DEM simulation results. This finding can explain the
 373 role of nanofillers in improving the nanomechanical properties of C-S-H gels in outer hydration products. In the case of a
 374 constant mix proportion, the volume ratio of outer hydration products is basically unchanged before or after adding low
 375 content of nanofillers. Moreover, the presence of inactive nanofillers does not significantly change the hydration degree of
 376 cement pastes [40]. Therefore, the volume of outer hydration products and substances therein change little in cement pastes

377 without or with nanofillers. Under these conditions, CH crystals formed by nanofillers adsorbed calcium ions, owing to
378 their tiny size, can participate in the accumulation of C-S-H gels like the nanoscale CH crystals in UHD C-S-H [66], thus
379 increasing the quantity of substances forming C-S-H gels in outer hydration products. Additionally, thanks to their low
380 packing density and high-performance nature, NEDLD C-S-H and NEDHD C-S-H make more outer hydration product
381 space occupied by C-S-H gels under the same amount of substances to decrease the defects and simultaneously improve
382 the mechanical performance of outer hydration products.

383 A former study proposed the concept of the nano-core effect zone that considers the action zone of nanofillers composed
384 of nanofillers themselves and adsorbed hydration products, i.e., the nano-core-shell elements [68]. Implementing this
385 concept, the action zone in cement pastes accounts for about 0.44 vol.%, assuming that 0.4 vol.% nano boron nitride is
386 added and the thickness of the shell is 2.5 nm. Such a small amount of action zone cannot explain the significant influence
387 of the tiny content of nanofillers on the overall performances of cement pastes at the macroscale. Therefore, the former
388 study only considered the short-range effect of nanofillers. The findings in the current study demonstrate that the nanofillers
389 have a long-range effect on the cement pastes at the same time. On the one hand, nanofillers, combined with adsorbed
390 hydration products, form nano-core-shell elements. Because of the existence of the hard core, the nano-core-shell elements
391 modify the nanoscale mechanical properties of hydration products in a short-range. On the other hand, nanofillers can
392 adsorb the ions in the early hydration solution, which refines and optimizes the hydration products near nanofiller particles.
393 Moreover, the nano-core-shell elements and the surrounding particles increase the integrality of C-S-H gels through the
394 interaction between the particles to increase the nanoscale mechanical properties of C-S-H gels under low packing densities.

395 The above findings have demonstrated nanofillers can modulate C-S-H gels, the major binding element in concrete,
396 through modulating their nanogranular nature. Such modulation, on the one hand, enhances the network of C-S-H basic
397 building blocks and the interaction among them, lessening the defects caused by internal volume changes (e.g. plastic,
398 autogenous, drying, and carbonation shrinkages [73,74]) or external loads (e.g. compression, tension, and flexure loads
399 [75–77]). On the other hand, the nanomodulation contributes to improve concrete durability due to the prevention of
400 harmful media corrosion through refining larger pores into smaller ones in concrete at the nanoscale [34]. The
401 aforementioned benefits lead to superior performance of nano-engineered concrete at the macroscale without increasing
402 cement content [78–80], in other words, the ideal performance of concrete can be achieved with less cement through
403 nanomodulation, thus cutting CO₂ emissions from reduced cement consumption or reducing CO₂ footprint by prolonging
404 concrete service life.

405 4 Conclusions

406 This study provides evidence that nanofillers can improve intrinsic nanoscale mechanical performances of C-S-H gels

407 of cement paste in concrete at the nanoscale. The nanofillers induce the formation of NEDLD and NEDHD C-S-H in outer
408 hydration products. The indentation modulus/hardness of NEDLD and NEDHD C-S-H reached 25.4/0.80 GPa and
409 46.7/2.72 GPa, respectively. Meanwhile, the packing densities of NEDLD and NEDHD C-S-H are slightly lower than that
410 of LD and HD C-S-H, respectively. The superior nanoscale mechanical performances of NEDLD and NEDHD C-S-H
411 derive from the formation of nano-core-shell elements rather than the increase in the packing density. In a short-range,
412 nanofillers together with adsorbed silica tetrahedrons form nano-core-shell elements during hydration of cement pastes in
413 concrete, improving the mechanical properties of C-S-H basic building blocks. In the long-range, the nano-core-shell
414 elements replace some C-S-H building blocks, thus improving the indentation modulus of C-S-H gels due to their high
415 modulus. Moreover, the nano-core-shell elements, together with the surrounding C-S-H building blocks, increase the
416 integrality of C-S-H gels through their interaction. The short-range and long-range effects proposed in this study provide a
417 fundamental understanding of the superior nanoscale mechanical performances of C-S-H gels in concrete, guiding its
418 design and applications. In addition to endowing C-S-H gels with superior mechanical properties at the nanoscale, the
419 nanomodulation of C-S-H gels is conducive to upgrading the macroscale performance of concrete (e.g. strength,
420 deformation behavior, volume stability, and harmful media resistance), on the basis of constant cement content.
421 Consequently, a nano-engineered concrete, with superior mechanical properties, excellent durability and low cement need,
422 can be developed through such nanomodulation, showing the great potential for mitigating the CO₂ footprint of concrete
423 industry by reducing cement consumption and prolonging concrete service life.

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