

Protonated portlandite precursor unlocks enhanced nucleation and growth for cement hydration

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

1. TEM (Fig. 1) shows defects, but could authors provide quantitative defect or orientation analysis?
2. Could authors provide the direct evidence on the growth model (Fig. 6) - CHP as the templates.
3. The compressive strength gains (Fig. 5d) at 8 h and 12 h (up to 29.5 MPa) are similar to the effects of C-S-H seeds, but CHP is derived from CH, suggesting seeding by fine particles rather than protonation.
4. Pore structure (Fig. 5f) suggests reduced maximum pore size, but the fractal dimension analysis (Fig. 5g) divides regions arbitrarily, could provide physical meaning for these regions?
5. ²⁹Si NMR (Fig. 5h) indicates slight hydration degree increase (51.6% to 53.3%) and mean chain length (MCL) from 3.02 to 3.65, attributed to Ca²⁺ supply, however similar effects also occur with nano-additives without protonation.

Reviewer #2

(Remarks to the Author)

This manuscript presents an interesting investigation into modulating cementitious materials properties through a mechanochemically synthesized calcium hydroxide precursor (CHP), demonstrating promising enhancements in elasticity and compressive strength. However, a thorough review reveals several fundamental concerns regarding the paper's core scientific premises, the robustness of its proposed mechanisms, and the completeness of its experimental methodology and data interpretation. Consequently, major revisions are required to address these significant issues and ensure the scientific rigor and clarity of the work.

1. The paper's emphasis on portlandite's inherent brittleness as the primary bottleneck for cement performance isn't accurately framed. Although the calcium hydroxide occupies a high mass fraction in hydrated cement (about 15 to 20%), the crystalline phase, i.e., portlandite, has a very small fraction around 6%. Therefore, portlandite is not the key player that dominates the mechanical properties of cement-based materials. Given that C-S-H is widely recognised as the main phase controlling mechanical properties and overall brittleness, it is confusing the claim of the authors. Does the title accurately reflect the work's scope in this regard? The authors must significantly revise their introduction and abstract to accurately frame the problem. They should acknowledge that C-S-H is the primary strength-giving phase and the main contributor to bulk brittleness. The morphology and distribution of CH, when improved by CHP, may enhance the overall integrity and mechanical performance of the C-S-H matrix, perhaps by eliminating local stress concentrations or improving the CH/C-S-H interface.

2. The cited references (specifically 9-11) do not truly support the claim that the nature of portlandite directly causes interlayer delamination and brittle fracture affecting the durability and mechanical properties of cement concrete. There is no direct link between the nature of portlandite and mechanical properties of cement. Ref. 11 shows that CH directly impacts the hydration of cement, which essentially modulates the C-S-H product.

3. What definitive evidence supports the claim of CHP protonation? Could the authors present the details of how they prepare the RHP and CHP samples for XRD measurement? Could the XPS signals attributed to adventitious OH of H₂O simply indicate incomplete drying or surface-adsorbed water? Is the proposed protonation of CH chemically plausible, or is

the $\text{Ca}(\text{OH})(\text{H}_2\text{O})^+$ species more accurately described as a dissolved ionic hydrate? Since CH is ground in wet condition, drying might change the crystallinity of fine CH particle or even carbonate them. Full XRD patterns should be provided.

4. The simulation component of this study aims to support the proposed protonation mechanism of CHP at an atomic level. However, the computational evidence for this claim is not sufficiently robust due to significant simplifications. Specifically, the adsorption energy calculations, which are foundational to the proposed mechanism's energetics, were performed in the gas phase. This highly unrealistic condition fundamentally neglects the profound influence of the aqueous environment, including solvation effects of water molecules and dissolved ions, and charge screening, rendering the calculated energy values and the inferred spontaneity of protonation unreliable for a real mineral-solution system. While WT-MetaD simulations do incorporate some explicit water, the inherent limitations of small, periodic simulation cells may still restrict their ability to fully capture bulk solution effects, thus providing only qualitative mechanistic insights rather than quantitatively predictive support for the specific protonation claim in the complex environment of hydrating cement.

5. Why was a control experiment comparing the effects of CHP with raw CH (or ideally, raw CH dry-ground to a similar particle size) not performed? Without such a comparison, how can the unique impact of the mechanochemical treatment (beyond particle size effects) be conclusively demonstrated? From the comparison in hydration heat and compressive strength of cement paste mixed with and without CHP, the addition of CHP indeed accelerates the growth of strength. However, it is not surprising the CHP has a seeding effect as the fine crystallite size and defective surface can lower the nucleation energy barrier of C-S-H.

6. How do the authors definitively conclude amorphization of CHP based solely on changes in FWHM and intensity from XRD, given that crystallite size reduction and lattice strain also significantly influence these parameters? Can the particle size distribution of the raw CH be provided for comparison before and after grinding? Does the particle size change with the grinding time?

7. The authors claimed in their manuscript that the addition of CHP decreases the fraction of CH whereas increases the amount of nano CH (or CH@CSH composites) based on their nanoindentation measurements. From their TG analysis, the mass content of total CH increases with the addition of CHP. Given that the indentation measurement only has 144 data points for each sample, it is not feasible enough for the statistical analysis. To increase the feasibility, the authors can do two things: 1) increase the indentation points on a larger area; 2) perform quantitative XRD analysis to show the fraction of each phase in the hydrated cement paste. In addition, the authors should also present their original histogram data of the indentation measurements and show the accuracy of the deconvolution of the PDFs. From the eyes, for the current results in Fig. 4e and f, it is doubtful to obtain the theoretical PDFs from accumulating the decomposed functions. Regarding those points have a elastic modulus larger than 80 GPa, they can be calcium carbonate as well.

8. To what extent do the observed changes in zeta potential, conductivity, and OH^- concentration genuinely indicate unique protonation of CHP, as opposed to simply accelerated dissolution due to smaller particle size and increased defect density? The dissolution of Ca could lead to the formation of ionic hydrates, which is a well-known common phenomenon of CH. It is not a unique phenomenon for CHP only. The reason for this can be that the CHP has smaller particle size (supporting data is needed) and more defective surface than raw CH, which can accelerate the dissolution of portlandite. There is nothing to do the protonation.

9. Can more explicit details be provided regarding the drying process for CHP and RCH samples for XRD, XPS, and TG, and what specific precautions were taken to prevent carbonation, given the high susceptibility of fine, wet CH to carbonation?

10. What is the detailed chemical composition of the Portland cement used in this study?

11. Can convergence analysis results and explicit details of the production runs be provided for the WT-MetaD simulations?

12. Could "silica" on Line 255 be corrected to "silicate" for accuracy?

13. Fig. S5, the captions are not consistent with the labels.

Reviewer #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #4

(Remarks to the Author)

The manuscript presents a combined experimental and computational investigation of an enhanced calcium hydroxide precursor (CHP) with protonated and disordered structure, assuming that CH is uniformly grown along the different crystal phases of CHP. The effect of CHP on the nucleation, the growth and the distribution of CH in C-S-H gel is also considered. The topic is relevant and of interest to researchers in cement chemistry and materials science. The work is well conducted and the results are generally sound. However, the quality of the writing requires revision. Several sections would benefit

from improved clarity, grammar, and style to enhance readability and precision. While the results are solid and contribute to the understanding of CHP behavior, their novelty and broader impact fall short of the high threshold expected for Nature Communications. The reviewer encourages the authors to consider submitting their work to more domain-specific journals, such as:

- Cement and Concrete Research
- Construction and Building Materials

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed the comments.

Reviewer #2

(Remarks to the Author)

Recommendation: Major Revision

The authors are thanked for the extensive additional work and revisions provided in this round. However, while the volume of data has increased, several critical scientific issues remain unresolved, and in some cases, the new data reveals further contradictions. The manuscript continues to overstate its findings, and the proposed mechanisms remain largely speculative without direct evidence to support the main conclusions.

1. Framing and Scope (Title and Abstract)

The title and central claims regarding "modulating growth dynamics" remain an overstatement of the actual study content. The manuscript does not provide explicit results or investigations into the actual growth process of CH and C-S-H; rather, it demonstrates that early-stage hydration kinetics are accelerated by the addition of ground CH. Furthermore, the "hydrogen-bond-regulated proton transfer" described is a precursor preparation process and should not be confused with the hydration dynamics themselves. The authors must reframe the title and discussion to accurately reflect that this is a study of hydration kinetics and early-age acceleration.

2. Mechanical Premises and Brittleness

The assertion that "CH acts as the main contributor to the bulk brittleness of cementitious materials" is scientifically inaccurate and misleading. Brittleness is a systemic property arising from the brittle nature of the hydrated paste, microcracking, stress concentrations, and the heterogeneous nature of the composite (C-S-H, CH, pores, and clinkers). Additionally, the authors propose modulating growth to overcome this "dilemma," yet they provide no direct evidence of increased toughness or enhanced interlayer bonding strength after the addition of CHP.

3. Characterization and Phase Identification (SEM)

The phase identification in Fig. 7 is highly questionable. The morphologies shown in panels (l), (m), and (n) exhibit thin plates, flakes, and rod-like structures typical of AFm and AFt phases, rather than CH. Given that much of the mechanistic discussion in the "Growth habits" section relies on these images, this misidentification undermines the paper's conclusions. Furthermore, the use of N₂ gas injection to preserve pores for SEM observation (Lines 463-469) likely creates artificial conditions that do not reflect actual CH formation in bulk cement hydration.

4. Scientific Contradictions and Data Inconsistency

There is a serious inconsistency between the nanoindentation results and the bulk mineralogical data. Comparison of the CH content derived from nanoindentation deconvolution (Fig. 7 and Supp. Fig. 21) with QXRD (Fig. 6c) and TGA (Supp. Fig. 17) reveals contradictory results. Even when accounting for UHD C-S-H as a composite, the fractions do not align. TGA is generally considered more reliable for phase quantification, and Supp. Fig. 17 shows that total CH content (including any potential "CH@C-S-H") does not differ significantly across samples, which directly contradicts the nanoindentation interpretations.

5. Silicate Chain Modeling

In Fig. 6i, the illustrations of (alumino) silicate chains are incorrect. Silicate chain lengths must follow the 3n-1 rule; therefore, 3-unit or 4-unit chains are not scientifically plausible in this context. These illustrations must be corrected to reflect established silicate chemistry.

6. Mechanism: Protonation vs. Adsorption

The results in Fig. 4 appear to demonstrate the adsorption of water molecules on a defective surface (CHP_OHv) rather than a unique protonation process. If a wet-grinding-induced protonation were truly present, the authors should have performed the same tests on CHP_H+; theoretically, a truly protonated surface should exhibit less water adsorption compared to the defective CHP_OHv. The "super-nucleation effect" also requires a precise definition. Furthermore, the fact that all CHP variants result in similar 28-day strengths suggests the effect is driven by the addition of CH itself, rather than the specific grinding conditions or protonation.

7. Methodological Clarifications

- Provide detailed preparation procedures for CH_Raw and CHP_Perf, including how particle size was controlled.
- Specify the CHP/water ratio used for ultrasonic dispersion and the criteria for selecting nanoindentation regions.
- Clarify the age of the samples in Fig. 7 (12 hours or 28 days).

Reviewer #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #4

(Remarks to the Author)

The authors make a significant and deeply revision of the paper. Therefore, I accept the publication of the paper in the present form.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors make a significant revision of the paper. Therefore, I accept the publication of the paper in the present form.

Reviewer #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

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RESPONSE TO REVIEWERS' COMMENTS

Dear Editor and Reviewers:

We are deeply grateful to the Editor and Reviewers for their valuable and constructive comments and suggestions, as well as your positive comments on this work and tolerance of shortcomings. We have studied each comment and suggestion carefully and have incorporated them as suggested. We sincerely hope that the revised manuscript can meet your expectations, and if there are any shortcomings, we hope to receive your guidance and help again. Thank you again!

Contents

Reviewer #1: P1~P11

Reviewer #2 and 3: P11~P47

Reviewer #4: P47-50

Blue text indicates responses to questions.

Red text indicates revisions in the manuscript.

Reviewer #1:

1. TEM (Fig. 1) shows defects, but could authors provide quantitative defect or orientation analysis?

Reply: Thanks for your suggestions. For “quantitative defect”, we supplemented with EPR tests, as shown in Fig.2 f. For “orientation analysis”, we supplemented with additional TEM tests and conducted further analysis in the manuscript, as shown in Fig. 1 and Supplementary Fig. 2. Notably, based on your suggestions in Questions 3 and 5, we have added two additional control groups: CHP_Perf. (chemically synthesized) and CHP_OH_v (dry grinding), both with average particle sizes similar to protonated CHP_H⁺ (wet grinding).

(1) Due to the strong metallic valence state (i.e., Ca) of CH, it interferes with vacancy monitoring, preventing quantitative fitting after multiple measurements. Therefore, we can only qualitatively compare the defect severity among the four types of CH. Detailed revisions are as follows:

Page 5, line 132-136:

As shown in Fig. 2 f, electron paramagnetic resonance (EPR) spectra reveal that the defect concentration of CHP_H^+ is markedly lower than that of CHP_OH_v but higher than that of CH_Raw and CHP_Perf ³². This observation implies that the oxygen vacancies generated during water-medium ball grinding are healed after protonation.

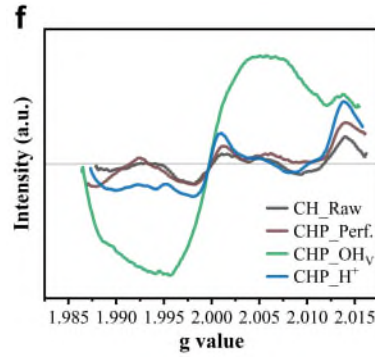


Fig. 2 f EPR spectra of 4 types of CH.

(2) On the other hand, we supplemented a large number of TEM images to conduct a detailed analysis of the lattice orientation of the four types of CH. Detailed revisions are as follows:

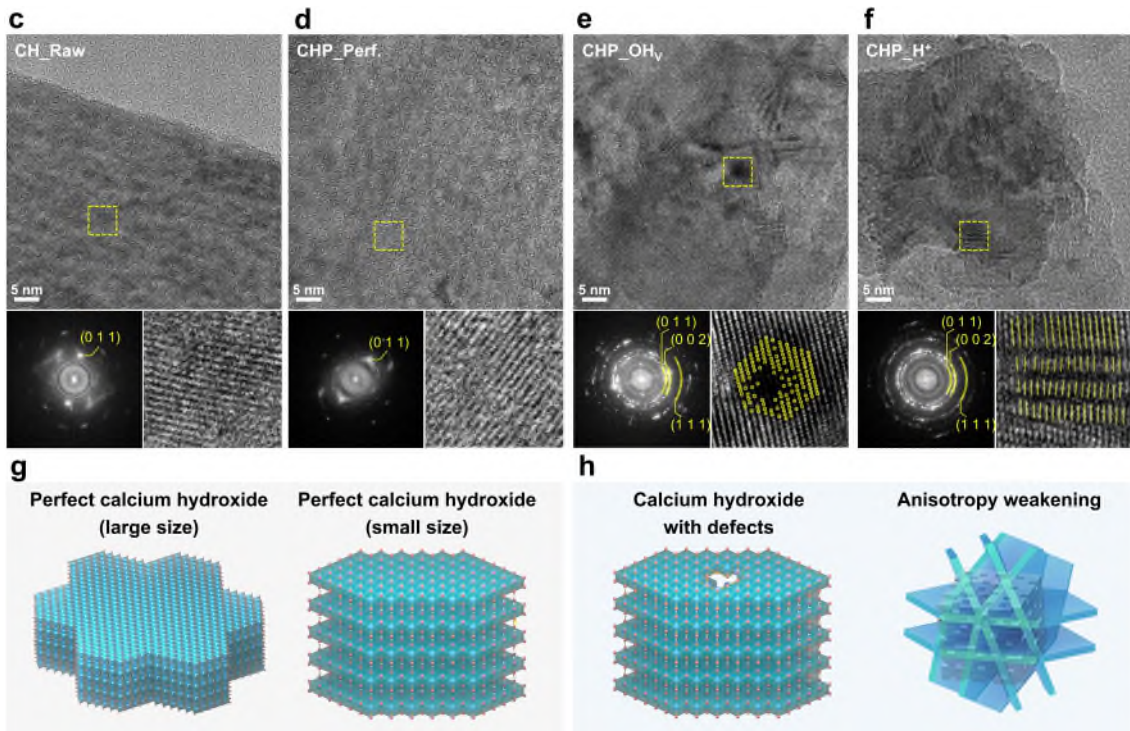
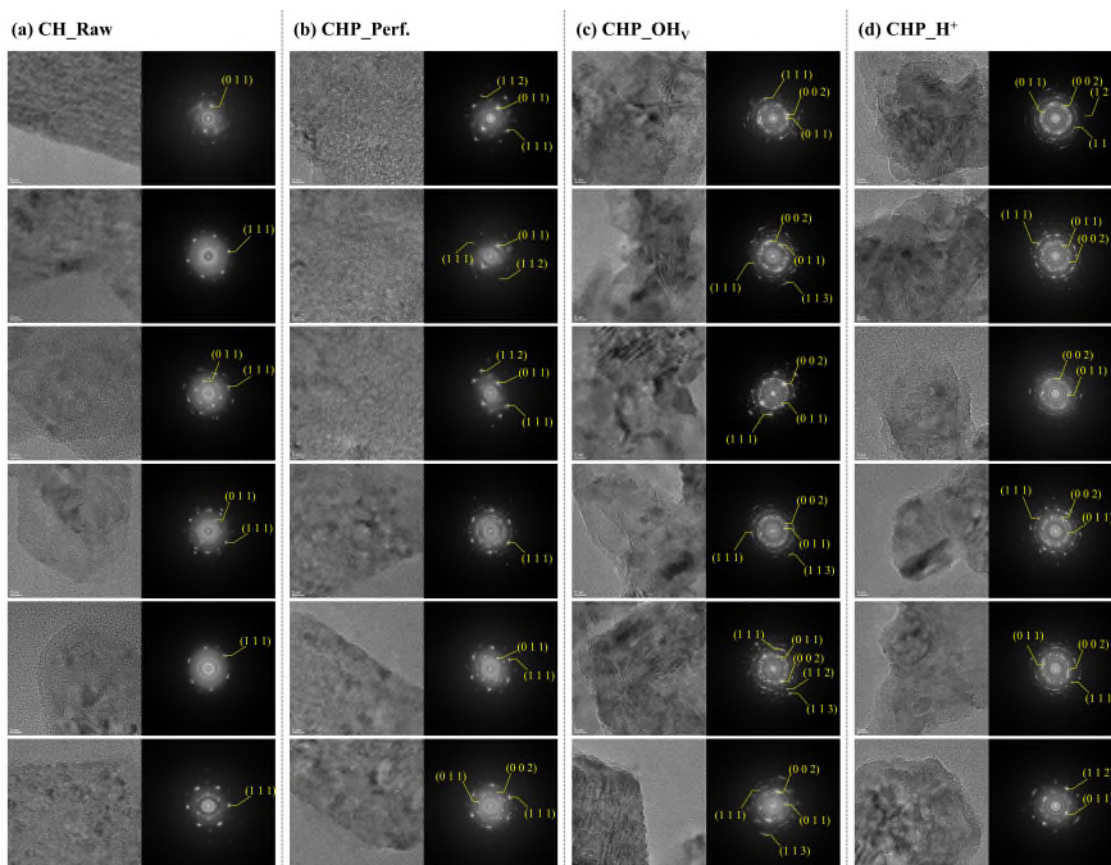


Fig. 1: **c-f** HRTEM images (top), FFT patterns (bottom left), and magnified local regions within yellow boxes (bottom right) for CH_Raw (c), CHP_Perf. (d), CHP_OH_v (e), and CHP_H^+ (f). **g** Perfect crystal structure of CH in different sizes. **h** Crystal structures of CH with defects and of CH with different crystal planes.



2. Could authors provide the direct evidence on the growth model (Fig. 6) - CHP as the templates.

Reply: Thanks for your comments. Systematically elucidating the template effect of CHP, particularly proving the heterogeneous nucleation of $[\text{SiO}_4]^{4-}$, not only enhances the scientific rigor and credibility of this study's conclusions but also expands its universal value and application prospects across multidisciplinary fields. We demonstrated this effect through a combination of simulation and experimental approaches, as shown in Fig. 5.

(1) Simulation section: We systematically refined and supplemented the simulation work, as detailed in Fig. 6 a-c. The focus was on the influence of solvation effects on the adsorption process. Detailed revisions are as follows:

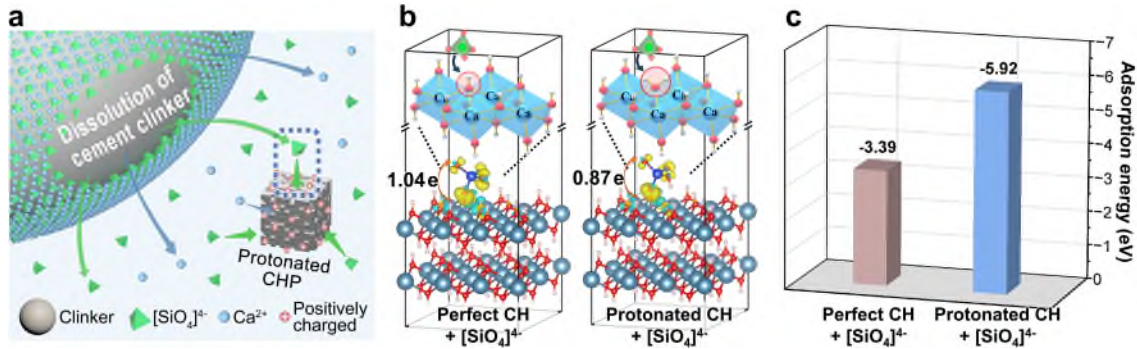


Fig. 5: **a** The schematic diagram of nucleation effect of protonated CHP. **b** Atomic models of $[\text{SiO}_4]^{4-}$ adsorption on perfect CH surfaces and protonated CH surfaces, and the corresponding charge transfer. **c** Adsorption energy of $[\text{SiO}_4]^{4-}$ on the surfaces of perfect CH and protonated CH.

Page 13, line 326-331:

Atomic models of $[\text{SiO}_4]^{4-}$ adsorption on the surfaces of perfect CH and protonated CH were established. As shown in Fig. 5 b, $[\text{SiO}_4]^{4-}$ tends to form ionic bonds on the CH surface, while on the protonated CH surface, it tends to form covalent bonds that are more stable. As shown in Fig. 5 c, the adsorption energy of $[\text{SiO}_4]^{4-}$ on the protonated CH surface reaches -5.92 eV, which is 1.75 times that of $[\text{SiO}_4]^{4-}$ on the CH surface (-3.39 eV). The results indicate that protonation enhances the affinity of CH towards $[\text{SiO}_4]^{4-}$, providing theoretical support for the super-nucleation effect.

(2) Experimental section: We extracted pore solution from fresh cement paste, which is rich in $[\text{SiO}_4]^{4-}$. And we investigated the C-S-H gel content and Si content on

the surface of three types of CHP in CPS, as well as the change in Si content in CPS before and after adding CHP. The results indicate that protonated CHP_H^+ exhibits stronger adsorption of Si and can act as a template to induce the formation of C-S-H gel. Detailed revisions are as follows:

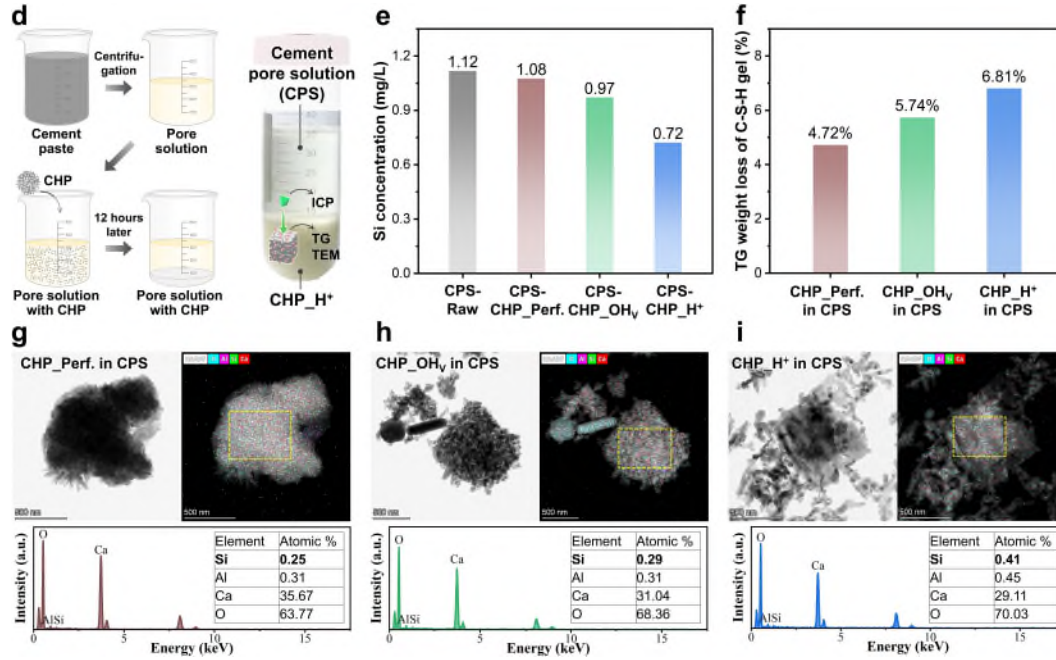


Fig. 5: **d** Experimental approach to verify the super-nucleation effect of protonated CHP. The mass ratio of CHP to the CPS is 1:200. **e** Si concentration in the pore solution after 12 hours with the addition of 3 types of CHP. **f** Thermal weight loss of C-S-H gel from 3 types of CHP in the pore solution after 12 hours. **g-i** TEM images of CHP_Perf. (g), CHP_OH_v (h), and CHP_H⁺ (i) in CPS. The HAADF-STEM image lies in the upper left corner, the EDS elemental mapping image in the lower right corner, and the atomic compositions are listed below.

Page 14, line 332-350:

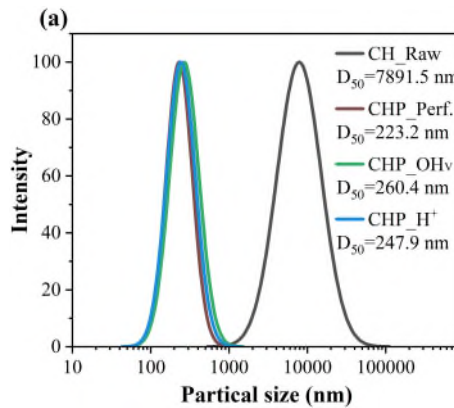
A series of comparative experiments was conducted to further validate the adsorption advantage of protonated CH towards $[\text{SiO}_4]^{4-}$. As shown in Fig. 5 d, three types of CHP were individually introduced into the extracted cement pore solution (CPS), and changes in Si content within both CPS and CHP were measured after 12 hours standing. As shown in Fig. 5 e, the addition of CHP_H^+ reduced the Si concentration in CPS by 35.7%, which was much higher than the effects observed in CHP_Perf. (3.6%) and CHP_OH_v (13.4%). As shown in Fig. 5 f and Supplementary Fig. 14, CHP_H^+ induces greater C-S-H gel formation in CPS, with the TG weight loss of

the C-S-H gel reaching 6.81%, which was much higher than that of CHP_Perf. (4.72%) and CHP_OH_v (5.74%). The microstructure and atomic content of CHP_Perf. (Fig. 5 g), CHP_OH_v (Fig. 5 h), and CHP_H⁺ (Fig. 5 i) after standing in CPS were investigated by TEM-EDS analysis. A substantial amount of gel adheres to the surface of CHP_H⁺, with Si content of 0.41%. In contrast, the gel content adhering to the surfaces of CHP_Perf. and CHP_OH_v is lower, with Si contents of 0.25% and 0.29%, respectively. Furthermore, consistent with the trend observed in Fig. 2 a, CHP_H⁺ maintained prolonged dispersion without rapid sedimentation in the CPS (Supplementary Fig. 15), which was favorable for the nucleation and growth of C-S-H gel on the CHP_H⁺ surface. The results indicate that protonated CHP can effectively captures [SiO₄]⁴⁻ and induces the formation of C-S-H gel, indicating its potential as a super nucleation promoter.

3. The compressive strength gains (Fig. 5d) at 8 h and 12 h (up to 29.5 MPa) are similar to the effects of C-S-H seeds, but CHP is derived from CH, suggesting seeding by fine particles rather than protonation.

Reply: Thanks for your suggestions. Indeed, previous experiments failed to exclude the influence of nucleation effects from CH itself, which could mislead readers.

(1) To address your concerns, we have added two control groups: chemically synthesized CH (CHP_Perf.) and dry grinding CH (CHP_OH_v). As shown in Supplementary Fig. 1, the average particle size (D₅₀) of protonated CHP_H⁺ is 247.9 nm, which is comparable to the average particle sizes of CHP_Perf. (D₅₀ = 223.2 nm) and CHP_OH_v (D₅₀ = 260.4 nm). The dosage of each type of CHP is 5 wt% by mass of cement. All types of CHP are first mixed with the water required for cement and ultrasonically dispersed for 10 min.



Supplementary Fig. 1. (a) Particle size distribution and median particle (D₅₀) for

CH_Raw, CHP_Perf., CHP_OH_v and CHP_H⁺.

(2) We discarded the previous data and re-conducted tests on compressive strength, hydration heat, XRD, TG, etc. In the latest data, we ensured that all four cement paste groups were tested simultaneously under identical conditions. The results indicate that the hydration heat release rate, early compressive strength, and early hydration product content of the cement paste with CHP_H⁺ were significantly higher than those of the CHP_Perf. and CHP_OH_v groups. Detailed revisions are as follows:

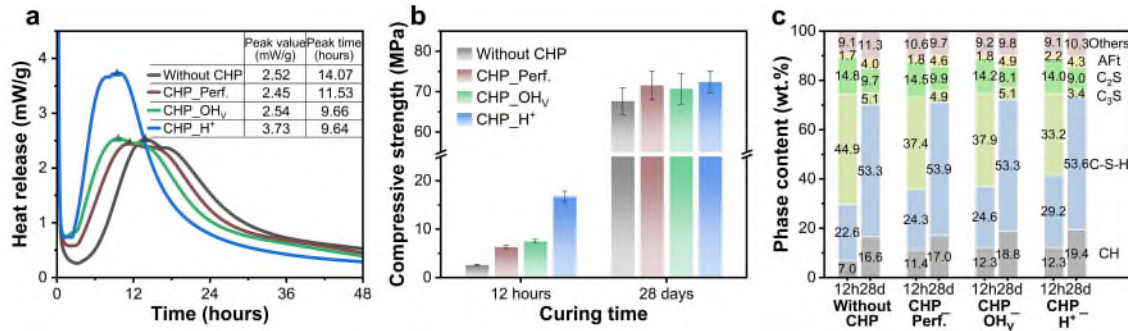
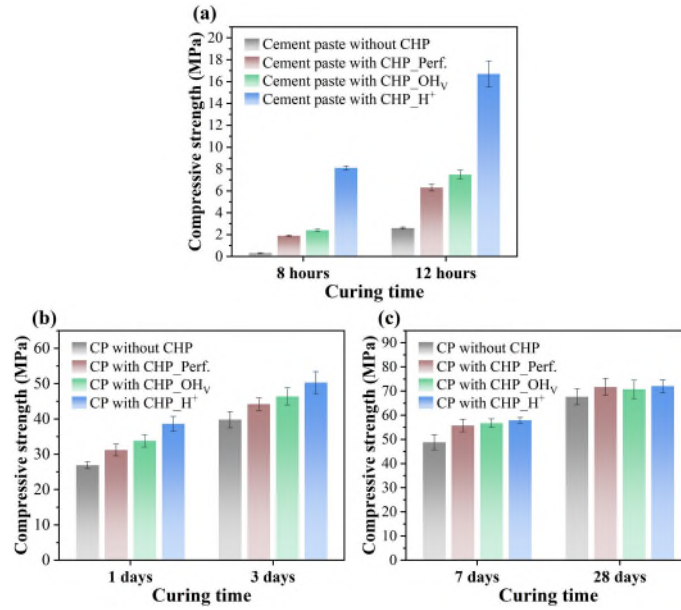


Fig. 6: **a** Hydration heat of cement pastes. The upper right corner shows the peak heat release and the corresponding time. **b** Compressive strength of cement pastes at 12 hours and 28 days. **c** The phase composition of cement pastes at 12 hours and 28 days.

Page 16, line 365-379:

The hydration heat release results are shown in Fig. 6 a. CHP_H⁺ had an accelerating effect on the cement hydration, with the value of the main hydration peak increasing by 48.0%, 52.2%, and 46.9% compared to the groups of without CHP, with CHP_Perf., and with CHP_OH_v, respectively. The time of main hydration peak of the CHP_H⁺ group was the shortest, reduced by 31.5% compared to the group without CHP. The compressive strength results are shown in Fig. 6 b and Supplementary Fig. 16. CHP_H⁺ has an excellent effect on improving the compressive strength, CHP_H⁺ exhibits excellent performance in enhancing compressive strength, and its 12-hour strength reaches 16.7 MPa, which is much higher than that of CHP_Perf. (6.3 MPa) and CHP_OH_v (7.5 MPa). Based on quantitative TG (Supplementary Fig. 17) and XRD (Supplementary Fig. 18) results, the phase composition of the samples at 12 hours and 28 days was quantified, as shown in Fig. 6 c. During the early hydration stage (12 hours), CHP_H⁺ can accelerate the hydration reaction of C₃S and induce the formation of more C-S-H gel. In the later hydration stages (28 days), the phase composition of the hydration products in all samples is similar except for CH content.



Supplementary Fig. 16. Compressive strength of cement pastes at different curing ages. (a) 8 hours and 12 hours. (b) 1 day and 3 days. (c) 7 days and 28 days.

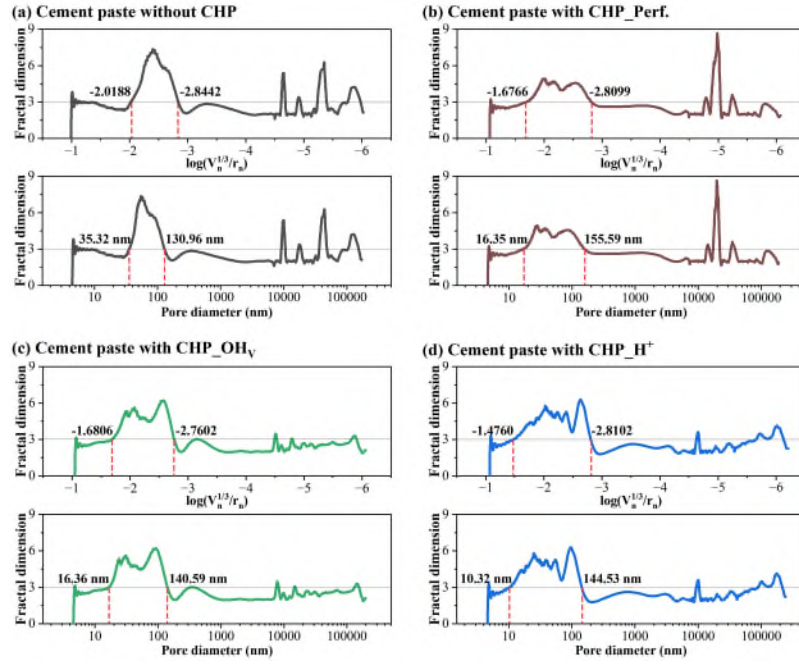
4. Pore structure (Fig. 5f) suggests reduced maximum pore size, but the fractal dimension analysis (Fig. 5g) divides regions arbitrarily, could provide physical meaning for these regions?

Reply: Thanks for your comments. Based on your suggestion, we have provided a scientific method for dividing fractal regions. We have also supplemented the physical meaning of these regions and their corresponding fractal dimensions. Additionally, similar to Question 3, we have added two extra control groups to exclude the influence of the nano-micro filling effect of CHP_H^+ on fractal dimension and fractal regions.

(1) The estimation of the fractal dimension on an average stand (with only one linear regression) may lead to erroneous result. The data in Fig. 6 e was differentiated to the first order, and $D = 3$ was used as the boundary for dividing different fractal regions, as shown in Supplementary Fig. 26. The Region II turns out to be a transition region and no clear fractal property is found for the internal pore surface. Finally, the original horizontal coordinate was replaced with pore diameter to obtain the values at the boundary.

Page 26-27, line 631-633:

The data in Fig. 6 e was differentiated to the first order, and $D = 3$ was used as the boundary for dividing different fractal regions, as shown in Supplementary Fig. 26.



Supplementary Fig. 26. Relationship between fractal dimension and $\log(V_n^{1/3} r_n^{-1})$, and relationship between fractal dimension and pore diameter of cement pastes at 28 days. (a) Cement paste without CHP. (b) Cement paste with CHP_Perf. (c) Cement paste with CHP_OH_v. (d) Cement paste with CHP_H⁺.

(2) Based on relevant literature, we have supplemented the physical meaning of each region in cement paste. Detailed revisions are as follows:

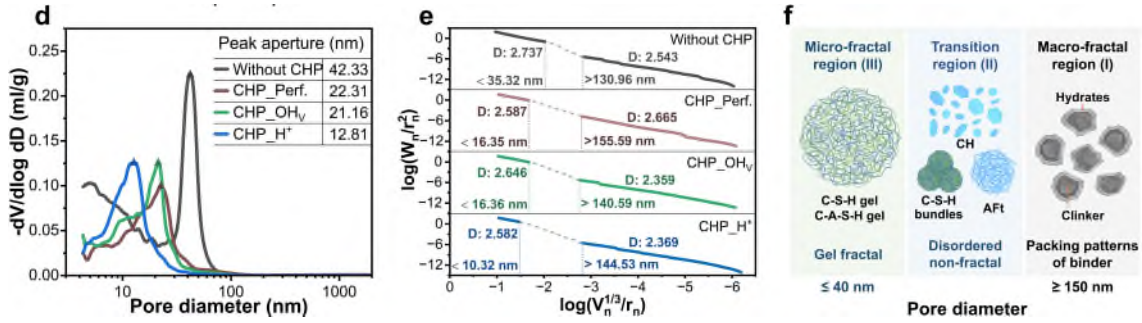


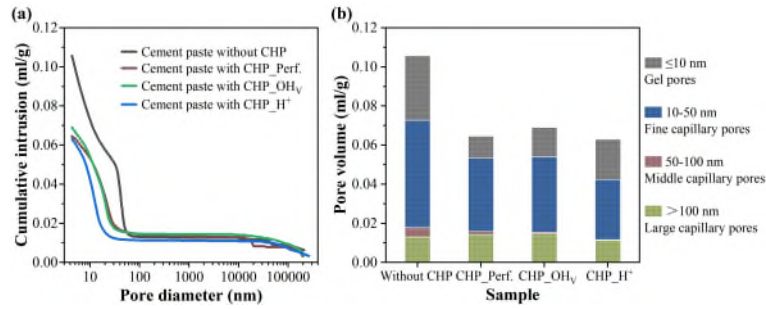
Fig. 6: d Pore structure of cement pastes at 28 days. e Pore surface fractal dimensions of cement pastes at 28 days. f The primary phases corresponding to different fractal regions.

Page 17, line 398-407:

As shown in Fig. 6 e, the pore structure shows two fractal regions with well-defined D value, separated by a transition region without clear fractal property. Research indicates that Region I, the macroscopic fractal region, represents the accumulation form of cement particles. Region II, the transition region, is more related to the random space left between C-S-H bundles and other larger hydrates, such as CH

and AFt⁴¹. Region III, the microscopic fractal region, reflects the microstructure of C-S-H hydrates. Fig. 6 f shows the primary phases corresponding to different fractal regions. Overall, compared to CHP_Perf. and CHP_OH_v, the Region II range of CHP_H⁺ extends toward lower pore sizes, which indicates an increased content of structurally complex CH and C-S-H bundles. This implies that the stacking patterns and microstructure of the hydration products have undergone alterations, which will be further verified in Fig. 7.

(3) We measured the MIP of four sample groups under identical conditions. Results indicate that the pore sizes in the cement paste containing CHP_H⁺ were smaller than those in the CHP_Perf. and CHP_OH_v groups. This indirectly proves that CHP_H⁺ serves as a template to form a more compact CH@C-S-H structure. Detailed revisions are as follows:



Supplementary Fig. 19. (a) Cumulative mercury exposure curve of cement pastes at 28 days. (b) Pore volume distribution of cement pastes at 28 days.

Page 16, line 384-392:

The pore structure of the samples at 28 days was explored as shown in Fig. 6 d. The pore size can be divided into 4 ranges as shown in Supplementary Fig. 19³⁹. All three types of CHP can effectively decrease the porosity of cement paste and refine its pore size distribution, an improvement that is primarily attributed to the nano-micron scale filling effect of the precursor particles. However, the most possible aperture of the CHP_H⁺ group is only 12.81 nm, much lower than that of CHP_Perf. (22.31 nm) and CHP_OH_v (21.16 nm). This indicates that CHP_H⁺ not only acts as a physical filler but also induces the heterogeneous nucleation and dense growth of C-S-H gel on its surface via the super-nucleation effect, which aligns with the results in Fig. 5.

5. ²⁹Si NMR (Fig. 5h) indicates slight hydration degree increase (51.6% to 53.3%) and mean chain length (MCL) from 3.02 to 3.65, attributed to Ca²⁺ supply,

however similar effects also occur with nano-additives without protonation.

Reply: Thanks for your suggestions. Indeed, the additional Ca^{2+} supply from CHP_H^+ would interfere with the assessment of the protonation effect. Consistent with the solutions for Questions 3 and 4, we have provided two control groups: CHP_Perf. and CHP_OH_v . As well, we ensured that all four sets of cement slurries were tested simultaneously under identical conditions. This demonstrates once again the unique nucleation induction effect of protonated CHP_H^+ . Detailed revisions are as follows:

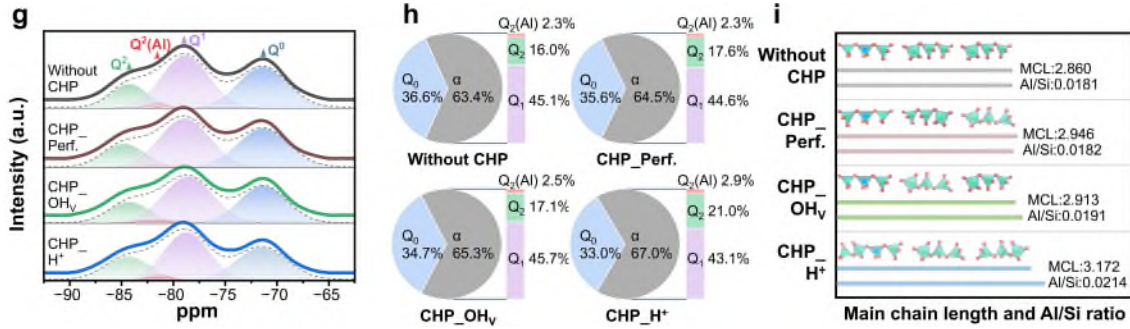


Fig. 6: **g** ^{29}Si NMR spectrum of cement pastes at 28 days. **h** The proportion of each coordination environment Si (Q_n , $n=1-2$) after deconvolution of the ^{29}Si NMR spectrum. **i** The main chain length and Al/Si ratio of cement pastes.

Page 17, line 415-423:

The addition of all three types of CHP enhanced α and MCL compared to the group without CHP, which involved multiple mechanisms such as solubilization and nucleation. CHP efficiently supplies Ca^{2+} and forms bridging during silicate polymerization, thereby promoting the formation of long-chain C-S-H gel¹³. Compared with other groups, the addition of CHP_H^+ had no significant effect on α (2.60%-5.68% increase), but it significantly affected Q^2 (19.32%-31.25% increase). Under similar α values, CHP_H^+ induced a larger MCL compared to group without CHP, increasing by 10.91%, which was much higher than that of CHP_Perf. (3.01%) and CHP_OH_v (1.85%).

Reviewer #2:

This manuscript presents an interesting investigation into modulating cementitious materials properties through a mechanochemically synthesized calcium hydroxide precursor (CHP), demonstrating promising enhancements in elasticity and

compressive strength. However, a thorough review reveals several fundamental concerns regarding the paper's core scientific premises, the robustness of its proposed mechanisms, and the completeness of its experimental methodology and data interpretation. Consequently, major revisions are required to address these significant issues and ensure the scientific rigor and clarity of the work.

Reply: Thank you very much for your comments and professional advice. These opinions help to improve scientific rigor and clarity of the work. Based on your suggestion and request, we have made corrected modifications on the revised manuscript. We also appreciate your clear and detailed feedback and hope that the explanation has fully addressed all of your concerns. Note: **blue text** indicates responses to questions, and the **red text** indicates revisions in the manuscript.

1. **(1)** The paper's emphasis on portlandite's inherent brittleness as the primary bottleneck for cement performance isn't accurately framed. Although the calcium hydroxide occupies a high mass fraction in hydrated cement (about 15 to 20%), the crystalline phase, i.e., portlandite, has a very small fraction around 6%. Therefore, portlandite is not the key player that dominates the mechanical properties of cement-based materials. Given that C-S-H is widely recognised as the main phase controlling mechanical properties and overall brittleness, it is confusing the claim of the authors. **(2)** Does the title accurately reflect the work's scope in this regard? The authors must significantly revise their introduction and abstract to accurately frame the problem. They should acknowledge that C-S-H is the primary strength-giving phase and the main contributor to bulk brittleness. The morphology and distribution of CH, when improved by CHP, may enhance the overall integrity and mechanical performance of the C-S-H matrix, perhaps by eliminating local stress concentrations or improving the CH/C-S-H interface.

Reply: Thanks for your suggestions. Q1 is divided into **2 parts** for detailed response.

Response to Part (1):

Indeed, we have overemphasized CH. We originally intended to illustrate that overcoming the intrinsic brittleness of CH is one of the important factors for enhancing the performance of cement-based materials, rather than to define it as the sole decisive factor. As you stated, "Given that C-S-H is widely recognised as the main phase controlling mechanical properties and overall brittleness". In other words, CH is often

considered a secondary phase with inferior properties compared to C-S-H. The focus of this paper is on the regulation of C-S-H and CH through protonated CH, yet the Abstract and Introduction insufficiently highlight C-S-H. Based on your suggestions, we acknowledge and emphasize the importance of C-S-H. In the revision, we avoided using absolute terms such as “primary bottleneck” and “dominant”. Nevertheless, based on the latest literature, we still regard CH as one of the critical phases determining the properties of cementitious materials. Specifically, C-S-H and CH, as the primary amorphous and crystalline phases of cement hydration products respectively, determine the properties of cementitious materials.

Additionally, regarding the content of the CH crystal phase, we have re-examined the literature, as shown in Table Q1. A review of the literature indicates that in the fully hydrated products of ordinary Portland cement, CH predominates as a crystalline phase (Portlandite), accounting for approximately 15-25% by mass or 20-30% by volume. CH is the most abundant crystalline phase product, consistent with the quantitative XRD results (Fig. 6 c and Fig. 18) presented in this paper. Therefore, we still maintain that the influence of CH on the properties of cementitious materials cannot be neglected.

Table Q1:

Corresponding content	Ref.
Although the existence of amorphous or microcrystalline CH in C-S-H seems established, the vast majority of this phase in cementitious systems occurs in the form of micrometer-sized crystals.	1.
Fig. 5 shows the amount of calcium hydroxide measured by four different methods: (1) XRD/Rietveld, (2) BSE/IA, (3) TGA, and (4) mass balance calculation, from the amounts of the anhydrous silicate phases reacted, measured by XRD/Rietveld.	2.
Calcium hydroxide, with the mineral name portlandite, constitutes about 27% of the volume in mature portland cement pastes and can participate in numerous beneficial or deleterious processes throughout concrete’s service life.	3.
This method leads to a portlandite mass content of 24.4±2.3%.	4.
Experiments were conducted to determine the portlandite mass content in hydrated	

C₃S pastes. According to the literature, values vary from 25% [9],[10] up to 35% [11],[12],[13].

References

1. Gallucci E, et al. *Cement and Concrete Research*, 2007, 37(4): 492-501.
2. Scrivener K L, et al. *Cement and Concrete Research*, 2004, 34(9): 1541-1547.
3. Han Y, et al. *Chemical Engineering Journal*, 2025, 515: 162484.
4. Henocq P, et al. *Cement and Concrete Research*, 2012, 42(2): 321-326.

Response to Part (2):

The title of this paper accurately reflects the scope of the research (i.e., C-S-H and CH), as demonstrated in the sections “Super-nucleation effect of protonated CHP” and “Growth habits of CH and C-S-H regulated by protonated CHP” within the Results. We acknowledge that the discussion of C-S-H in the Introduction and Abstract was insufficient. We have supplemented this to recognize the significance of C-S-H. Furthermore, regarding your insight that CHP improves the morphology and distribution of CH, we find it entirely correct and highly insightful. Consequently, we have appropriately modified and incorporated it into the manuscript. Detailed revisions are as follows:

Abstract

Page 1, line 4-9:

Calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) are the dominant hydration products of Portland cement; among them, C-S-H constitutes the primary strength-giving phase, while CH acts as the main contributor to the bulk brittleness of cementitious materials. Collectively, the targeted modulation of these two phases is the core prerequisite for achieving super performance or leapfrog performance breakthroughs in advanced construction materials.

Introduction

Page 1-2, line 28-31:

The CH may form microcrystals within the C-S-H gel structure to enhance its mechanical properties^{10, 11, 12, 13}, or it may accumulate into crystal-oriented and large-sized particles, thereby impairing the mechanical and durability performance of cementitious materials^{14, 15, 16, 17}.

Page 2, line 51-57:

Crystal refinement is expected to suppress coarse grain growth in CH crystals, eliminate localized stress concentrations, and mitigate mechanical property defects caused by lattice anisotropy. Furthermore, the introduction of CH precursors with surface functionalization and lattice disorder as templates is expected to induce heterogeneous nucleation of C-S-H, thereby achieving synergistic enhancement of both the interface properties between CH and C-S-H and the microstructure of C-S-H.

Page 3, line 62-71:

In this work, we proposed a hydrogen-bond-regulated proton transfer strategy to prepare protonated CH (CHP_H^+) with disordered structure, and regulated the growth behavior of CH and C-S-H, achieving super-nucleation of hydrates and breakthroughs in mechanical strength. Furthermore, the structure-disordered CHP_H^+ served as a molecular template to improve the morphology and distribution of CH, thereby facilitating to eliminate its oriented crystallization and coarse grain growth.

2. The cited references (specifically 9-11) do not truly support the claim that the nature of portlandite directly causes interlayer delamination and brittle fracture affecting the durability and mechanical properties of cement concrete. There is no direct link between the nature of portlandite and mechanical properties of cement. Ref. 11 shows that CH directly impacts the hydration of cement, which essentially modulates the C-S-H product.

Reply: Thanks for your comments. We acknowledge that the claims proposed regarding portlandite are not entirely accurate, and some of the referenced literature fails to provide sufficient support for these assertions. Moreover, the present statement does not correspond to the central argument of this section, specifically the proposition that “Their anisotropy and interface effects could be key to high-performance design but could also be the source of material failure.”

CH has both positive and negative effects on cementitious materials, necessitates strategies to maximize its benefits and mitigate potential drawbacks. Therefore, we have rephrased this statement to emphasize the positive impact of CH on C-S-H while acknowledging the adverse effects of CH. The relevant references and corresponding sentences are listed in Table Q2. Additionally, all references in this paper have been updated to accurately support the respective arguments.

Page 1-2, line 28-31:

The CH may form microcrystals within the C-S-H gel structure to enhance its mechanical properties ^{10, 11, 12, 13}, or it may accumulate into crystal-oriented and large-sized particles, thereby impairing the mechanical and durability performance of cementitious materials ^{14, 15, 16, 17}.

Table Q2:

Corresponding content	Attitude	Ref.
It was observed that CH crystallises according to two main patterns, the first consisting of a few, large, convoluted and unevenly distributed clusters, while the second consists of numerous smaller particles, evenly and closely distributed in the matrix.	Neutral	1.
Results indicate that, in the selected microvolumes where C-S-H and nanoscale $\text{Ca}(\text{OH})_2$ (CH) are present, increasing fractions of CH increase the local indentation modulus (and hardness), yielding values above those reported for high-density (HD) C-S-H. Micromechanical analyses show that C-S-H and CH are associated, not merely as a simple biphasic mixture, but as an intimate nanocomposite where nanoscale CH reinforces C-S-H by partially filling the latter's gel pores.	Positive	2.
Conclusions: At the nanoscale, the intrinsic modulus of portlandite and limestone is slightly higher than that of C-S-H, but their cohesion is lower.	Positive	3.
Introduction: The other essential structural distinction of the ITZ in comparison to HCP is the textured state of calcium hydroxide (CH) crystallites close to the aggregate surface [3], [4]. The higher porosity and, in part, the textured state of the CH crystallites favor the appearance and development of the microcracks in the ITZ.	Negative	4.
Abstract: Additionally, incorporating GGBS avoids the build-up of $\text{Ca}(\text{OH})_2$ within ITZ and provides a more uniform microstructure.	Negative	5.
A study shown that the CH crystals within ITZ are large and orientated due to the large number and size of pores [45]. Ma et al. [30] found that the microhardness of ITZ decreases with increasing CH crystal orientation. Qiu et al. [46] found that adding fly ash can consume CH within ITZ and densify its microstructure, thus reducing the ITZ thickness.	Negative	6.

References

1. Gallucci E, et al. *Cement and Concrete Research*, 2007, 37(4): 492-501.
2. Chen J J, et al. *Journal of the American Ceramic Society*, 2010, 93(5): 1484-1493.
3. Zhang Z, et al. *Cement and Concrete Research*, 2025, 189: 107781.
4. Harutyunyan V S, et al. *Cement and Concrete Research*, 2000, 30(5): 709-713.
5. Wu K, et al. *Cement and Concrete Research*, 2016, 79: 243-256.
6. Gao X, et al. *Cement and Concrete Research*, 2025, 187: 107675.

3. (1) What definitive evidence supports the claim of CHP protonation? (2) Could the authors present the details of how they prepare the RHP and CHP samples for XRD measurement? (3) Could the XPS signals attributed to adventitious OH of H₂O simply indicate incomplete drying or surface-adsorbed water? (4) Is the proposed protonation of CH chemically plausible, or is the Ca(OH)(H₂O)⁺ species more accurately described as a dissolved ionic hydrate? (5) Since CH is ground in wet condition, drying might change the crystallinity of fine CH particle or even carbonate them. Full XRD patterns should be provided.

Reply: Thanks for your suggestions. Q3 is divided into **5 parts** for detailed response.

Response to Part (1).

To further evidence the protonation process in CHP, we have supplemented the following: 1. Added new control groups and tests (Fig. 2); 2. Supplemented with isotope tracer experiments and in-situ experiments (Fig. 4). Based on your suggestion in Question 5, we have added two control groups: chemically synthesized CH (CHP_Perf.) and dry-grinding CH (CHP_OH_v). Both the raw CH (CH_Raw) and the wet-grinding protonated CHP (CHP_H⁺) were remeasured to ensure consistent testing conditions for the samples. The average particle sizes of CHP_H⁺ (247.9 nm), CHP_OH_v (260.4 nm), and CHP_Perf. (223.2 nm) are comparable.

The protonation process influences both the macroscopic behavior and microscopic properties of CHP. We will provide both macroscopic and microscopic evidence.

1) Macroscopic evidence

Under eliminating interference from factors such as particle size, pH, and conductivity etc., CHP_OH⁺ exhibits outstanding dispersibility and stability (Supplementary Fig. 3), with a significantly higher zeta potential than CHP_Perf. and CHP_OHV (Fig. 2 a-c). This indicates that the surface charge of CHP_OH⁺ has changed following wet grinding treatment. Detailed revisions are as follows:

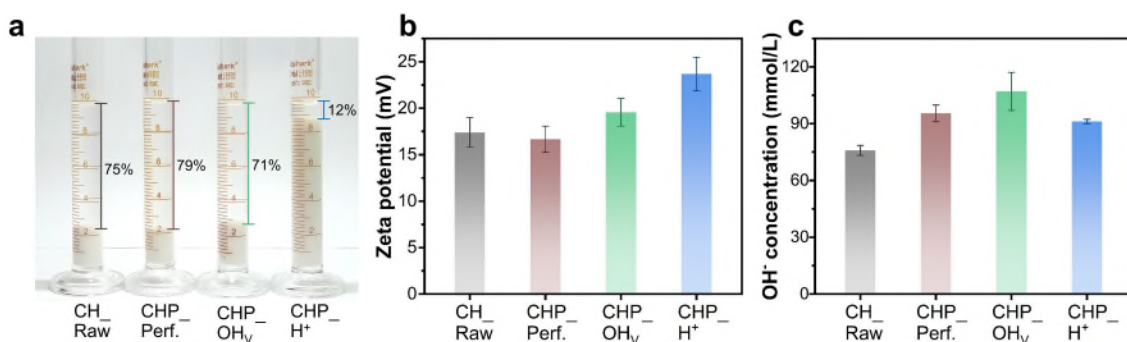
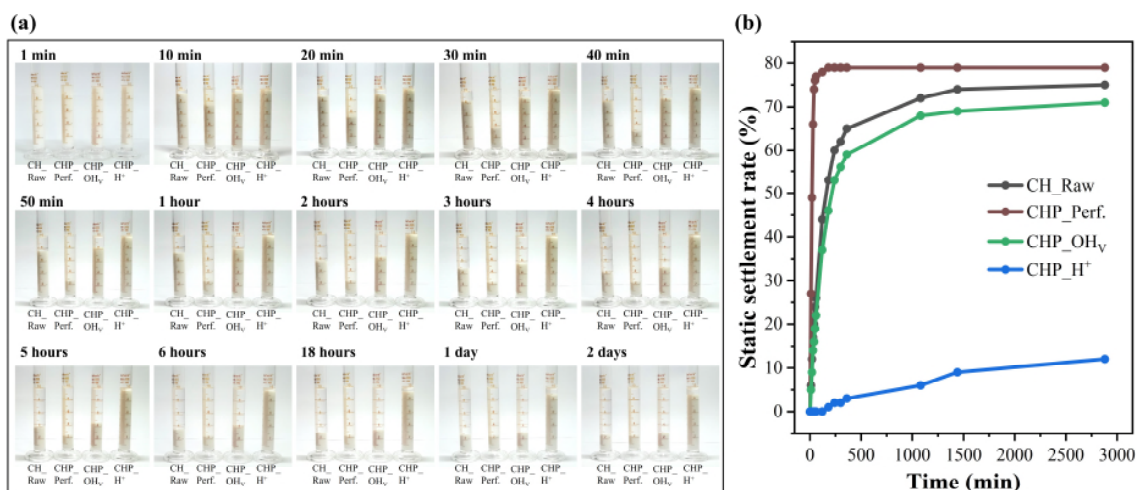


Fig. 2: **a** Photograph of slurries (water/CH = 20/1) prepared from 4 types of CH after settling for 2 days. The number in the photograph means the static settlement rate. **b** Zeta potential of 4 types of CH. **c** OH⁻ concentration of 4 types of CH.

Page 5, line 112-115:

The protonation phenomenon of CH was initially revealed through experimental observations, as shown in Fig. 2 a and Supplementary Fig. 3. The protonated CHP_H⁺ dispersed in water exhibited superior dispersibility and stability, with a static sedimentation rate of only 12% after 2 days. As shown in Fig. 2 b, the increase in zeta potential indicates that the positive charge density on the surface of CHP_H⁺ has been enhanced. The absence of significant variation in both OH⁻ concentration (Fig. 2 c) and conductivity (Supplementary Fig. 4) in the CHP_H⁺ dispersion suggested that the observed enhancement in zeta potential is not primarily governed by solution ion concentrations.



Supplementary Fig. 3. (a) Photograph of slurries (water/CH = 20/1) prepared from 4 types of CH at different settling times. (b) Static settlement rate curves of 4 types of CH at different settling times.

2) Microscopic evidence

The definitive evidence for protonation comprises three critical components: **Step**

I, Evidence for the formation of OH vacancies; **Step II**, Evidence that CH with OH vacancies reacts with H₂O (or D₂O); **Step III**, Observation of the $\equiv\text{Ca}-\text{OH}_2^+$ signal peak characteristic of protonated CHP. The experimental observation strategy for protonation is shown in Fig. 4 a.

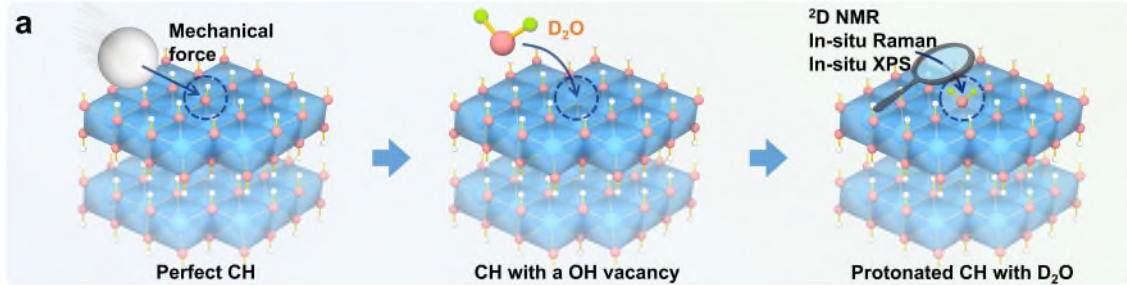


Fig. 4: a Schematic diagram of tracking protons based on the isotope labeling method to verify protonation.

Step I: Evidence for the formation of OH vacancies:

TEM test (Fig. 1 and Supplementary Fig. 2) and EPR test (Fig. f) were supplemented. The results showed that defects formed on the surfaces of CHP_OH_v and CHP_H⁺ after high-energy ball grinding, with CHP_OH_v exhibiting a higher defect content.

Page 3-4, line 84-94 :

The crystal structures of 4 types of CH were investigated using TEM, as shown in Fig. 1 c-f and Supplementary Fig. 2. CH_Raw and CHP_Perf. possess relatively intact single-crystal structures, characterized by highly ordered atomic arrangements and a unique, continuously consistent crystallographic orientation throughout the crystal (Fig. 1 g). In contrast, CHP_OH_v and CHP_H⁺ exhibit substantial crystalline distortions, dislocations, and vacancies (Fig. 1 h). This phenomenon is commonly observed after mechanical grinding, as prolonged mechanical force disrupts the crystal lattice, interferes with the regular atomic packing, and reduces the long-range order of the crystal²⁷. The appearance of diffraction rings in the FFT patterns, originating from randomly oriented grains, confirms the transition of the CH sample from a single-crystalline to a polycrystalline state after grinding.

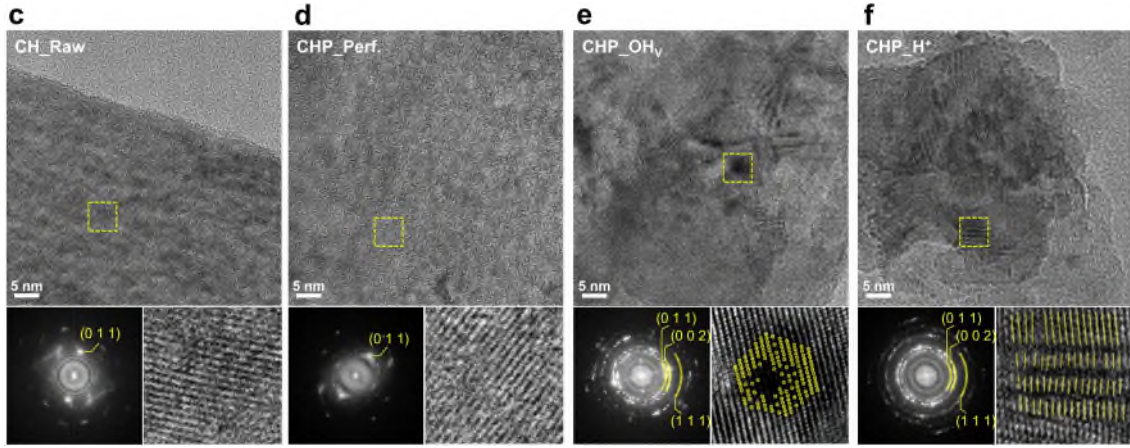


Fig. 1: c-f HRTEM images (top), FFT patterns (bottom left), and magnified local regions within yellow boxes (bottom right) for CH_Raw (c), CHP_Perf. (d), CHP_OH_v (e), and CHP_H⁺ (f).

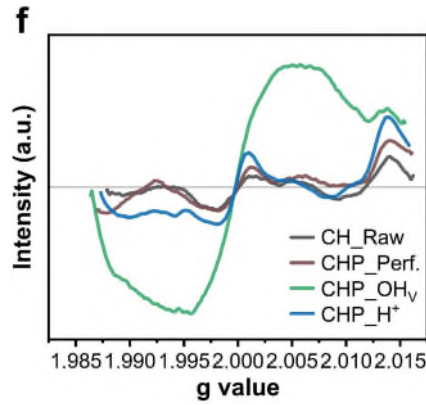


Fig. 2: f EPR spectra of 4 types of CH.

Step II: Evidence that CH with OH vacancies reacts with H₂O (or D₂O)

The isotope deuterium (D) is incorporated as a tracer to eliminate interference from wet grinding, atmospheric H₂O, and -OH in CH, thus clarifying the characteristic signal of the protonated product (i.e., -OH₂⁺). Specifically, deuterated water (D₂O) serves as the proton source and contacts the surface of CHP_OH_v, thereby tracing the occurrence and pathways of protonation. Meanwhile, CHP_Perf. is employed as the control group to distinguish the exchange between OH⁻ and DO⁻ induced by the ionization of CH in D₂O. Finally, the occurrence of adsorption reactions was detected using BET, ²D NMR and in-situ Raman measurements. Detailed revisions are as follows:

Page 10-11, line 243-273:

As shown in Fig. 4 b-d, D₂O molecules were controllably adsorbed onto the CHP surface of the CH in a monolayer form based on BET theory guidance, and then ²D NMR testing was performed after desorption and drying. This experiment effectively

eliminates signal interference caused by CH ionization in D₂O, thereby providing crucial evidence to determine whether surface reactions occur. Firstly, based on the H₂O adsorption-desorption isotherms (Fig. 4 b), a pressure condition (420 Pa) was determined where the adsorption capacities of the two samples were comparable and both exhibited monolayer adsorption. Secondly, D₂O cyclic adsorption-desorption experiments were conducted at a maximum pressure of 420 Pa (Fig. 4 c). The results showed that the adsorption capacity of CHP_OH_v decreased by 22.7% in the second adsorption cycle compared to the first, while that of CHP_Perf. decreased by only 6.6%, indicating the presence of chemical adsorption on the surface of CHP_OH_v. Finally, ²D NMR test (Fig. 4 d) and Raman test (Supplementary Fig. 9) were conducted on the samples after D₂O adsorption-desorption. Both the ²D NMR spectrum and Raman spectrum of CHP_OH_v revealed signal peaks associated with D, whereas CHP_Perf. showed no distinct signal peaks. The results indicate that D₂O undergoes chemical adsorption on the CHP_OH_v surface and generates deuterated hydroxyl groups, thereby experimentally confirming the thermodynamic feasibility of protonation of CH with defect.

As shown in Fig. 4 e-g, the proton transfer process was monitored by in-situ Raman testing in a D₂O gas atmosphere. The A_{1g} (internal stretching vibrations) peaks of Ca(OH)₂ and Ca(OD)₂ are located at 3610 cm⁻¹ and 2664 cm⁻¹ respectively³⁵. CHP_Perf. exhibited its initial -OD peak at 25 min (Fig. 4 e), attributed to proton exchange induced by CH ionization. In contrast, CHP_OH_v exhibited a -OD peak as early as 7 min (Fig. 4 f), attributed to proton transfer induced by protonation. Based on the deconvolution results of the in-situ Raman testing (Supplementary Fig. 10), the variation in -OD proportion is shown in Fig. 4 g. During the 15-20 min period, the Ca(OD)₂ content in CHP_OH_v tends to stabilize, potentially indicating that the protonation reaction is nearly complete. Then, at 25 min, its content increased again, suggesting that CH ionization began to dominate the subsequent proton exchange process. The results further confirm the feasibility of the protonation process and enable a preliminary quantification of the protonation degree.

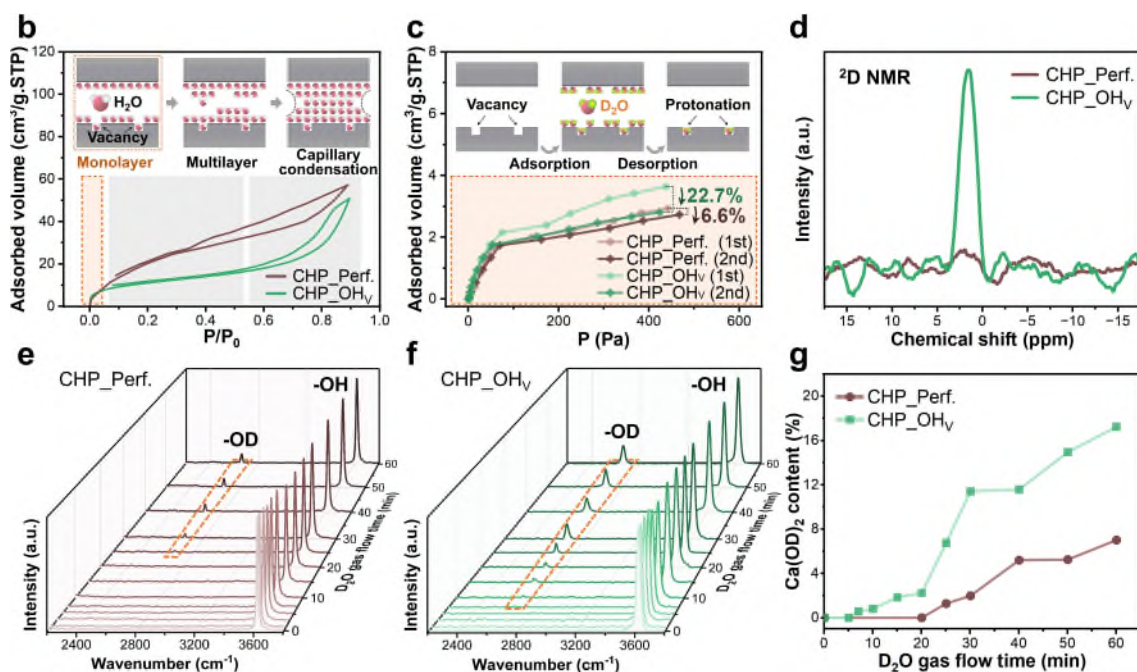


Fig. 4: **b** H₂O adsorption/desorption isotherms of CHP_Perf. and CHP_OH_v. The maximum pressure is about 6638.4 Pa. The schematic diagram above the curve shows the three stages of H₂O adsorption on the CH surface: monolayer adsorption, multilayer adsorption, and capillary condensation. **c** D₂O adsorption isotherms of CHP_Perf. and CHP_OH_v. The maximum pressure is about 420 Pa. Each sample was adsorbed and desorbed twice. The schematic diagram above the curve shows D₂O monolayer adsorption on the CH surface followed by desorption. **d** ²D NMR spectra of CHP_Perf. and CHP_OH_v after two cycles of D₂O adsorption and desorption. The samples used were those recycled after testing in figure c. **e and f** In-situ Raman spectra of CHP_Perf. (e) and CHP_OH_v (f) in D₂O gas atmospheres at different times. The internal stretching vibrations involving -OH and -OD occur at 3610 cm⁻¹ and 2664 cm⁻¹, respectively. **g** The proportion of deconvoluted peaks of -OD in figures (e) and (f).

Step III: Observation of the Ca-OH₂⁺ signal peak characteristic of protonated CHP.

We have supplemented the XPS O1s spectra of four types of CH (Fig. 2 d) to identify the position of O_v (oxygen vacancy) and preliminarily determine the position of O_p (protonated -OH₂⁺). Furthermore, we supplemented in situ XPS of CHP_Perf. and CHP_OH_v during H₂O vapor adsorption and thermal desorption processes (Fig. 4 h-j) to determine the O_A (adsorbed water) peak position and clarify the O_p (protonated -OH₂⁺) position. As shown in Supplementary Fig. 13, the shoulder peak at 533.6 eV observed in the CHP_H⁺ group after wet grinding does not belong to O_A or O_v, but rather represents a peak characteristic of protonation. Detailed revisions are as follows:

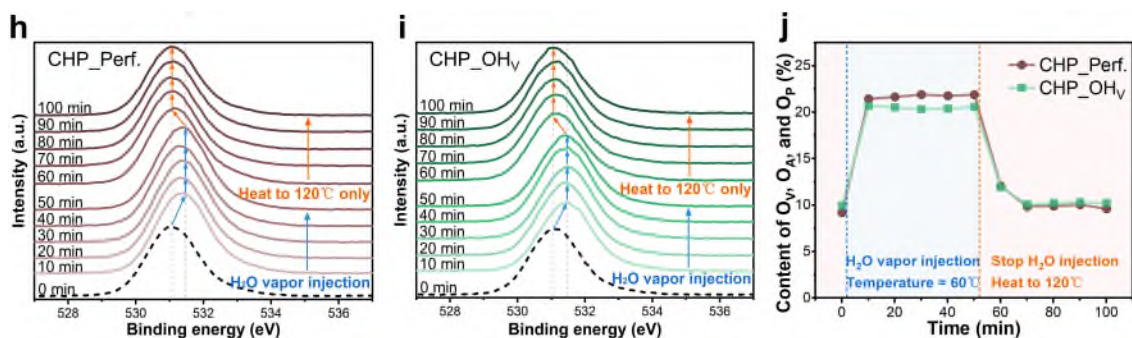
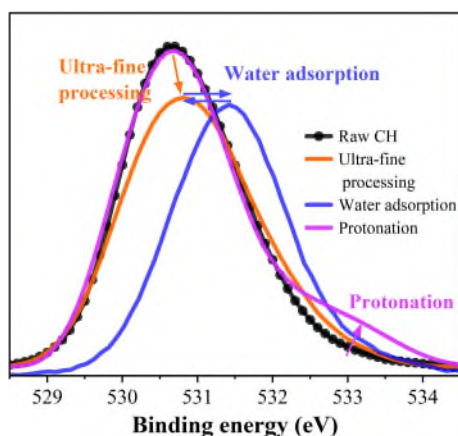


Fig. 4: h and i In-situ XPS spectra of CHP_Perf. (h) and CHP_OH_v (i) during 50 min in H₂O gas atmosphere followed by 50 min heating at 120°C. **j** The proportion of the deconvoluted peak (O_V, O_A, and O_P) at 532–533 eV in figures (h) and (i).

Page 11-12, line 274-292:

As shown in Fig. 4 h-j, in-situ XPS was used to investigate the evolution of the evolution of O1s binding energy of the samples during H₂O vapor adsorption and thermal desorption processes. The objective of this test is to determine the peak positions of OA (adsorbed water) and to provide experimental evidence to support the assignment of the protonation characteristic peak (O_P) in Fig. 2 d. After 10 min of H₂O vapor exposure, the O 1s spectra of both CHP_Perf. (Fig. 4 h) and CHP_OH_v (Fig. 4 i) shifted collectively toward higher binding energies by 0.4 eV; correspondingly, the percentages of the deconvoluted peaks at 532-533 eV (Fig. 4 j and Supplementary Fig. 11) increased from 9.17% and 9.94% to 21.44% and 20.69%, respectively. Beyond 10 min, prolonging the H₂O vapor exposure duration did not induce a further shift in the binding energy, indicating that adsorbed water has a limited effect on the O1s binding energy. After ceasing H₂O injection and heating for desorption, the O1s spectra of both samples shifted toward lower binding energies and gradually recovered to their initial state (0 min). But a weak shoulder peak remained near 533.6 eV for CHP_OH_v, while no significant signal was observed for CHP_Perf. (Supplementary Fig. 12). Further normalized comparison revealed that neither CH refinement nor physically adsorbed water induced significant shoulder formation at 533.6 eV (Supplementary Fig. 13), indicating that the characteristic signal at this position does not originate from defects or molecular water adsorption but should be attributed to the distinctive O_P peak formed during protonation.

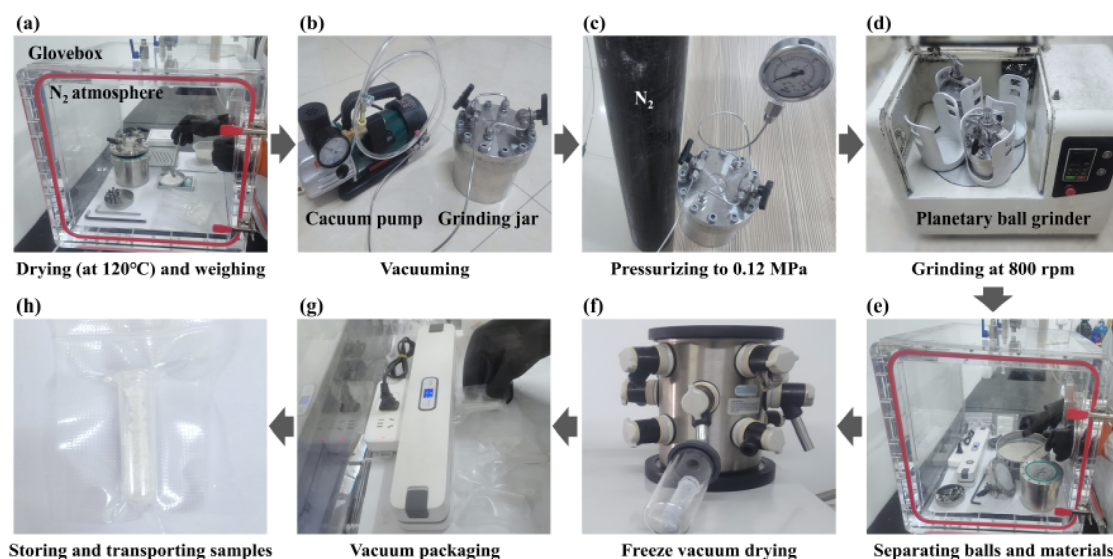


Supplementary Fig. 13. The trend of normalized XPS O1s spectra for CH under different treatment conditions

Response to Part (2) and Part (5). “Could the XPS signals attributed to adventitious OH of H₂O simply indicate incomplete drying or surface-adsorbed water? Since CH is ground in wet condition, drying might change the crystallinity of fine CH particle or even carbonate them. Full XRD patterns should be provided.”

We fully understand your concern that water and CO₂ in the air may affect the test results. Two methods to prevent the influence of air. First, all experiments were conducted in a hermetically sealed, N₂ atmosphere, as shown in Supplementary Fig. 6. Second, as mentioned earlier, two additional control groups were added.

All sample treatments were conducted in an acrylic glovebox under a nitrogen (N₂) atmosphere, including weighing, heating and drying, sealing of grinding jars, sieving, and vacuum packaging, as shown in Supplementary Fig. 6 a, e, g, and h. During the grinding step (Supplementary Fig. 6 b-d), the grinding jar was first evacuated and then purged with N₂ to a pressure of 0.12 MPa. The CHP_H⁺ slurry was sealed into test tubes within a glove box, then frozen for 6 hours, and promptly transferred to a vacuum dryer for drying. Following drying, the samples were immediately sealed, transferred to the glovebox, and subjected to heat-drying (120°C for 30 minutes) and sieving, prior to final vacuum packaging. In contrast, CHP_OH_v did not require freezing or vacuum drying and was directly vacuum-sealed. CH_Raw and CHP_Perf. only require heating for drying and vacuum packaging within the glove box. Additionally, although samples inevitably come into contact with air during testing, this portion of error and interference can be eliminated through comparison with control groups.



Supplementary Fig. 6. Experimental flowchart for the preparation of CHP_OH_v and CHP_H⁺. (a) Drying and weighing of CH samples in a glove box under N₂ atmosphere. For CHP_OH_v samples, CH_Raw, grinding balls, and grinding jars must each undergo heating and drying at 120°C for 30 min. (b) Vacuuming of the grinding jar. The purpose is to remove residual water and CO₂ from the internal piping of the grinding tank during CHP_OH_v preparation. (c) Pressurize the grinding jar. This prevents the grinding jar from drawing in air during the grinding process. (d) Grinding treatment. During operation, cold air is continuously introduced for cooling. (e) Separation of grinding balls from materials in a glove box under N₂ atmosphere. (f) Freeze vacuum drying process. Only CHP_H⁺ slurry is required. CHP_H⁺ slurry was sealed into test tubes within a glove box, then frozen for 6 hours followed by freeze vacuum drying for 48 hours. Finally, CHP_H⁺ was dried on a heating plate for 30 min in a glove box under N₂ atmosphere. (g) Vacuum packaging in a glove box under N₂ atmosphere. Prior to this, CH_Raw and CHP_Perf. will be heated and dried at 120°C for 30 minutes. (h) Storage and transport of samples.

Following your suggestions, full XRD patterns are provided, as shown in Fig. 2 h. The results indicate that no significant carbonation occurred in any of the four sample groups. Furthermore, additional DTG and Raman were supplemented for the four samples, and the results further validate that all samples exhibited no obvious carbonation and possessed low adsorbed water content.

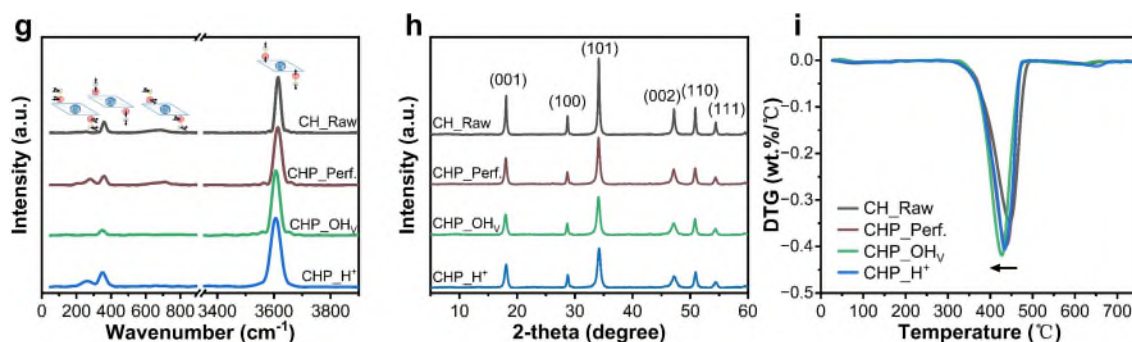


Fig. 2: **g** Raman spectra of 4 types of CH. **h** XRD spectra of 4 types of CH. **i** DTG spectra of 4 types of CH.

Response to Part (3): “Could the XPS signals attributed to adventitious OH of H₂O simply indicate incomplete drying or surface-adsorbed water?”

As mentioned in Part (1), we employed in situ XPS to eliminate the influence of adsorbed water. The in situ XPS tests comprised two steps: 1. Water vapor introduction, 2. Stop the water vapor introduction and dry at 120°C. The results indicate that the O1s peak associated with adsorbed water has a center energy of 532-533 eV. The shoulder peak center of protonated CHP_H⁺ after drying appears around 533.6 eV. Overall, in-situ XPS effectively eliminates interference from adsorbed water.

Page 11-12, line 274-292:

As shown in Fig. 4 h-j, in-situ XPS was used to investigate the evolution of the evolution of O1s binding energy of the samples during H₂O vapor adsorption and thermal desorption processes. The objective of this test is to determine the peak positions of OA (adsorbed water) and to provide experimental evidence to support the assignment of the protonation characteristic peak (O_P) in Fig. 2 d. After 10 min of H₂O vapor exposure, the O 1s spectra of both CHP_Perf. (Fig. 4 h) and CHP_OH_v (Fig. 4 i) shifted collectively toward higher binding energies by 0.4 eV; correspondingly, the percentages of the deconvoluted peaks at 532-533 eV (Fig. 4 j and Supplementary Fig. 11) increased from 9.17% and 9.94% to 21.44% and 20.69%, respectively. Beyond 10 min, prolonging the H₂O vapor exposure duration did not induce a further shift in the binding energy, indicating that adsorbed water has a limited effect on the O1s binding energy. After ceasing H₂O injection and heating for desorption, the O1s spectra of both samples shifted toward lower binding energies and gradually recovered to their initial state (0 min). But a weak shoulder peak remained near 533.6 eV for CHP_OH_v, while no significant signal was observed for CHP_Perf. (Supplementary Fig. 12). Further

normalized comparison revealed that neither CH refinement nor physically adsorbed water induced significant shoulder formation at 533.6 eV (Supplementary Fig. 13), indicating that the characteristic signal at this position does not originate from defects or molecular water adsorption but should be attributed to the distinctive O_P peak formed during protonation.

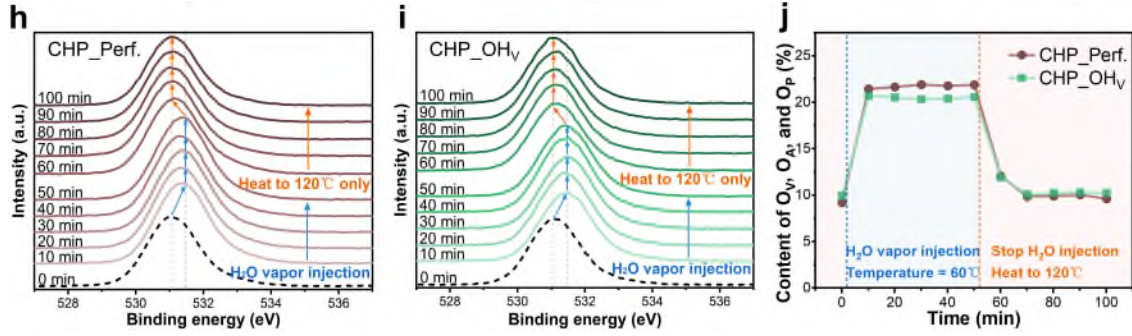


Fig. 4: h and i In-situ XPS spectra of CHP_Perf. (h) and CHP_OH_V (i) during 50 min in H₂O gas atmosphere followed by 50 min heating at 120°C. **j** The proportion of the deconvoluted peak (O_V , O_A , and O_P) at 532-533 eV in figures (h) and (i).

Response to Part (4): “Is the proposed protonation of CH chemically plausible, or is the $\text{Ca}(\text{OH})(\text{H}_2\text{O})^+$ species more accurately described as a dissolved ionic hydrate?”

The protonation of CH proposed in this paper falls within the scope of defect chemistry [1] and is chemically plausible. Defect chemistry is a research direction which mainly studies the generation, balance, properties, and regulation of defects in solid materials. In recent decades, many studies about solid defect chemistry have been reported [2, 3]. Furthermore, the Lewis acid-base theory can also well rationalize the chemical feasibility of the protonation proposed in this work [4]. Wet-grinding induces the formation of hydroxyl vacancies on the CH surface, leading to the exposure of adjacent Ca^{2+} ions due to coordination unsaturation, thus forming isolated Lewis acid sites. Water is considered a classical Lewis base due to the lone pair electrons on its oxygen atom [5]. The oxygen in water can be adsorbed at vacancy sites and coordinate with calcium to form $\equiv\text{Ca}-\text{OH}_2^+$.

You have raised an insightful point, i.e., the hydrate. The notation $\text{Ca}(\text{OH})(\text{H}_2\text{O})^+$ is misleading, so we have revised it to $\equiv\text{Ca}-\text{OH}_2^+$ or $\text{Ca}(\text{OH})_{2-\delta}\cdot\delta\text{H}_2\text{O}(\delta^+)$. From a local and microscopic perspective, the coordination between OH vacancies on the CH surface and H₂O molecules to form $\equiv\text{Ca}-\text{OH}_2^+$, which is similar to the hydration process. However, in reality, various defects form during the grinding process, and the content

and types of these defects are difficult to quantify, resulting in an unpredictable final product. Therefore, the protonation process of CH in wet grinding cannot be entirely regarded as a hydration process. Sentences and formulas related to $\text{Ca}(\text{OH})(\text{H}_2\text{O})^+$ have been revised.

The second is a unique protonation pathway we propose for the aqueous mechanochemical environment, based on Lewis acid-base theory³³. Mechanical force elicits the formation of hydroxyl vacancies on the CH surface; this induces local coordination unsaturation, which in turn exposes adjacent Ca^{2+} and forms discrete isolated Lewis acid sites. Water is a classic Lewis base whose oxygen contains a Lewis base site³⁴. The oxygen in water can be adsorbed at vacancy sites and coordinate with calcium to form $\equiv\text{Ca}-\text{OH}_2^+$ (Fig. 3 b).



References

- [1] Fuller C S. *Journal of the American Chemical Society*, 1964, 86(20): 4514-4515.
- [2] Li Z, et al. *Journal of the American Chemical Society*, 2016, 138(45): 14810-14819.
- [3] Schweke D, et al. *Advanced Materials*, 2018, 30(41): 1706300.
- [4] Stephan D W. *Science*, 2016, 354(6317): 7229.
- [5] Corma A, et al. *Chemical Reviews*, 2003, 103(11): 4307-4366.

4. The simulation component of this study aims to support the proposed protonation mechanism of CHP at an atomic level. However, the computational evidence for this claim is not sufficiently robust due to significant simplifications. Specifically, the adsorption energy calculations, which are foundational to the proposed mechanism's energetics, were performed in the gas phase. This highly unrealistic condition fundamentally neglects the profound influence of the aqueous environment, including solvation effects of water molecules and dissolved ions, and charge screening, rendering the calculated energy values and the inferred spontaneity of protonation unreliable for a real mineral-solution system. While WT-MetaD simulations do incorporate some explicit water, the inherent limitations of small, periodic simulation cells may still restrict their ability to fully capture

bulk solution effects, thus providing only qualitative mechanistic insights rather than quantitatively predictive support for the specific protonation claim in the complex environment of hydrating cement.

Reply: Thanks for your suggestions. Regarding your concern that “the computational evidence for this claim is not sufficiently robust,” this study adopted a strategy combining simulation calculations with experimental verification. For the experimental section: we employed deuterated water (D_2O) as the proton source in surface contact with CHP_{OH_V} , verifying the occurrence and pathways of protonation via ^2D NMR, in-situ Raman, and in-situ XPS. The experimental section has been discussed in detail in Question 3 (Part I) and will not be repeated herein. For the simulations section: **(1)** Revised the manuscript to emphasize mechanistic insights rather than evidence and predictions for protonation. **(2)** Upgraded and optimized the simulations as suggested, and supplemented with metadynamics simulations to provide further insights into the protonation process.

(1) The revision regarding the emphasis on mechanistic insights is as follows:

Page 8-9, line 212-220:

Overall, in Path I, the energy of FS is much higher than that of IS which means that the reaction is more difficult to occur. While, in Path II, the energy of FS is lower than that of IS, and the reaction energy barrier is lower, which implies that the reaction has the potential to proceed spontaneously. This finding provides a novel approach for experimentally verifying protonation. Rather than tracking the protonation on the CH surface under dynamic-grinding conditions, the Path II can be directly verified by statically observing the interaction between the CH with OH_V (i.e. CHP_{OH_V}) and water molecules. The experimental verification derived from this theoretical prediction is presented in Fig. 4.

(2) We have updated and supplemented the simulation calculations. Indeed, the adsorption behavior in vacuum is difficult to accurately represent for the protonation mechanism, and the influence of the aqueous environment is crucial. Therefore, we further incorporated an aqueous environment using VASPsol++ (*The Journal of Chemical Physics* **159**, (2023)) and recalculated the adsorption energies under these conditions. The corresponding adsorption energy values and the resulting trend is consistent with the protonation mechanism we identified. Additionally, we

supplemented the density of states and charge transfer to further complement insights into the protonation mechanism. As you rightly pointed out, we performed metadynamics simulations primarily to investigate the kinetic mechanism of protonation, uncover the reaction pathway, and provide a qualitative mechanistic insight into the protonation process. Detailed revisions are as follows:

Page 7, line 173-184:

The thermodynamic behaviors of the two protonation pathways were explained based on density functional theory (DFT) calculations. Two models were constructed: one for perfect CH and another for CH with OH_V, as shown in [Supplementary Fig. 8](#). The density of states (DOS) is presented in Fig. 3 c. For the perfect CH model, the valence band maximum near the Fermi level is primarily contributed by the electronic states of O, which exhibits a high occupied electronic state and an electron-donating tendency. This suggests that the O sites readily act as electron donors to form coordination bonds with H⁺, which is consistent with the electron transfer trend shown in Fig. 3 d. For the CH with OH_V model, the entire electronic structure shifts toward lower energy. The conduction band minimum, predominantly composed of Ca electronic states, moves closer to the Fermi level, indicating that Ca sites possess empty orbitals with a tendency to accept electrons. This electronic feature supports the role of Ca as an electron acceptor, enabling coordination with oxygen atoms in water molecules, which is consistent with the electron transfer trend shown in Fig. 3 e. As shown in Fig. 3 f, the adsorption energy of H⁺ adsorbed on the perfect CH surface is +1.93 eV, indicating that it cannot form spontaneously and needs external environment to provide energy. The adsorption energy of H₂O adsorbed on the hydroxyl vacancies of CH is -0.99 eV, indicating that the process is spontaneous.

Page 8-9, line 215-220:

This finding provides a novel approach for experimentally verifying protonation. Rather than tracking the protonation on the CH surface under dynamic-grinding conditions, the Path II can be directly verified by statically observing the interaction between the CH with OH_V (i.e. CHP_OH_V) and water molecules. The experimental verification derived from this theoretical prediction is presented in Fig. 4.

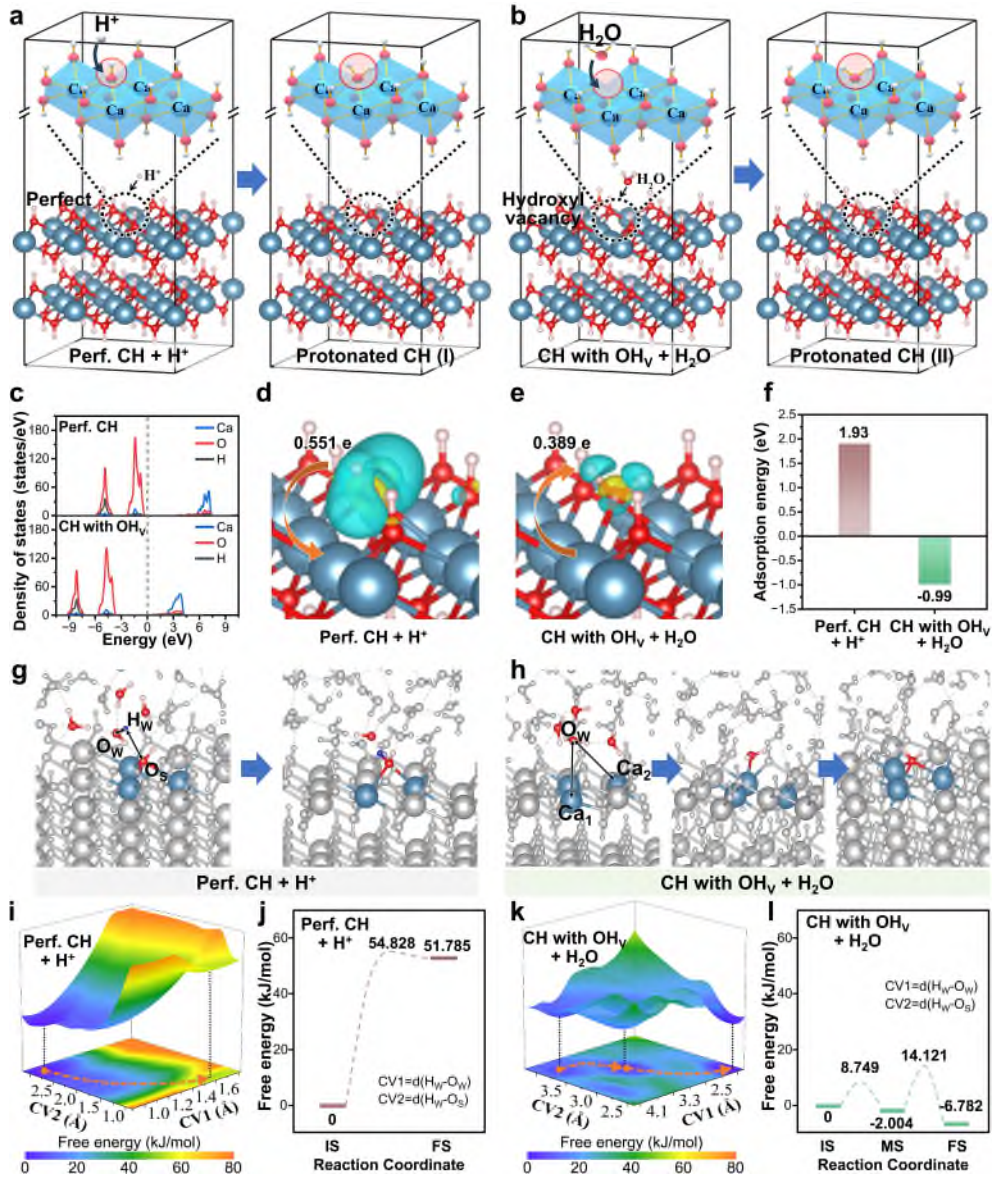


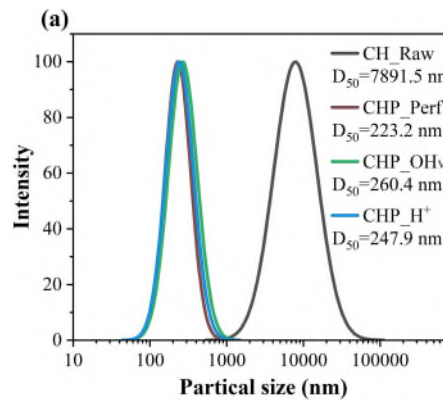
Fig. 3: Atomic structure, electronic structure and energy landscape of the surface protonation process. **a and b** The protonation process of the perfect CH (a) and CH with OH_v (b). **c** Density of states (DOS) of perfect CH and CH with OH_v . **d and e** Charge transfer during adsorption of H^+ on perfect CH (d) and during adsorption of H_2O on CH with OH_v (e). **f** Adsorption energies for 2 types of protonation processes. **g and h** Schematic diagram of the changes in the structure of perfect CH (g) and CH with OH_v (h) during protonation. The O, H and Ca involved in the reaction are highlighted in red, white and blue spheres, respectively. In Path I (a and c), HW and OW represent H and O in H_2O and OS represents oxygen ions on the surface. In Path II (b and d), Ca1 and Ca2 represent the two calcium atoms of CH. **i and k** 3D free energy surfaces of perfect CH and CH with OH_v during protonation. **j and l** The Free energy changes

during the protonation process of the perfect CH and CH with OH_v.

5. Why was a control experiment comparing the effects of CHP with raw CH (or ideally, raw CH dry-ground to a similar particle size) not performed? Without such a comparison, how can the unique impact of the mechanochemical treatment (beyond particle size effects) be conclusively demonstrated? From the comparison in hydration heat and compressive strength of cement paste mixed with and without CHP, the addition of CHP indeed accelerates the growth of strength. However, it is not surprising the CHP has a seeding effect as the fine crystallite size and defective surface can lower the nucleation energy barrier of C-S-H.

Reply: Thanks for your suggestions. Indeed, previous experiments failed to exclude the influence of nucleation effects from CH itself, which could mislead readers.

(1) To address your concerns, we have added two control groups: chemically synthesized CH (CHP_Perf.) and dry grinding CH (CHP_OH_v). As shown in Supplementary Fig. 1, the average particle size (D_{50}) of protonated CHP_H⁺ is 247.9 nm, which is comparable to the average particle sizes of CHP_Perf. (D_{50} = 223.2 nm) and CHP_OH_v (D_{50} = 260.4 nm). The dosage of each type of CHP is 5 wt% by mass of cement. All types of CHP are first mixed with the water required for cement and ultrasonically dispersed for 10 min.



Supplementary Fig. 1. (a) Particle size distribution and median particle (D_{50}) for CH_Raw, CHP_Perf., CHP_OH_v and CHP_H⁺.

(2) We discarded the previous data and re-conducted tests on compressive strength, hydration heat, XRD, TG, MIP, NMR, etc. In the latest data, we ensured that all four cement paste groups were tested simultaneously under identical conditions. The results indicate that the hydration heat release rate, early compressive strength, and early

hydration product content of the cement paste with CHP_H^+ were significantly higher than those of the CHP_Perf. and CHP_OH_v groups. Question 5 involves revisions to the full manuscript, so only the sections you are concerned about (strength and hydration heat) are listed below.

Page 15-16, line 363-379:

The influence of CHP_Perf. , CHP_OH_v , and CHP_H^+ at a 5 wt.% dosage on the properties of cement paste was investigated to further explore the super-nucleation effect of protonated CHP. The hydration heat release results are shown in Fig. 6 a. CHP_H^+ had an accelerating effect on the cement hydration, with the value of the main hydration peak increasing by 48.0%, 52.2%, and 46.9% compared to the groups of without CHP, with CHP_Perf. , and with CHP_OH_v , respectively. The time of main hydration peak of the CHP_H^+ group was the shortest, reduced by 31.5% compared to the group without CHP. The compressive strength results are shown in Fig. 6 b and Supplementary Fig. 16. CHP_H^+ has an excellent effect on improving the compressive strength, CHP_H^+ exhibits excellent performance in enhancing compressive strength, and its 12-hour strength reaches 16.7 MPa, which is much higher than that of CHP_Perf. (6.3 MPa) and CHP_OH_v (7.5 MPa). Based on quantitative TG (Supplementary Fig. 17) and XRD (Supplementary Fig. 18) results, the phase composition of the samples at 12 hours and 28 days was quantified, as shown in Fig. 6 c. During the early hydration stage (12 hours), CHP_H^+ can accelerate the hydration reaction of C_3S and induce the formation of more C-S-H gel. In the later hydration stages (28 days), the phase composition of the hydration products in all samples is similar except for CH content. The enhancement of 28-days strength by CHP_H^+ could be attributed to its optimization of the microstructure and distribution of hydration products. The acceleration effect of CHP_H^+ is comparable to that of C-S-H seed^{36, 37, 38}, with no negative impact on later-stage strength, which is expected to serve as a new accelerator.

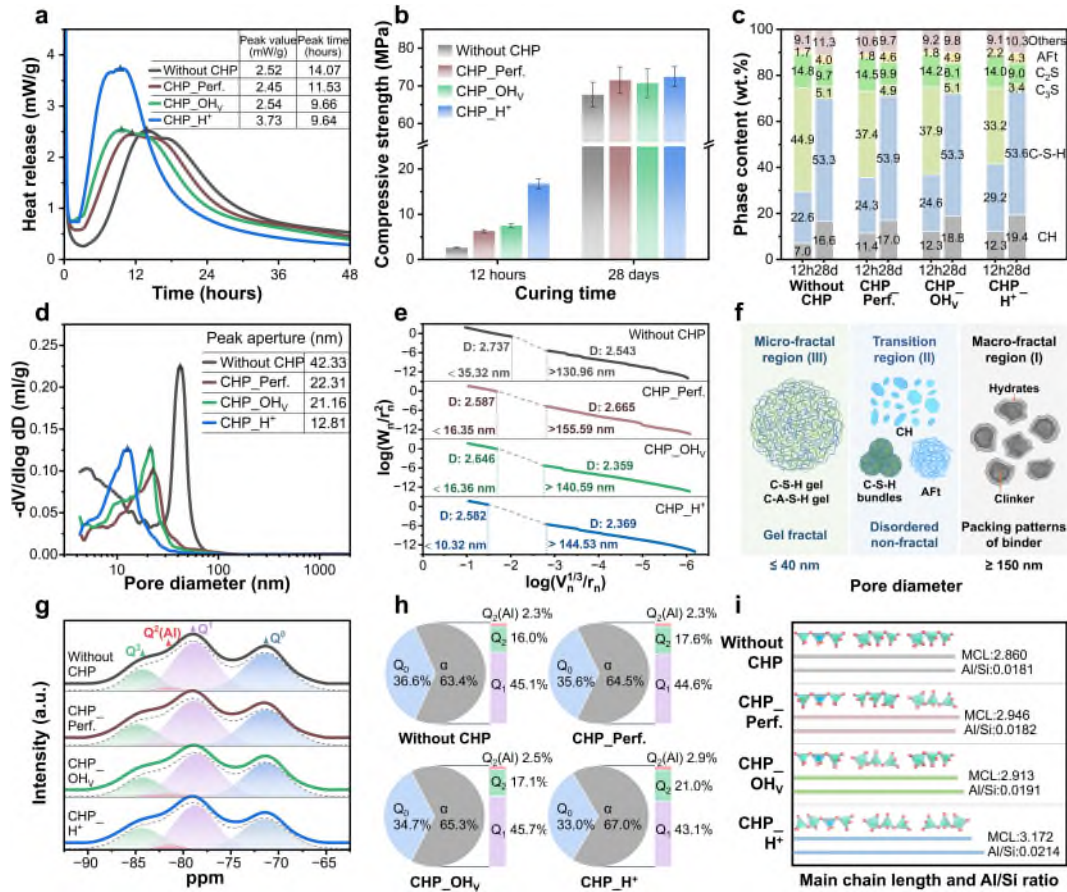


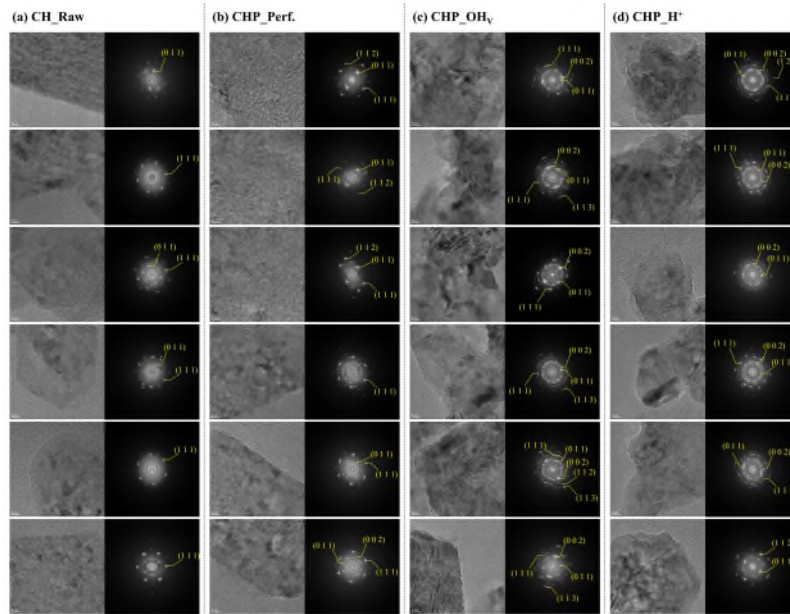
Fig. 6: Effect of protonated CHP on cement paste properties. **a** Hydration heat of cement pastes. The upper right corner shows the peak heat release and the corresponding time. **b** Compressive strength of cement pastes at 12 hours and 28 days. **c** The phase composition of cement pastes at 12 hours and 28 days. **d** Pore structure of cement pastes at 28 days. **e** Pore surface fractal dimensions of cement pastes at 28 days. **f** The primary phases corresponding to different fractal regions. **g** ^{29}Si NMR spectrum of cement pastes at 28 days. **h** The proportion of each coordination environment Si (Q_n , $n=1-2$) after deconvolution of the ^{29}Si NMR spectrum. **i** The main chain length and Al/Si ratio of cement pastes.

6. (1) How do the authors definitively conclude amorphization of CHP based solely on changes in FWHM and intensity from XRD, given that crystallite size reduction and lattice strain also significantly influence these parameters? (2) Can the particle size distribution of the raw CH be provided for comparison before and after grinding? Does the particle size change with the grinding time?

Reply: Thanks for your suggestions. Q6 is divided into 2 parts for detailed response.

Response to Part (1):

We acknowledge that the conclusion regarding amorphization was an overinterpretation. Based on XRD and TEM results, we have revised the corresponding section to state that “the crystal structure transitions from a single crystal to a polycrystalline structure”. As you anticipated, both grain size reduction and lattice strain influence XRD-related parameters (see Supplementary Fig. 7). Therefore, we supplemented extensive TEM data and demonstrated that CH transforms from a single crystal to a polycrystalline structure after grinding (see Supplementary Fig. 2). Detailed revisions are as follows:

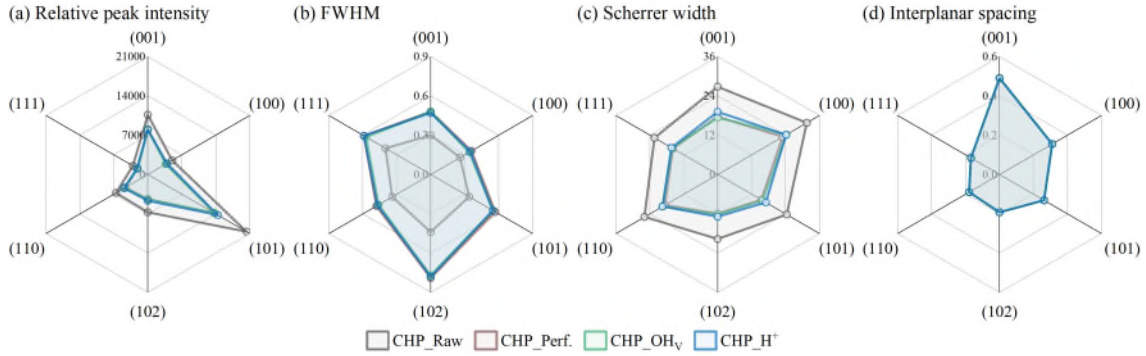


Supplementary Fig. 2. Transmission electron microscopy (TEM) images and their corresponding fast Fourier transform (FFT) images of 4 types of (a) CH_Raw, (b) CHP_Perf., (c) CHP_OH_v, and (d) CHP_H⁺.

Page 3, line 84-94 :

The crystal structures of 4 types of CH were investigated using TEM, as shown in Fig. 1 c-f and Supplementary Fig. 2. CH_Raw and CHP_Perf. possess relatively intact single-crystal structures, characterized by highly ordered atomic arrangements and a unique, continuously consistent crystallographic orientation throughout the crystal (Fig. 1 g). In contrast, CHP_OH_v and CHP_H⁺ exhibit substantial crystalline distortions, dislocations, and vacancies (Fig. 1 h). This phenomenon is commonly observed after mechanical grinding, as prolonged mechanical force disrupts the crystal lattice, interferes with the regular atomic packing, and reduces the long-range order of the crystal²⁷. The appearance of diffraction rings in the FFT patterns, originating from

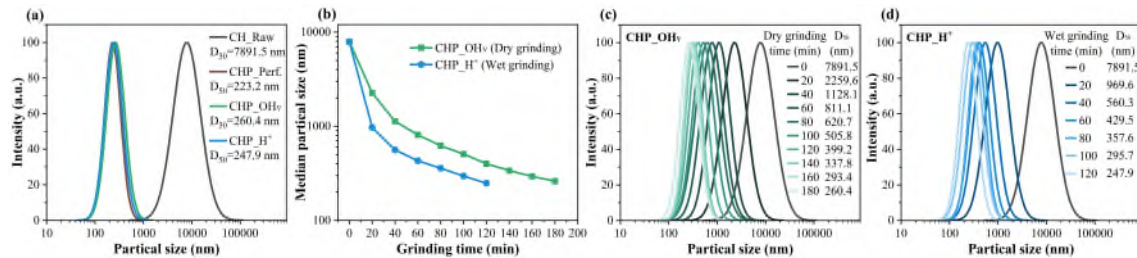
randomly oriented grains, confirms the transition of the CH sample from a single-crystalline to a polycrystalline state after grinding.



Supplementary Fig. 7. Crystallographic parameters in the XRD spectra of the four types of CH. (a) relative peak intensity. (b) Full width at half maximum (FWHM). (c) Scherrer width. (d) Interplanar spacing.

Response to Part (2):

We have provided the particle size distribution of raw CH (CH_Raw) and CH with different wet grinding times, as shown in Supplementary Fig. 1. Wet grinding causes changes in the particle size of CH. To eliminate the interference of particle size variation on protonation, we have added two control groups: chemically synthesized CH (CHP_Perf.) and dry grinding CH (CHP_OH_v), as shown in Fig. 1 a-b.



Supplementary Fig. 1. Particle size of the four types of CH. (a) Particle size distribution and median particle (D_{50}) for CH_Raw, CHP_Perf., CHP_OH_v and CHP_H⁺. (b) Median particle size of CHP_OH_v and CHP_H⁺ at different grinding times. (c) Particle size distribution of CHP_OH_v at different grinding times. (d) Particle size distribution of CHP_H⁺ at different grinding times.

Page 3, line 75-83:

We propose a mechanochemical strategy based on water-medium ball grinding to induce protonation on the CH surface. To demonstrate the unique properties of protonated CHP (CHP_H⁺), raw CH before grinding (CH_Raw), chemically synthesized CHP (CHP_Perf.) with similar particle size, and dry-grinding CHP with hydroxyl-vacancy (CHP_OH_v) were selected as control groups. CH_Raw and

CHP_Perf. were chemically synthesized using a bottom-up approach (Fig. 1 a), with average particle sizes of 7891.5 nm and 223.2 nm, respectively. CHP_OH_v and CHP_H⁺ were both prepared from CH_Raw via a top-down approach (Fig. 1 b), i.e., with D₅₀ of 260.4 nm and 247.9 nm, respectively. The particle size distribution curves for the 4 types of CH are shown in Supplementary Fig. 1.

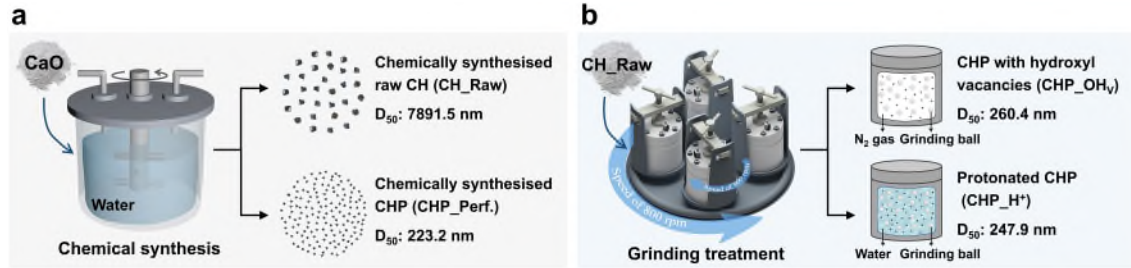


Fig. 1: **a** Preparation methods (chemical synthesis) and average particle size of CH_Raw and CHP_Perf. **b** Preparation methods (grinding) and average particle sizes of CHP_OH_v and CHP_H⁺.

7. The authors claimed in their manuscript that the addition of CHP decreases the fraction of CH whereas increases the amount of nano CH (or CH@CSH composites) based on their nanoindentation measurements. From their TG analysis, the mass content of total CH increases with the addition of CHP. Given that the indentation measurement only has 144 data points for each sample, it is not feasible enough for the statistical analysis. To increase the feasibility, the authors can do two things: (1) increase the indentation points on a larger area; (2) perform quantitative XRD analysis to show the fraction of each phase in the hydrated cement paste. In addition, the authors should also present their original histogram data of the indentation measurements and show the accuracy of the deconvolution of the PDFs. From the eyes, for the current results in Fig. 4e and f, it is doubtful to obtain the theoretical PDFs from accumulating the decomposed functions. Regarding those points have a elastic modulus larger than 80 GPa, they can be calcium carbonate as well.

Reply: Thanks for your comments. Q7 is divided into 2 parts for detailed response.

Response to Part (1):

Following your comments, the test points for each sample have been expanded to 1024 points to enhance feasibility. The current number of test points exceeds the quantity commonly used in relevant literature. Furthermore, the number of samples was

increased from the original 2 groups to 4 groups (Without CHP, CHP_Perf., CHP_OH_v, and CHP_H⁺). The updated data has been integrated into Fig. 7. The new data further validates our initial conclusions, with results indicating that the addition of CHP_H⁺ leads to the formation of more CH@C-S-H (i.e., UHD C-S-H), while CHP_Perf. and CHP_OH_v increase the content of HD C-S-H.

In addition, the original histogram data is shown in Supplementary Fig. 20. The horizontal axis is spaced at 1 GPa intervals, while the vertical axis displays the number and frequency of 1024 data points within each interval. The deconvolution of PDFs exhibits excellent accuracy, with R² values of 0.997 (e), 0.997 (f), 0.998 (g), and 0.996 (h) in Fig. 7 e-h. Regarding the point you mentioned about the elastic modulus >80 GPa, we agree that it may originate from phases such as calcium carbonate or quartz.

Page 19, line 446-458:

Previous studies have indicated that under low water-to-cement ratios, the restricted hydration space allows nanoscale CH to be tightly embedded within the C-S-H gel, resulting in a CH@C-S-H composite structure that contributes to the enhanced mechanical performance of the gel phase ^{11, 12, 13}. The size of CHP reaches the nano-micron scale, providing the initial conditions for the formation of the CH@C-S-H composite structure. This is also the critical reason for the notable increase in HD C-S-H and UHD C-S-H phase content in Groups with three types of CHP.

Another interesting finding is that the addition of CHP_H⁺ increased the UHD C-S-H content from 3.9% in the group without CHP to 17.4%. Typically, UHD C-S-H exhibits higher content in ultra-high performance concrete with low water-cement ratios ⁴⁶. Although the mechanical identification of UHD as CH remains feasible ⁴⁷, the UHD C-S-H content in the CHP_Perf. and CHP_OH_v groups was only 8.6% and 9.3%, respectively, ruling out interference from exogenous CH addition. Two key mechanisms underpin this observed phenomenon. Firstly, the protonated precursor (CHP_H⁺) triggers the formation of CH@C-S-H composite structures via heterogeneous nucleation, with this process being directly driven by surface protonation. Secondly, the reduction in anisotropy of the CH crystal structure results in a decline in the overall modulus of CH, as illustrated in Fig. 7 i and g. The mechanical properties of anisotropic CH in the c direction are balanced, yet they simultaneously diminish the mechanical properties in the a and b directions.

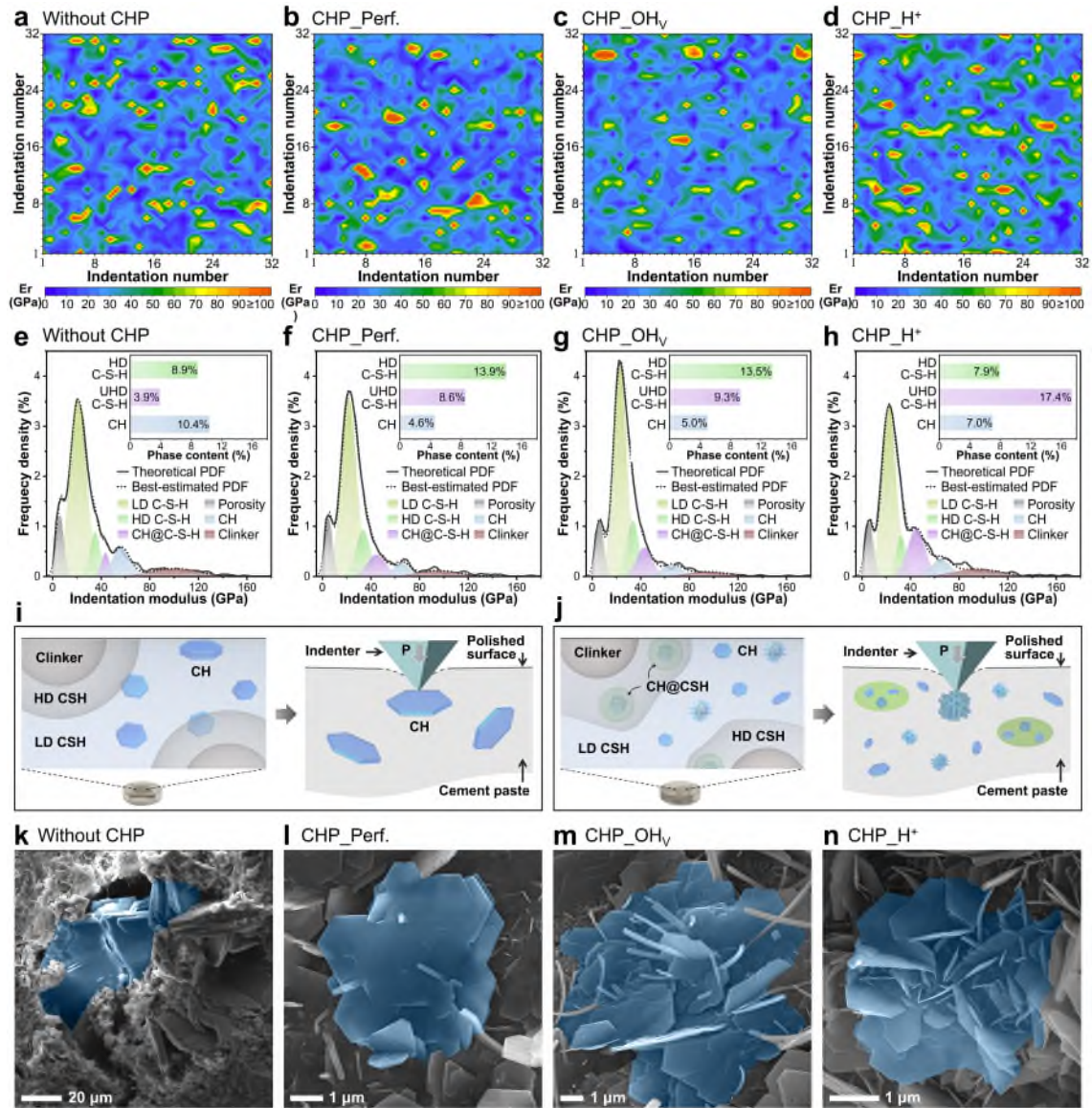
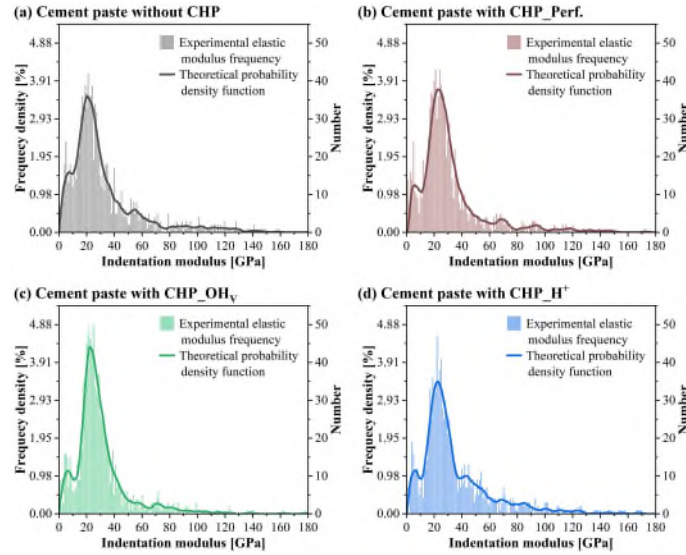


Fig. 7: Effect of protonated CHP on C-S-H modulus and CH structure in cement paste. **a-d** Elastic modulus maps of cement paste for **Without CHP** (a), **CHP_Perf.** (b), **CHP_OH_v** (c), and **CHP_H⁺** (d). The indentation matrix for the 4 samples was $32 \times 32 = 1024$, with a spacing of 10 μm . **e-h** Deconvolution results of the theoretical frequency counts for **Without CHP** (e), **CHP_Perf.** (f), **CHP_OH_v** (g), and **CHP_H⁺** (h). The bar chart (upper right corner) is the proportion of different hydration products based on deconvolution analysis and reference values. **i and j** Schematic diagram of indentation test with Bergdahl indenter on the surface of cement paste **without** (i) and **with** (j) **protonated CHP**. **k-n** SEM image of CH in the retained pore region of cement pastes for **Without CHP** (k), **CHP_Perf.** (l), **CHP_OH_v** (m), and **CHP_H⁺** (n).



Supplementary Fig. 20. Experimental elastic modulus frequency (bar size is 1 GPa.) and theoretical probability density function of cement pastes at 28 days. (a) Cement paste without CHP. (b) Cement paste with CHP_Perf. (c) Cement paste with CHP_OH_v. (d) Cement paste with CHP_H⁺.

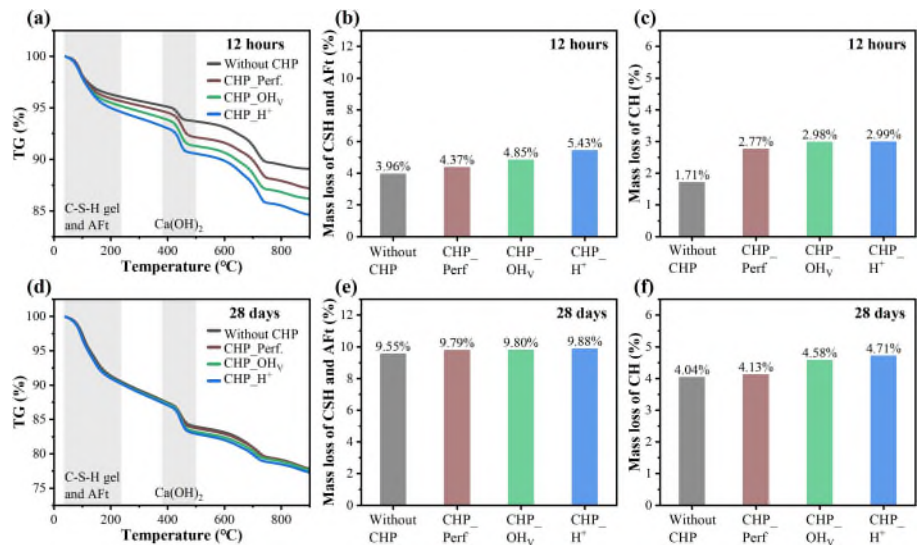
Response to Part (2):

Following your suggestion, we performed quantitative XRD analysis on four samples at 12 hours and 28 days, as shown in Supplementary Fig. 18. However, the phase composition of cement hydration products is highly complex, and the overlapping of their XRD diffraction peaks significantly impairs the accuracy of XRD quantitative analysis. Therefore, we have supplemented the analysis with TG tests, as shown in Supplementary Fig. 17. TG allows for the accurate quantification of key phases in cement hydration products, such as CH, C-S-H, and AFt. The TG results were used to calibrate the XRD quantification process, leading to the final composition of hydration products presented in Fig. 6 c.

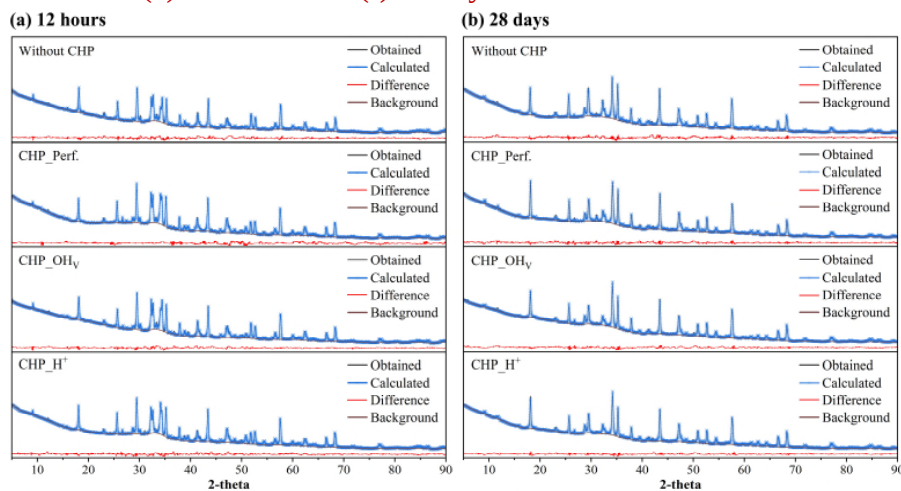
Page 16, line 374-379:

Based on quantitative TG (Supplementary Fig. 17) and XRD (Supplementary Fig. 18) results, the phase composition of the samples at 12 hours and 28 days was quantified, as shown in Fig. 6 c. During the early hydration stage (12 hours), CHP_H⁺ can accelerate the hydration reaction of C₃S and induce the formation of more C-S-H gel. In the later hydration stages (28 days), the phase composition of the hydration products in all samples is similar except for CH content. The enhancement of 28-days strength by CHP_H⁺ could be attributed to its optimization of the microstructure and distribution of hydration products. The acceleration effect of CHP_H⁺ is comparable to

that of C-S-H seed ^{36, 37, 38}, with no negative impact on later-stage strength, which is expected to serve as a new accelerator.



Supplementary Fig. 17. Thermal gravimetry (TG) spectra of cement pastes at (a) 12 hours and (d) 28 days. Mass loss of C-S-H gel and Aft at (b) 12 hours and (e) 28 days. Mass loss of CH at (c) 12 hours and (f) 28 days.



Supplementary Fig. 18. X-ray diffraction patterns of cement pastes at different curing ages. (a) 12 hours. (b) 28 days.

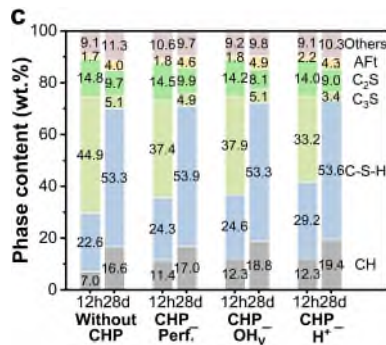


Fig. 6: b c The phase composition of cement pastes at 12 hours and 28 days.

8. To what extent do the observed changes in zeta potential, conductivity, and OH⁻ concentration genuinely indicate unique protonation of CHP, as opposed to simply accelerated dissolution due to smaller particle size and increased defect density? The dissolution of Ca could lead to the formation of ionic hydrates, which is a well-known common phenomenon of CH. It is not a unique phenomenon for CHP only. The reason for this can be that the CHP has smaller particle size (supporting data is needed) and more defective surface than raw CH, which can accelerate the dissolution of portlandite. There is nothing to do the protonation.

Reply: Thanks for your suggestions. Zeta potential is one of the critical test methods for the preliminary determination of protonation. However, as you stated, the reduction in particle size and increase in defect density accelerate the dissolution rate of CH, thereby causing changes in zeta potential, conductivity, and OH⁻ concentration. Therefore, we supplemented two additional control groups, as previously mentioned: synthesized CH (CHP_Perf.) and dry grinding CH (CHP_OH_v). The particle size of CHP_Perf. is smaller than that of protonated CHP_H⁺ (Supplementary Fig. 1), while the defect density of CHP_OH_v is higher than that of protonated CHP_H⁺ (Fig. 2 f). As shown in Fig. 2 a-c and Supplementary Fig. 4, CHP_H⁺ exhibits the best dispersion properties and the highest increase in zeta potential, while CHP_OH_v exhibits the most significant increases in conductivity and OH⁻ concentration. This indicates that the increase in the zeta potential of CHP_H⁺ is independent of the ionic concentration in the solution, providing preliminary evidence that proton transfer occurs on the surface of CHP_H⁺.

In addition, the results in Fig. 2 a-c provide preliminary and simplified evidence for protonation. In Questions 3 and 4, we describe in detail the process of verifying protonation through simulations that mimic experimental conditions. In Questions 3 and 4, we further validated protonation through a combined approach of simulations and experiments.

Page 5, line 112-115:

The protonation phenomenon of CH was initially revealed through experimental observations, as shown in Fig. 2 a and Supplementary Fig. 3. The protonated CHP_H⁺ dispersed in water exhibited superior dispersibility and stability, with a static sedimentation rate of only 12% after 2 days. As shown in Fig. 2 b, the increase in zeta

potential indicates that the positive charge density on the surface of CHP_H^+ has been enhanced. The absence of significant variation in both OH^- concentration (Fig. 2 c) and conductivity (Supplementary Fig. 4) in the CHP_H^+ dispersion suggested that the observed enhancement in zeta potential is not primarily governed by solution ion concentrations.

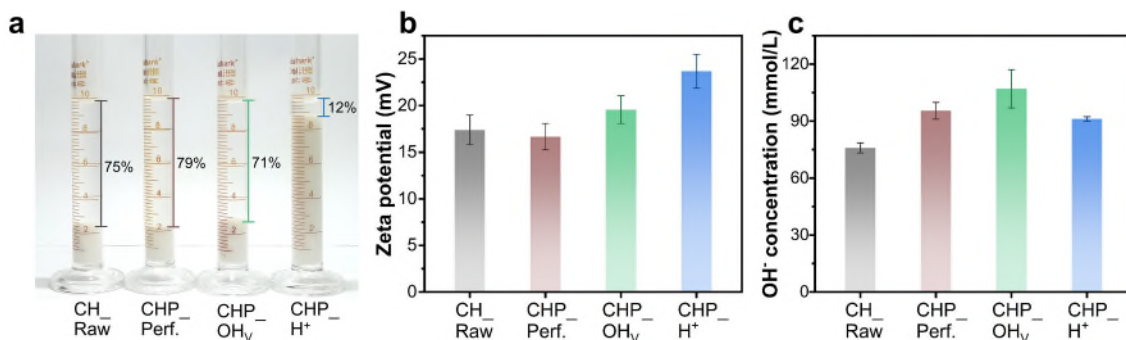


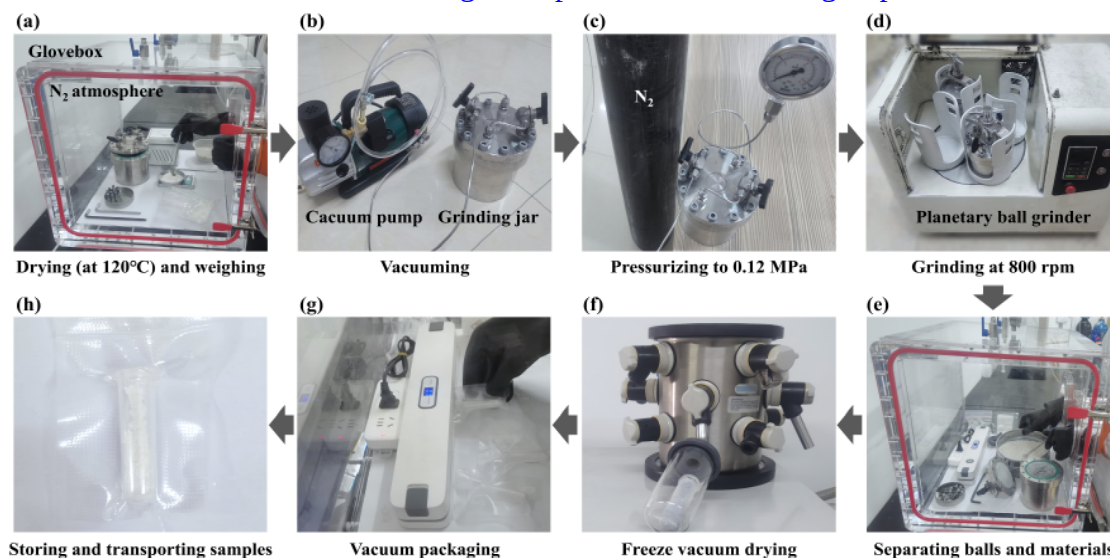
Fig. 2: **a** Photograph of slurries (water/CH = 20/1) prepared from 4 types of CH after settling for 2 days. The number in the photograph means the static settlement rate. **b** Zeta potential of 4 types of CH. **c** OH^- concentration of 4 types of CH.

9. Can more explicit details be provided regarding the drying process for CHP and RCH samples for XRD, XPS, and TG, and what specific precautions were taken to prevent carbonation, given the high susceptibility of fine, wet CH to carbonation?

Reply: Thanks for your comments. To avoid the interference of water vapor and CO_2 in the air on the test results, two approaches were adopted. First, all experiments were conducted in a hermetically sealed, N_2 atmosphere, as shown in Supplementary Fig. 6. Second, as mentioned earlier, two additional control groups were added.

All sample treatments were conducted in an acrylic glovebox under a nitrogen (N_2) atmosphere, including weighing, heating and drying, sealing of grinding jars, sieving, and vacuum packaging, as shown in Supplementary Fig. 6 a, e, g, and h. During the grinding step (Supplementary Fig. 6 b-d), the grinding jar was first evacuated and then purged with N_2 to a pressure of 0.12 MPa. The CHP_H^+ slurry was sealed into test tubes within a glove box, then frozen for 6 hours, and promptly transferred to a vacuum dryer for drying. Following drying, the samples were immediately sealed, transferred to the glovebox, and subjected to heat-drying (120°C for 30 minutes) and sieving, prior to final vacuum packaging. In contrast, CHP_OH_v did not require freezing or vacuum drying and was directly vacuum-sealed. CH_Raw and CHP_Perf. only require heating for drying and vacuum packaging within the glove box. Additionally, although samples

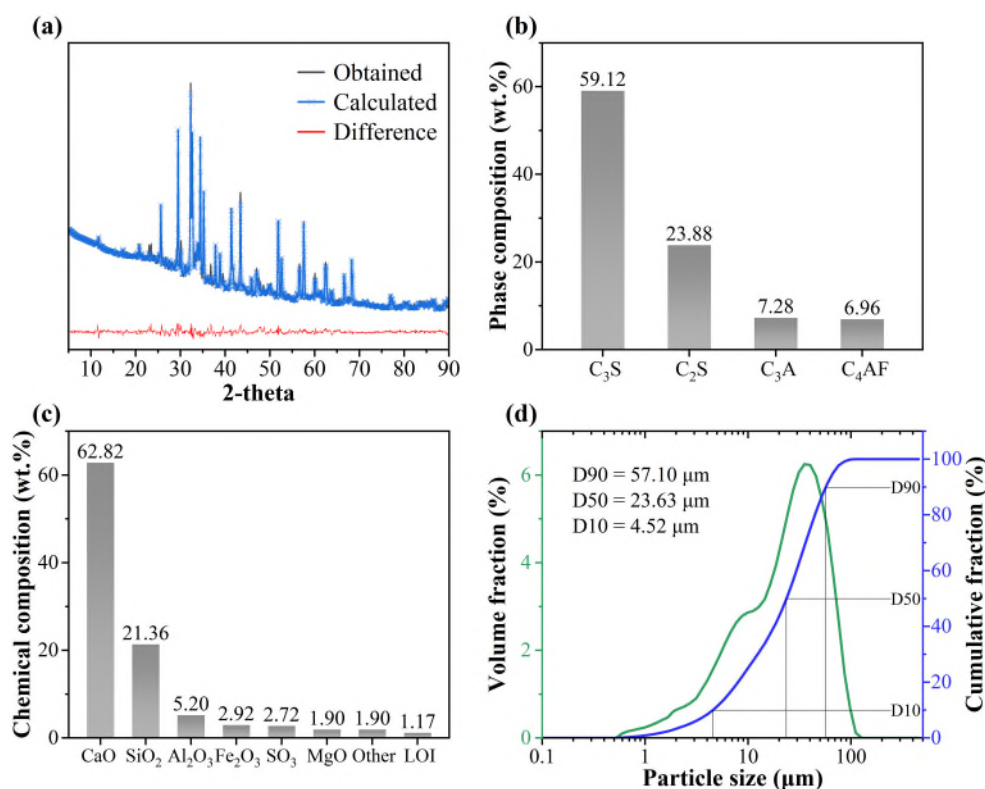
inevitably come into contact with air during testing, this portion of error and interference can be eliminated through comparison with control groups.



Supplementary Fig. 6. Experimental flowchart for the preparation of CHP_OH_v and CHP_H⁺. (a) Drying and weighing of CH samples in a glove box under N₂ atmosphere. For CHP_OH_v samples, CH_Raw, grinding balls, and grinding jars must each undergo heating and drying at 120°C for 30 min. (b) Vacuuming of the grinding jar. The purpose is to remove residual water and CO₂ from the internal piping of the grinding tank during CHP_OH_v preparation. (c) Pressurize the grinding jar. This prevents the grinding jar from drawing in air during the grinding process. (d) Grinding treatment. During operation, cold air is continuously introduced for cooling. (e) Separation of grinding balls from materials in a glove box under N₂ atmosphere. (f) Freeze vacuum drying process. Only CHP_H⁺ slurry is required. CHP_H⁺ slurry was sealed into test tubes within a glove box, then frozen for 6 hours followed by freeze vacuum drying for 48 hours. Finally, CHP_H⁺ was dried on a heating plate for 30 min in a glove box under N₂ atmosphere. (g) Vacuum packaging in a glove box under N₂ atmosphere. Prior to this, CH_Raw and CHP_Perf. will be heated and dried at 120°C for 30 minutes. (h) Storage and transport of samples.

10. What is the detailed chemical composition of the Portland cement used in this study?

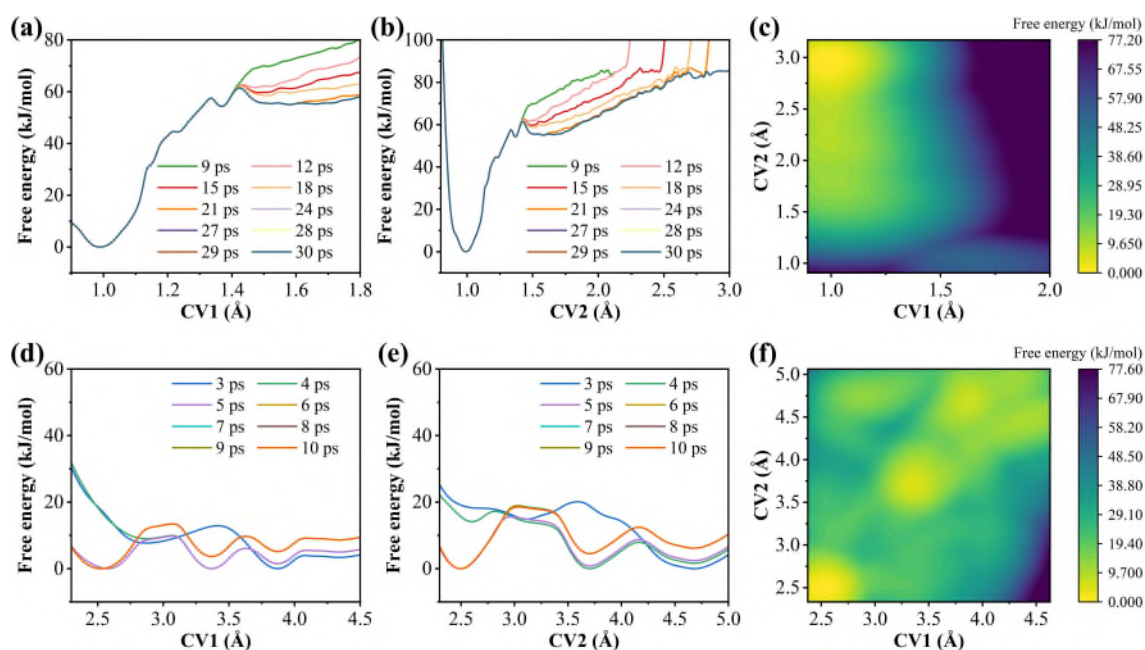
Reply: Thanks for your suggestions. As shown in Supplementary Fig. 24, we have supplemented the basic information on Portland cement, including its phase composition, chemical composition, and particle size distribution.



Supplementary Fig. 24. Characterisation of Ordinary Portland cement (P.O. 42.5 type). (a) X-ray diffraction (XRD) patterns. (b) Phase composition. (c) Chemical composition. (d) Particle size distribution.

11. Can convergence analysis results and explicit details of the production runs be provided for the WT-MetaD simulations?

Reply: Thanks for your comments. Here we provide the time-evolution free energy profiles, which demonstrate the convergence of the metadynamics simulations. Specifically, convergence is achieved when the free energy profile remains unchanged over time. As shown in Supplementary Fig. 27, our simulations ultimately reached a point where the free energy profiles remained stable with further simulation time, indicating that the metadynamics calculations have converged. Specifically, the perfect CH (a and b) exhibits a constant curve in the range of 24 ps to 30 ps, while the CH with OH vacancy (a and b) shows a constant curve of 6 ps to 10 ps.



Supplementary Fig. 27. (a) and (b) Time-evolution free energy profiles of (a) CV1 (Å) and (b) CV2 (Å) of perfect CH during protonation. (c) 2D free energy surfaces at 30 ps of perfect CH during protonation. (d) and (e) Time-evolution free energy profiles of (d) CV1 (Å) and (e) CV2 (Å) of CH with OH vacancy during protonation. (f) 2D free energy surfaces at 10 ps of CH with OH vacancy during protonation.

12. Could "silica" on Line 255 be corrected to "silicate" for accuracy?

Reply: Thank you for your thorough review of our work. "silica" has been revised to "silicate". We conduct thorough checks and revisions of manuscripts to prevent the recurrence of similar issues.

13. Fig. S5, the captions are not consistent with the labels.

Reply: Thanks for your kind comment. We have corrected Supplementary Fig. 5 (now updated to **Supplementary Fig. 22**) and reviewed the entire manuscript to avoid similar errors.

Reviewer #3

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reply: We would like to express our sincere gratitude to you and the co-reviewers for your constructive comments and suggestions on the revision of our manuscript. We have made comprehensive revisions to the manuscript as suggested

Reviewer #4

The manuscript presents a combined experimental and computational investigation of an enhanced calcium hydroxide precursor (CHP) with protonated and disordered structure, assuming that CH is uniformly grown along the different crystal phases of CHP. The effect of CHP on the nucleation, the growth and the distribution of CH in C-S-H gel is also considered. The topic is relevant and of interest to researchers in cement chemistry and materials science. The work is well conducted and the results are generally sound. However, the quality of the writing requires revision. Several sections would benefit from improved clarity, grammar, and style to enhance readability and precision. While the results are solid and contribute to the understanding of CHP behavior, their novelty and broader impact fall short of the high threshold expected for Nature Communications. The reviewer encourages the authors to consider submitting their work to more domain-specific journals, such as:

- Cement and Concrete Research
- Construction and Building Materials

Reply: Thanks for your suggestions. We appreciate your inquiry regarding the novelty of this study, which may stem from our insufficient emphasis on its contributions in the main text. Cementitious materials, as the world's most widely used man-made materials, play an irreplaceable role in global infrastructure construction. However, numerous core scientific issues associated with them, such as the formation mechanisms of key hydration products and the principles governing performance regulation, remain unsolved to this day. This work addresses a persistent challenge in cement science and materials engineering: the inherent mechanical anisotropy and limited toughness of calcium hydroxide (CH, portlandite), a ubiquitous but structurally flawed component in cementitious materials. The work unveils a fundamental proton-transfer mechanism governing the crystallization dynamics of CH and calcium silicate hydrate (C-S-H). It provides the first strategy to achieve isotropic protonated CH and engineer its synergistic integration with C-S-H at the nanoscale (i.e., CH@CSH).

This represents a paradigm shift in designing cementitious materials, moving from mitigating inherent weaknesses to fundamentally reprogramming growth pathways at the atomic level. It enables a new class of high-performance, durable cementitious composites with transformative potential for sustainable construction and infrastructure resilience. The insights into hydrogen-bond-mediated growth control are confined not only to the nucleation mechanism of C-S-H in the cement field (*Nat Commun* 2023, 14, 7979), but also extend to fields like biomineralization, geochemistry, and crystal engineering (*Nat Commun* 2025, 16, 713; *Matter* 2025, 102100; *Nat Commun* 2024, 15, 10790).

In recent years, fundamental research in building materials has garnered increasing attention in *Nature Communications*, which has established a related collection: **Cement and Concrete Innovation for Construction**. We are confident that the discovery of this protonation-driven isotropic growth mechanism and its dramatic impact on mechanical performance presents a pivotal advance worthy of Nature Communications' broad audience.

We have extensively revised the entire manuscript, including enhancing clarity, grammar, and style to improve readability and precision, and providing further evidence for protonation and CH@CSH formation. Here, we hope to gain your appreciation of our research value by reviewing its innovative aspects and our latest findings.

(1) Novelty

We report the first observation of proton transfer in $\text{Ca}(\text{OH})_2$ under wet grinding conditions. Conventionally, protonation typically occurs in acidic environments, e.g., $\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$. After wet grinding, the zeta potential of $\text{Ca}(\text{OH})_2$ significantly increased, even affecting its macroscopic dispersion, as shown in Fig. 2. Furthermore, novel signal peaks have been preliminarily identified via XPS and ^1H NMR tests.

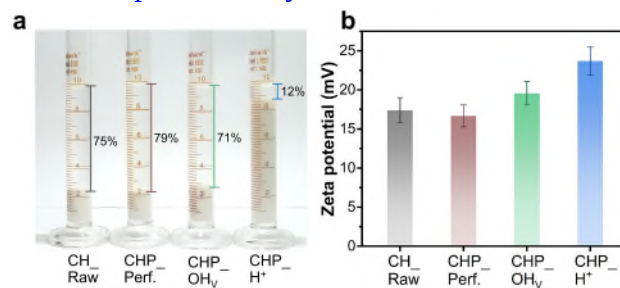


Fig. 2: **a** Photograph of slurries (water/CH = 20/1) prepared from 4 types of CH after settling for 2 days. **b** Zeta potential of 4 types of CH.

To explain this phenomenon, this paper proposes a novel protonation pathway and

demonstrates it through a combined approach of simulation (Fig. 3) and experiment (Fig. 4). Under wet grinding conditions, OH vacancies are first formed in CH, followed by H₂O adsorption at these vacancies and subsequent coordination with calcium to form $\equiv\text{Ca}-\text{OH}_2^+$. Simulation results indicate that this pathway exhibits a lower energy barrier and provides mechanistic insights into the protonation process. The feasibility of this pathway has been confirmed through isotope tracing and in situ experiments.

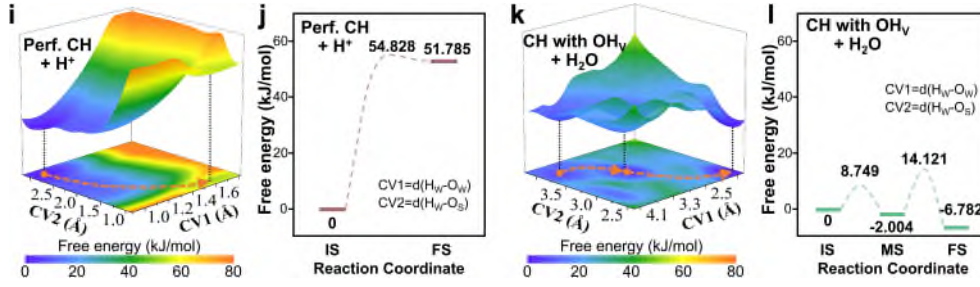


Fig. 3: i and k 3D free energy surfaces of perfect CH and CH with OH_v during protonation. **j and l**

The Free energy changes during the protonation process of the perfect CH and CH with OH_v.

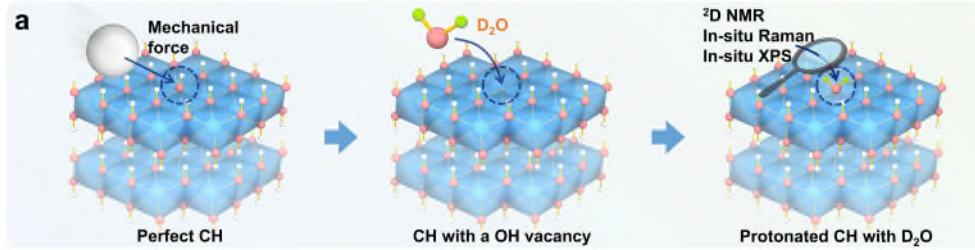


Fig. 4: a Schematic diagram of tracking protons based on the isotope labeling method to verify protonation.

Leveraging the performance characteristics of protonated CH, this study introduced it as a precursor into cementitious materials, thereby regulating and enhancing its primary hydration products, i.e., CH and C-S-H. CHP_H⁺ induced the formation of CH@C-S-H structures through heteronuclear nucleation, thereby enhancing the mechanical properties of C-S-H. CHP_H⁺ reduces the size of CH and mitigates the anisotropy of CH crystals.

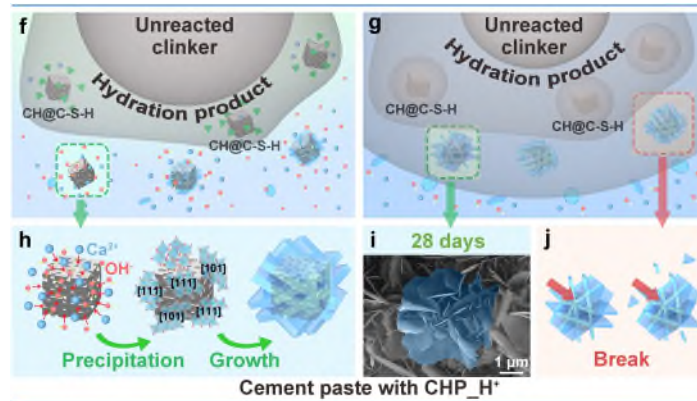


Fig. 8: Microstructural modeling of portlandite growth as the hydration of the cement.

(2) Broader impact

The protonation process disrupts the electrostatic interactions, maintaining the CHP surface in a state of positive charge. It is foreseeable that protonated CH will exhibit adsorption advantages toward anionic groups such as SiO_4^{4-} , CO_3^{2-} , SO_3^{2-} , and CrO_4^{2-} , etc., demonstrating broad application prospects. We supplemented the relevant experimental verification, as shown in Fig. 5. The results indicate that the adsorption capacity of protonated CH towards SiO_4^{4-} significantly increases. It has potential application value in fields such as water treatment, gas purification, and catalysis.

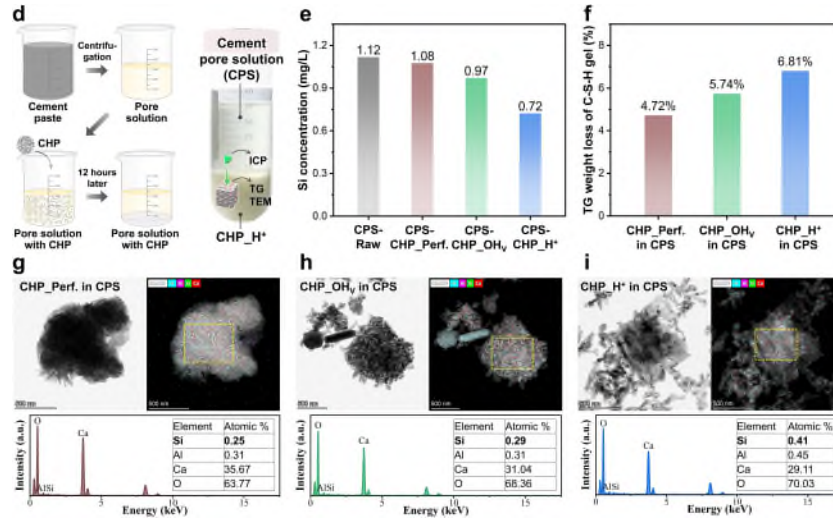


Fig. 5: Effect of protonated CHP on super-nucleation induction in C-S-H gels.

Furthermore, the protonation regulation strategy proposed in this study provides a both universal and innovative design paradigm for the surface functionalization and targeted performance optimization of inorganic functional materials such as metal hydroxides and layered double hydroxides (LDHs).

RESPONSE TO REVIEWERS' COMMENTS

Dear Editor and Reviewers:

We thank all reviewers for their constructive comments on the article. The paper has been further improved following their suggestions. We have responded to the reviewers' comments point-by-point in blue below, and have indicated the revised text in the manuscript in red.

Reviewer #1 (Remarks to the Author):

The authors have addressed the comments.

Reply: We greatly appreciate your recognition. Thank you again for your efforts and time spent in reviewing our research.

Reviewer #2 (Remarks to the Author):

Recommendation: Major Revision

The authors are thanked for the extensive additional work and revisions provided in this round. However, while the volume of data has increased, several critical scientific issues remain unresolved, and in some cases, the new data reveals further contradictions. The manuscript continues to overstate its findings, and the proposed mechanisms remain largely speculative without direct evidence to support the main conclusions.

Reply: We sincerely appreciate your thorough review and valuable comments. We have taken all your concerns very seriously and addressed them one by one with targeted revisions. We have further clarified the key scientific issues, carefully tempered our conclusion statements, and added additional experiments to support the proposed protonation-induced super-nucleation mechanism. Regarding the perceived contradictions arising from the new data, we have added more detailed data analysis and methodological descriptions to thoroughly clarify any misunderstandings. Detailed responses to your comments are mentioned below.

1. Framing and Scope (Title and Abstract)

The title and central claims regarding "modulating growth dynamics" remain an overstatement of the actual study content. The manuscript does not provide explicit

results or investigations into the actual growth process of CH and C-S-H; rather, it demonstrates that early-stage hydration kinetics are accelerated by the addition of ground CH. Furthermore, the "hydrogen-bond-regulated proton transfer" described is a precursor preparation process and should not be confused with the hydration dynamics themselves. The authors must reframe the title and discussion to accurately reflect that this is a study of hydration kinetics and early-age acceleration.

Reply: Thanks for your valuable comments. We fully agree with your insightful comment that the content of this manuscript should be strictly framed as early-age cement hydration acceleration kinetics. Protonation greatly enhances the adsorption capacity of CH surfaces toward $[\text{SiO}_4]^{4-}$, effectively reducing the heterogeneous nucleation energy barrier of C-S-H and thus endowing protonated CH with a "super-nucleation" effect. The most direct experimental evidence for this effect is as follows: 1) In Fig. 5, simulation calculations show an increase in the adsorption energy of $[\text{SiO}_4]^{4-}$, while experiments reveal an increase in the surface C-S-H content. 2) In Fig. 6, the addition of protonated CH accelerates the hydration rate, enhances early-strength, and increases the amount of hydration products. 3) In Fig. 7, the addition of protonated CH increases the UHD C-S-H content and results in the formation of heterogeneous CH products. These data require no indirect inference and provide direct and sufficient substantiation for the core conclusion that protonation promotes nucleation and accelerates hydration. The title and all relevant discussions throughout the manuscript have been precisely revised accordingly.

(1) For the title. We have adopted your suggestion, removed the expression "modulating growth dynamics" which was beyond the scope of this study, and precisely revised the title to focus exclusively on the super-nucleation effect of the protonated CH precursor and the accelerated early-age cement hydration kinetics induced by it, which aligns well with the actual content of this manuscript. The revised title is as follows:

Title

Protonated Portlandite Precursor Unlocks Super-Nucleation for Cement Hydration

(2) For the Abstract. We have removed the descriptions related to "regulation of the actual growth process of CH and C-S-H". In addition, through revision, we have further highlighted the aspects of hydration kinetics and early acceleration. Detailed revisions are as follows:

Abstract

Calcium silicate hydrate (C-S-H) and calcium hydroxide (CH, portlandite) are the dominant hydration products of Portland cement. However, the anisotropic layered CH and uncoordinated nucleation of C-S-H and CH severely restrict the macroscopic performance of cementitious materials. Here, we report a hydrogen-bond-regulated proton transfer strategy to mechanochemically synthesize a positively charged, isotropic disordered CH precursor (CHP_H^+). This precursor serves as a super-growth nucleus to trigger dual heterogeneous nucleation of CH and C-S-H, in situ forming a CH@C-S-H composite. Free energy calculations reveal that hydroxyl vacancies on CH surfaces drive spontaneous water adsorption to generate $\equiv\text{Ca-OH}_2^+$ sites, which stabilize silicate clusters and promote composite growth. The resulting cementitious material shows accelerated hydration kinetics, higher hydration heat release, and greatly improved elastic modulus and compressive strength, delivering a 5.4-fold improvement in 12 h strength over the control. This work provides an atomic-scale design principle for advanced cementitious materials by reprogramming the nucleation and growth pathways of hydration products via protonation regulation.

(3) For the Discussion section. We revised the control group from the CHP-free group to the CHP_Perf. group, aiming to highlight the super-nucleation effect of CHP_H^+ and make it consistent with the core research theme of the manuscript title. Meanwhile, we further elaborated on the acceleration mechanism of early hydration and the microstructure regulation effect at late hydration stage. In light of these revisions, Fig. 8 has been redrawn. Detailed revisions are as follows:

Page 21, line 495-515.

This study reveals the kinetic mechanism of protonation on the surface of CH, and further elucidates the super-nucleation effect of protonated CHP on the hydration process and microstructure evolution of Portland cement. The corresponding hydration behavior and structural evolution are shown in Fig. 8a-e. During the early hydration period (Fig. 8d), protonation endows the surface of CHP_H^+ with $\equiv\text{Ca-OH}_2^+$ active sites (Fig. 8a), enabling it to break through the limitation of conventional CH precursors that only induce homogeneous nucleation of themselves, thus exerting a dual nucleation effect (Fig. 8b). On the one hand, CHP_H^+ provides sites for the oriented nucleation and growth of the CH phase. On the other hand, CHP_H^+ adsorbs $[\text{SiO}_4]^{4-}$ via electrostatic interaction and induces C-S-H nucleation

(Fig. 5a-e), accelerates the nucleation and growth of C-S-H gel (Fig. 6a-c), and forms the CH@C-S-H composite hydration product (Fig. 5f, i). During the hydration process (Fig. 8e), CHP_H^+ continuously exerts a dual regulatory effect (Fig. 8c). It effectively inhibits the coarse and anisotropic growth of the CH phase (Fig. 7k-n), while promoting the formation of UHD C-S-H (Fig. 7d, h, i) and resulting in a dense microstructure (Fig. 6d-i). In contrast, non-protonated CHP can only induce homogeneous growth of CH (Fig. 8h, i), refine the CH crystal structure, and form a conventional HD C-S-H (Fig. 8j). It is difficult to achieve the synergistic regulation and structural optimization of hydration products as seen with CHP_H^+ (Fig. 8f, g). Protonation regulation fundamentally reprograms the growth pathways of cement hydration products at the atomic level, offering a approach to the theoretical design and performance optimization of advanced cementitious materials.

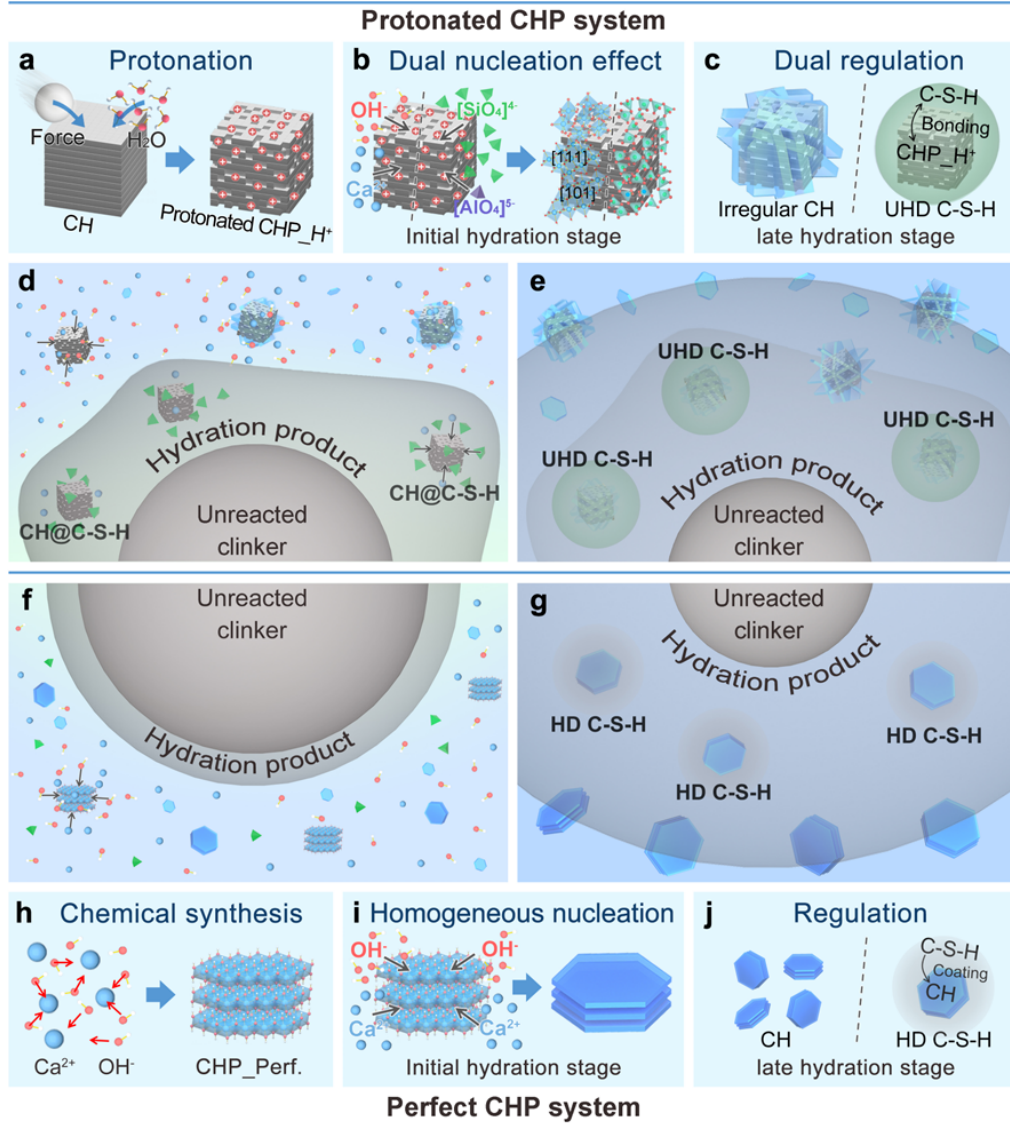


Fig. 8: Schematic showing the dual regulation of cement hydration through the

super-nucleation effect of protonated CHP. **a** Protonation of CH to form CHP_H^+ with positively charged. **b** Dual nucleation effect of CHP_H^+ at the initial hydration stage. **c** Dual regulation of CHP_H^+ on the growth of CH and C-S-H at the late hydration stage. **d and e** Schematic morphological evolution of main hydration products during early (d) and late (e) hydration stages for the protonated CHP system. **f and g** Schematic morphological evolution of main hydration products during early (f) and late (g) hydration stages for the perfect CHP system. **h** Chemical synthesis of perfect CHP. **i** Homogeneous nucleation of perfect CHP at the initial hydration stage. **j** Regulation of perfect CHP on the growth of CH and C-S-H at the late hydration stage.

2. Mechanical Premises and Brittleness

(1) The assertion that "CH acts as the main contributor to the bulk brittleness of cementitious materials" is scientifically inaccurate and misleading. Brittleness is a systemic property arising from the brittle nature of the hydrated paste, microcracking, stress concentrations, and the heterogeneous nature of the composite (C-S-H, CH, pores, and clinkers). **(2)** Additionally, the authors propose modulating growth to overcome this "dilemma," yet they provide no direct evidence of increased toughness or enhanced interlayer bonding strength after the addition of CHP.

Reply: Thanks for your suggestions. Q2 is divided into **2 parts** for detailed response.

Response to Part (1):

We agree with your valuable comment and have revised the abstract accordingly to remove the inaccurate statement attributing bulk brittleness to CH. The revised description more precisely reflects the role of CH in modulating the composite behavior, without mischaracterizing it as the exclusive cause of brittleness. Detailed revisions are as follows:

Page 1, line 4-7.

Calcium silicate hydrate (C-S-H) and calcium hydroxide (CH, **portlandite**) are the dominant hydration products of Portland cement. **However, the anisotropic layered CH and uncoordinated nucleation of C-S-H and CH severely restrict the macroscopic performance of cementitious materials.**

Response to Part (2):

We have revised the relevant parts of the Introduction to describe this dilemma

more rigorously. For example, we have replaced absolute expressions such as “enhance their interfacial bonding strength” with a more appropriate description: “interfacial compatibility with the host matrix (e.g., C-S-H)”. This wording is consistent with our experimental and simulation results. The enhanced adsorption energy from DFT calculations verifies the optimized interfacial interaction between protonated CHP and silicate clusters, and the increased UHD C-S-H fraction from nanoindentation tests confirms the refined interfacial microstructure in the cementitious matrix. Detailed revisions are as follows:

Page 2, line 32-35.

Therefore, the critical barrier in the field is how to optimize the interlayer properties of layered materials (e.g., CH) and enhance their interfacial compatibility with the host matrix (e.g., C-S-H) to break through the bottlenecks restricting the performance and application of these materials.

Page 3, line 62-65.

In this work, we proposed a hydrogen-bond-regulated proton transfer strategy to prepare protonated CH (CHP_H^+) with disordered structure, and guided the heterogeneous nucleation and cooperative formation of CH and C-S-H, achieving super-nucleation of hydrates and breakthroughs in mechanical strength.

3. Characterization and Phase Identification (SEM)

(1) The phase identification in Fig. 7 is highly questionable. The morphologies shown in panels (l), (m), and (n) exhibit thin plates, flakes, and rod-like structures typical of AFm and AFt phases, rather than CH. Given that much of the mechanistic discussion in the "Growth habits" section relies on these images, this misidentification undermines the paper's conclusions. (2) Furthermore, the use of N_2 gas injection to preserve pores for SEM observation (Lines 463-469) likely creates artificial conditions that do not reflect actual CH formation in bulk cement hydration.

Reply: Thanks for your suggestions. Q3 is divided into 2 parts for detailed response.

Response to Part (1):

We have provided SEM-EDS images of typical AFt/AFm phases to more clearly distinguish them from CH, as shown in Supplementary Fig. 25. This clearly demonstrates the needle-rod morphology of the AFt/AFm phase and the prominent Al and S peaks in its EDS spectrum, consistent with existing literature [1, 2]. In addition,

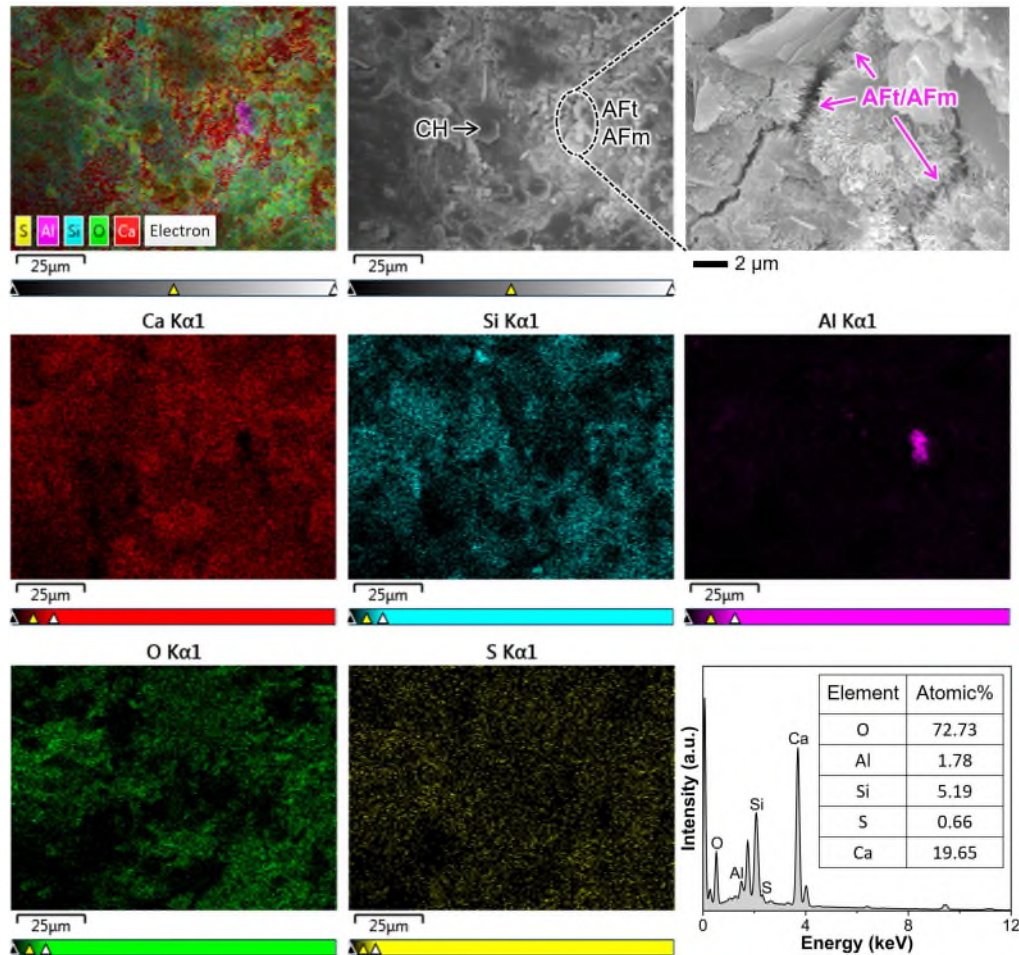
we have provided SEM-EDS surface scan images of Fig. 7k-n (see Supplementary Fig. 26) and re-stained the regions in Fig. 7l-n to correspond to the CH phase, thereby ruling out the potential AFt/AFm phases. The CH regions identified in Supplementary Fig. 26 are rich in Ca and O, with negligible Al and S, in excellent agreement with the expected chemical composition of CH. This revision has further reinforced the reliability of this section of the discussion. Detailed revisions are as follows:

Page 19, line 473-474.

In addition, SEM-EDS of ettringite was provided to distinguish it from CH (Supplementary Fig. 25 and 26).

References

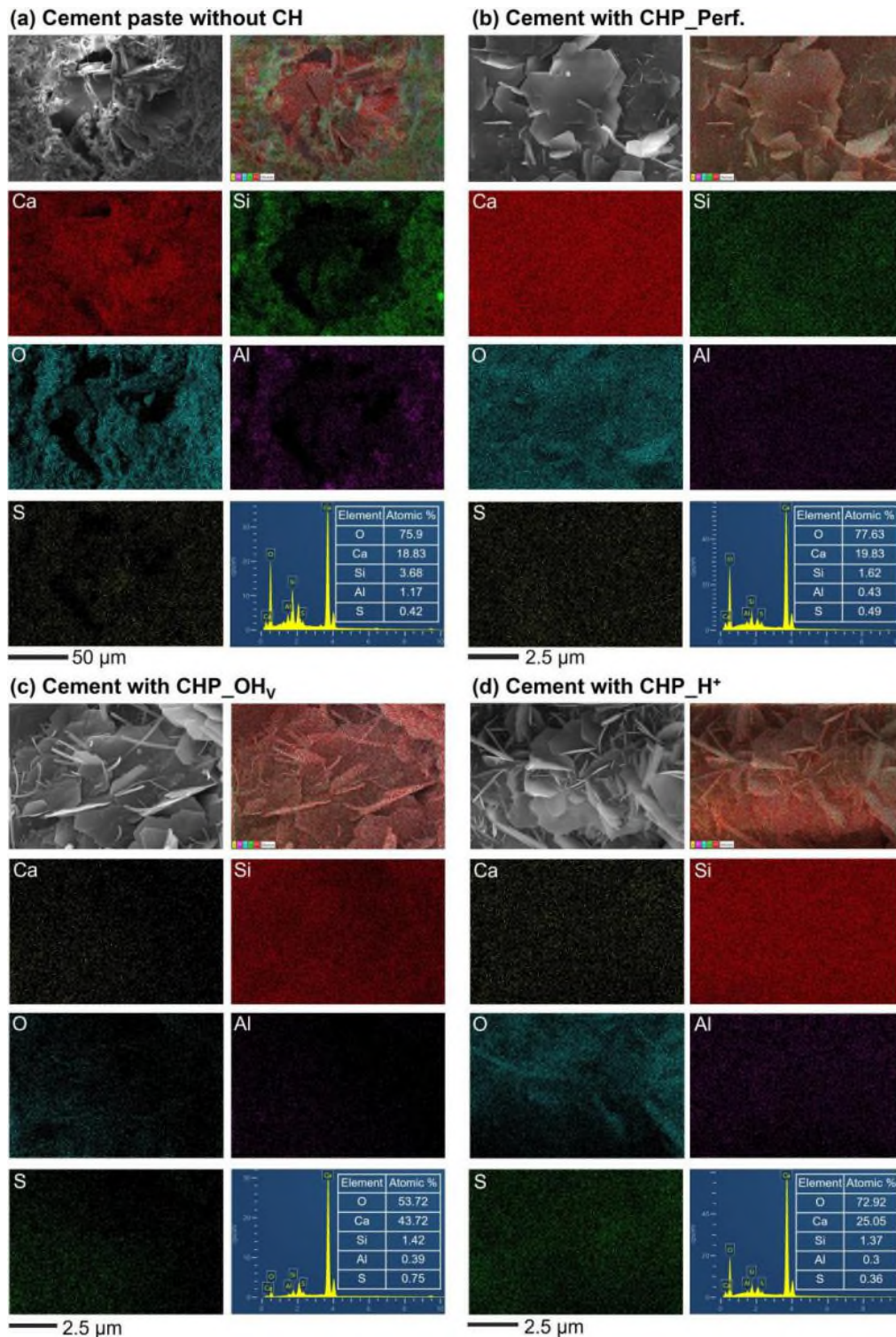
- [1] Georget, Fabien, et al. *Cement and Concrete Research*, 2021,141: 106327.
[2] Nelson, Shaun, et al. *Cement and Concrete Composites*, 2026, 165: 106355.



Supplementary Fig. 25. SEM-EDS surface scan images and element distribution maps of AFt/AFm and CH in cement paste.

Note: AFt/AFm in cement hydration products are mainly rod-shaped or needle-shaped, while CH exhibits a hexagonal plate-like morphology^{7,8}. AFt and AFm correspond to

$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ and $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$, respectively, and Ca, O, Al, and S are detectable in their EDS spectra.

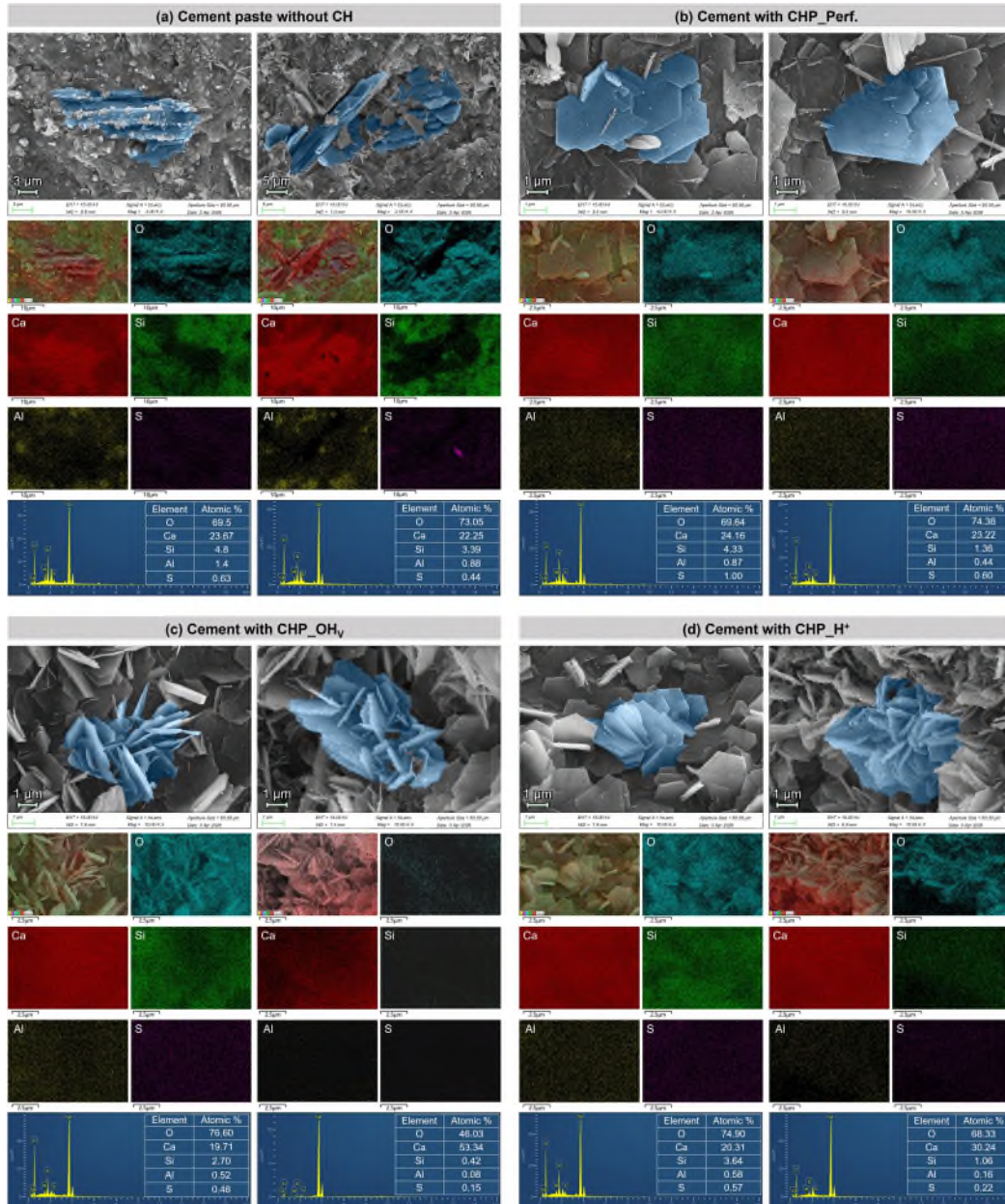


Supplementary Fig. 26. SEM-EDS surface scan images and element distribution maps of CH in cement paste containing artificial micropores at 28 days. (a) Cement paste without CHP. (b) Cement paste with CHP_Perf. (c) Cement paste with CHP_OH_v. (d) Cement paste with CHP_H⁺.

Response to Part (2):

We have provided SEM-EDS images of CH in the conventional samples (without N₂ injection). The results show that the morphological characteristics of CH are consistent between the two types of samples, as presented in Supplementary Fig. 23. These supplementary results effectively improve the reliability and rigor of the corresponding conclusions.

Detailed revisions are as follows:



Supplementary Fig. 23. SEM-EDS surface scan images and element distribution maps of CH in conventional cement paste at 28 days. (a) Cement paste without CHP. (b) Cement paste with CHP_Perf. (c) Cement paste with CHP_OH_v. (d) Cement paste with CHP_H⁺.

Page 18, line 439-443.

The nanoindentation technique addresses the limitations of the test in Fig. 6c in distinguishing gel products and provides deeper insights into the effects of various CHPs on the microstructural mechanical properties of C-S-H gels. Supplementary Fig. 21 shows the proportion of each component and the reasons for discrepancies with quantitative XRD/TG results.

Page 19, line 467-474.

As CH is difficult to observe directly due to encapsulation by C-S-H gel, CH in natural micropore regions was selected for characterization, as shown in Supplementary Fig. 23. Given the randomness in the size and distribution of natural micropores, which could cause observational deviations, we introduced an equal volume of fine N₂ bubbles into fresh samples to create artificial micropores (Supplementary Fig. 24). These artificial micropores further mitigate the inhibitory effect of spatial confinement on CH growth⁵⁰ and provide a stable observation window. In addition, SEM-EDS of ettringite was provided to distinguish it from CH (Supplementary Fig. 25 and 26).

Furthermore, we understand your concern that N₂ injection may introduce artificial factors and affect the representativeness of the observed results. Here we further elaborate on the rationale behind the experimental design. The creation of artificial micropores is both necessary and complementary. During SEM sample preparation, we found that CH encapsulated in the C-S-H gel was damaged during sample cutting, and only CH located in naturally formed micropores or microcracks can retain its intact morphology. However, the occurrence and size of such natural micropores or microcracks are random, which introduces considerable experimental errors and artificial interference. Consequently, sufficient parallel experiments must be performed to obtain statistically reliable results. To resolve this issue, we adopted a targeted strategy: injecting equal volumes of fine N₂ bubbles to induce artificial micropores. This eliminates such random interference, enabling controlled observation of the morphology and distribution of CH. This method does not create non-existent CH; instead, it provides a stable “observation window” for reproducible and traceable characterization of CH.

Detailed revisions are as follows:

Supplementary Fig. 24. Note: Direct characterization of CH morphology within the cementitious matrix is inherently compromised by mechanical sample preparation.

Sectioning and polishing inevitably disrupt the delicate CH lamellae encapsulated within the C-S-H gel, leaving intact morphology observable only within fortuitously exposed natural micropores or microcracks. However, the stochastic distribution and variable dimensions of these natural voids preclude systematic, reproducible observation and introduce significant sampling bias. Therefore, we adopted the method shown in Fig. S24 to induce fine and uniform artificial micropores. This method does not create non-existent CH; instead, it provides a stable “observation window” for reproducible and traceable characterization of CH.

4. Scientific Contradictions and Data Inconsistency

There is a serious inconsistency between the nanoindentation results and the bulk mineralogical data. Comparison of the CH content derived from nanoindentation deconvolution (Fig. 7 and Supp. Fig. 21) with QXRD (Fig. 6c) and TGA (Supp. Fig. 17) reveals contradictory results. Even when accounting for UHD C-S-H as a composite, the fractions do not align. TGA is generally considered more reliable for phase quantification, and Supp. Fig. 17 shows that total CH content (including any potential "CH@C-S-H") does not differ significantly across samples, which directly contradicts the nanoindentation interpretations.

Reply: Thanks for your comments. The inconsistency between nanoindentation results and TGA/QXRD mainly arises from the different testing ranges and distinct physical meanings of the data measured by the two techniques. Nanoindentation and TGA/QXRD provide complementary rather than contradictory information. Detailed explanations are given below:

1. The two testing methods have different ranges of applicability. Nanoindentation covers three types of C-S-H gels (LD, HD, and UHD) and micro-defects. It is effective in distinguishing microregions with different modulus, but struggles to differentiate crystalline phases such as AFt/AFm, C_2S/C_3S , and C_3A , which may be incorporated into other mechanical phases. XRD can precisely identify different crystalline phases. Therefore, the difference in phase identification capability leads to inconsistencies in component quantification between the two methods. In addition, the load-displacement curves obtained from indentation testing are abnormal and unusable for regions containing large pores or cracks, which are precisely the areas susceptible to CH enrichment. Therefore, it is reasonable that nanoindentation testing inevitably underestimates CH content.

2. The physical significance of the results from the two tests differs. The CH content in nanoindentation approximates the volume fraction, whereas the CH content in TG/QXRD test results represents the mass fraction. Specifically, nanoindentation reflects the contribution percentage of each phase in localized mechanical behavior through mechanical response, yielding the volume fraction of mechanical phases. TG/QXRD measures mass percentage. Therefore, the results from these two tests are not directly comparable in physical significance, and numerical differences between them are to be expected.

3. The two tests serve distinct purposes, with complementary capabilities in phase identification. Nanoindentation effectively addresses the limitations of TG/QXRD in identifying gel-type hydration products, and distinguishes the mechanical contributions at the microscopic scale from the CH@C-S-H composite structures derived from different types of CHP. The macroscopic homogeneity revealed by TG/QXRD results and the microscopic mechanical inhomogeneity exposed by nanoindentation authentically reflect the material's properties at different scales, respectively.

Owing to these factors, phase fractions from nanoindentation are typically subject to an inevitable discrepancy with quantitative XRD results in fundamental studies of cementitious materials [1-3]. We have added a note in the appendix to explain the reasons for the quantitative discrepancies between nanoindentation and XRD/TG. In addition, as this study primarily aims to explore the effect of CHP on the mechanical properties of C-S-H gel, macropores and unhydrated clinker-enriched regions were excluded from all indentation test areas to ensure sufficient valid data points. Differences in indentation region selection criteria from prior studies may cause slight discrepancies between our quantitative results and literature reports.

Detailed revisions are as follows:

Supplementary Fig. 21. Note: The quantitative discrepancy between nanoindentation and TG/QXRD results arises from inherent differences between the two techniques, which provide complementary rather than contradictory information for cement-based material characterization. Specifically, they differ in physical meaning: nanoindentation yields volume fractions of mechanical phases via local micromechanical response, while TG/QXRD measures mass fractions of bulk crystalline phases^{3,4}. They also have complementary phase identification capabilities and observation scales, with nanoindentation distinguishing various C-S-H gels but

underestimating CH content from invalid pore-region data, while TG/QXRD accurately quantifies crystalline phases at the macroscopic bulk scale but fails to identify amorphous phases such as C-S-H. In addition, as this study primarily aims to explore the effect of CHP on the mechanical properties of C-S-H gel, macropores and unhydrated clinker-enriched regions were excluded from all indentation test areas to ensure sufficient valid data points.

References

- [1] Liu, Yunze, et al. *Cement and Concrete Composites*, 2022, 134: 104815.
- [2] Zhang, Zhen, et al. *Cement and Concrete Composites*, 2023, 138: 104990.
- [3] Pedrosa, Herman Camilo, et al. *Cement and Concrete Research*, 2020, 129: 105978.

5. Silicate Chain Modeling

In Fig. 6i, the illustrations of (alumino) silicate chains are incorrect. Silicate chain lengths must follow the $3n-1$ rule; therefore, 3-unit or 4-unit chains are not scientifically plausible in this context. These illustrations must be corrected to reflect established silicate chemistry.

Reply: Thanks for your suggestions. We have removed the inset in Fig. 6i. We fully acknowledge that the $3n-1$ rule, which is commonly employed to describe the thermodynamically stable chain-length configurations in the dreierketten structure of ideal C-A-S-H crystals, is a well-accepted principle in silicate chemistry. However, it should be noted that the C-S-H/C-A-S-H gel in cementitious materials exhibits structural disorder and abundant defects. This results in the MCL in ^{29}Si NMR testing potentially not being strictly confined to discrete values of $3n-1$. By removing this inset illustration, we aim to eliminate potential interpretation biases. Detailed revisions are as follows:

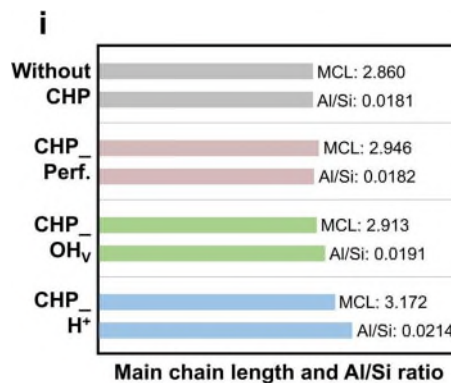


Fig. 6: i The main chain length and Al/Si ratio of cement pastes.

6. Mechanism: Protonation vs. Adsorption

(1) The results in Fig. 4 appear to demonstrate the adsorption of water molecules on a defective surface (CHP_OH_v) rather than a unique protonation process. If a wet-grinding-induced protonation were truly present, the authors should have performed the same tests on CHP_H⁺; theoretically, a truly protonated surface should exhibit less water adsorption compared to the defective CHP_OH_v. (2) The "super-nucleation effect" also requires a precise definition. (3) Furthermore, the fact that all CHP variants result in similar 28-day strengths suggests the effect is driven by the addition of CH itself, rather than the specific grinding conditions or protonation.

Reply: Thanks for your suggestions. Q6 is divided into 3 parts for detailed response.

Response to Part (1):

We acknowledge your point and have supplemented all tests (BET, ²D NMR, in-situ Raman and in-situ XPS) in Fig. 4 with the CHP_H⁺ group, and the results align with your hypothesis. The summary data results are as follows:

First, BET-²D NMR results (Fig.4b-e) show that after two D₂O adsorption-desorption cycles, the reduction in D₂O adsorbed capacity of CHP_H⁺ is smaller than that of CHP_OH_v but larger than that of CHP_Perf., which supports the conclusion that protonation can be induced by water-medium ball grinding. Second, in-situ Raman results (Fig. 4f-i and Supplementary Fig. 11) reveal that -OD characteristic peaks appear for CHP_OH_v and CHP_H⁺ at 7 min and 10 min, respectively, which are attributed to proton transfer driven by protonation. Third, in-situ XPS results (Fig. 4j-m and Supplementary Fig. 12) indicate that the total content of O_v, O_a and O_p in CHP_H⁺ is markedly higher than that in the other two groups, owing to the enhanced characteristic signal at 533.6 eV caused by protonation. Detailed revisions are as follows:

Page 10-11, line 253-259.

The slightly larger reduction rate for CHP_H⁺ relative to CHP_Perf. arises from incomplete protonation of OH vacancies on its surface during water-medium ball milling. Finally, ²D NMR test (Fig.4e) and Raman test (Supplementary Fig. 10) were conducted on the samples after D₂O adsorption-desorption. Both the ²D NMR spectrum and the Raman spectrum of CHP_OH_v and CHP_H⁺ revealed signal peaks associated with D, whereas CHP_Perf. showed no distinct signal peaks.

Page 11, line 265-274.

CHP_Perf. exhibited its initial -OD peak at 25 min (Fig. 4f), attributed to proton exchange induced by CH ionization. In contrast, CHP_OH_v (Fig. 4g) and CHP_H⁺ (Fig. 4h) exhibited -OD peaks at 7 min and 10 min, respectively, attributed to proton transfer induced by protonation. Based on the deconvolution results of the in-situ Raman testing (Supplementary Fig. 11), the variation in -OD proportion is shown in Fig. 4i. Before 20 min, the Ca(OD)₂ contents of CHP_OH_v and CHP_H⁺ increased slowly, corresponding to proton exchange driven by protonation. After 20 min, the Ca(OD)₂ content in all groups rose sharply, suggesting that CH ionization began to dominate the subsequent proton exchange process.

Page 11, line 276-290.

As shown in Fig. 4j-m, in-situ XPS was used to investigate the evolution of the O1s binding energy of the samples during H₂O vapor adsorption and thermal desorption processes. The purpose of this test is to provide experimental evidence for the assignment of the protonated characteristic peak (O_P) in Fig. 2d, and to exclude interference from the O_A and O_V peaks within the overlapping region regarding the assignment of the O_P peak. The three peaks (O_V, O_A, and O_P) near 532-533 eV were deconvoluted into a single composite peak to eliminate the systematic errors caused by subjective peak splitting fitting (Supplementary Fig. 12). After H₂O vapor injection, the relative proportion of the peaks in the 532-533 eV range increased for both CHP_Perf. and CHP_OH_v, and their main peaks shifted toward higher binding energy by 0.4 eV. After stopping H₂O injection and heating for desorption, the O1s spectra of both samples gradually recovered to their initial state. The peak shift is attributed to the variation in the intensity of the O_A peak (ca. 532 eV). In contrast, due to the presence of a signal peak at 533.6 eV for CHP_H⁺, the total content of O_V, O_A, and O_P at each time point is markedly higher than that of the other two groups (Fig. 4m), while its main peak shows a shift of only 0.2 eV (Fig. 4l).

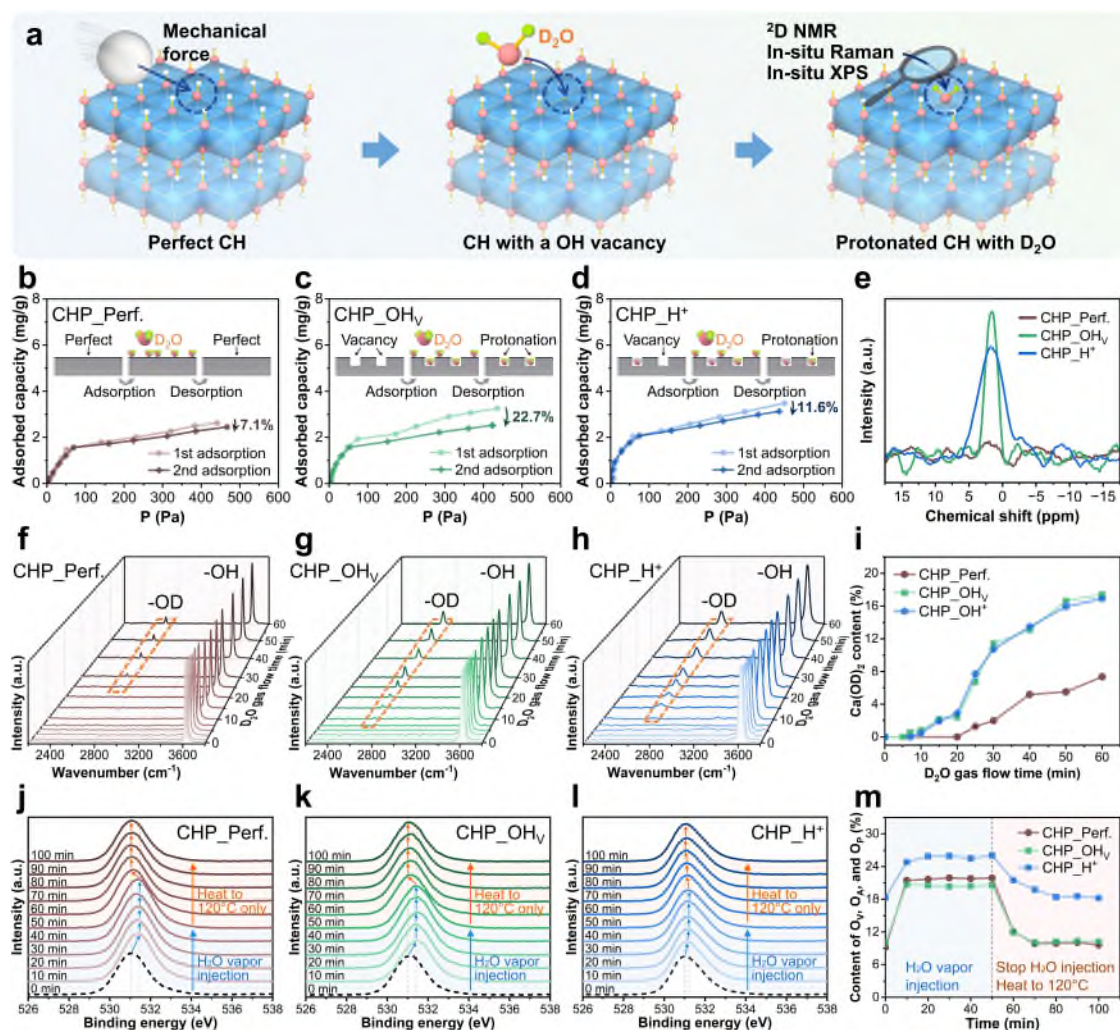
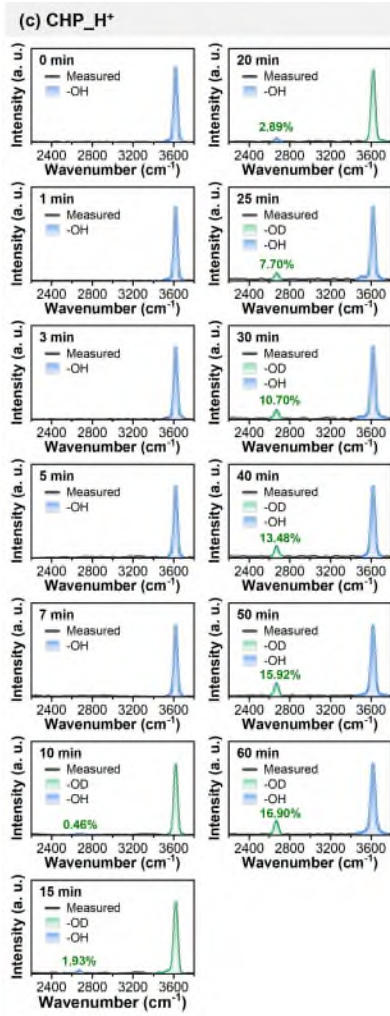
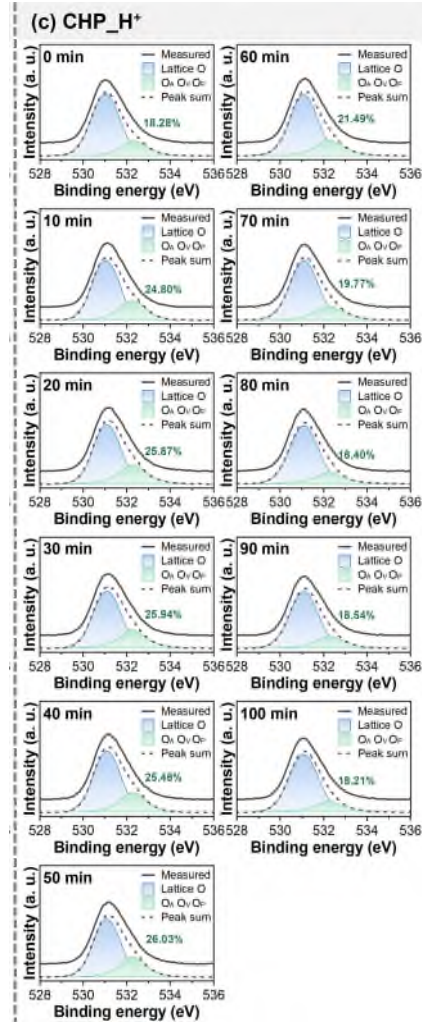


Fig. 4: Mechanism of protonation on CHP surfaces induced by lattice defects. **a** Schematic diagram of tracking protons based on the isotope labeling method to verify protonation. **b-d** D_2O adsorption isotherms of **CHP_Perf.** (b), **CHP_OH_v** (c) and **CHP_H⁺** (d). Each sample was subjected to two consecutive D_2O adsorption-desorption cycles. The schematic diagram above the curve shows D_2O monolayer adsorption on the CH surface followed by desorption. **e** ^2D NMR spectra of the samples after two cycles of D_2O adsorption and desorption. The samples used were those recycled as shown in Fig. 4b-d. **f-h** In-situ Raman spectra of **CHP_Perf.** (f), **CHP_OH_v** (g) and **CHP_H⁺** (h) in D_2O gas atmospheres at different times. The internal stretching vibrations involving -OH and -OD occur at 3610 cm^{-1} and 2664 cm^{-1} , respectively. **i** The proportion of deconvoluted peaks of -OD in Fig. 4f-h. **j-l** In-situ XPS spectra of **CHP_Perf.** (j), **CHP_OH_v** (k) and **CHP_H⁺** (l) during 50 min in H_2O vapor atmosphere followed by 50 min heating at 120°C . **m** The proportion of the deconvoluted O_v , O_a and O_p peaks in Fig. 4j-l.



Supplementary Fig. 11. In-situ Raman spectra of (a) CHP_Perf., (b) CHP_OH_v and (c) CHP_H⁺, along with the percentage of deconvoluted peaks in -OD.



Supplementary Fig. 12. In-situ XPS O1s spectra of (a) CHP_Perf., (b) CHP_OH_v and (c) CHP_H⁺, along with the percentage of deconvoluted peaks (O_V, O_A, and O_P).

Response to Part (2):

We provide a more precise definition of the “super-nucleation effect,” which is crucial for clarifying the innovative contributions of this paper. Here, the “super-nucleation effect” specifically refers to an enhanced nucleation effect induced by mechanochemical methods following the protonation of CHP. This effect represents an extension of the classical nucleation effect within the cement system. Following protonation, the physicochemical properties of the CHP surface undergo fundamental changes (e.g., the formation of $\equiv\text{Ca}-\text{OH}_2^+$ active sites). Compared to unmodified CHP, it exhibits a stronger surface charge, higher adsorption energy for $[\text{SiO}_4]_4^-$, and an enhanced ability to improve the structure and particle size of the CH

products. We have provided a detailed and precise description in the manuscript, as follows:

Page 21, line 495-515.

This study reveals the kinetic mechanism of protonation on the surface of CH, and further elucidates the super-nucleation effect of protonated CHP on the hydration process and microstructure evolution of Portland cement. The corresponding hydration behavior and structural evolution are shown in Fig. 8a-e. During the early hydration period (Fig. 8d), protonation endows the surface of CHP_H^+ with $\equiv\text{Ca-OH}_2^+$ active sites (Fig. 8a), enabling it to break through the limitation of conventional CH precursors that only induce homogeneous nucleation of themselves, thus exert a dual nucleation effect (Fig. 8b). On the one hand, CHP_H^+ provides sites for the oriented nucleation and growth of the CH phase. On the other hand, CHP_H^+ adsorbs $[\text{SiO}_4]^{4-}$ via electrostatic interaction and induces C-S-H nucleation (Fig. 5a-e), accelerates the nucleation and growth of C-S-H gel (Fig. 6a-c), and forming the CH@C-S-H composite hydration product (Fig. 5f, i). During the hydration process (Fig. 8e), CHP_H^+ continuously exerts a dual regulatory effect (Fig. 8c). It effectively inhibits the coarse and anisotropic growth of the CH phase (Fig. 7k-n), while promoting the formation of UHD C-S-H (Fig. 7d, h, i) and resulting in a dense microstructure (Fig. 6d-i). In contrast, non-protonated CHP can only induce homogeneous growth of CH (Fig. 8h, i), refine the CH crystal structure, and form a conventional HD C-S-H (Fig. 8j). It is difficult to achieve the synergistic regulation and structural optimization of hydration products as seen with CHP_H^+ (Fig. 8f, g). Protonation regulation fundamentally reprograms the growth pathways of cement hydration products at the atomic level, offering a approach to the theoretical design and performance optimization of advanced cementitious materials.

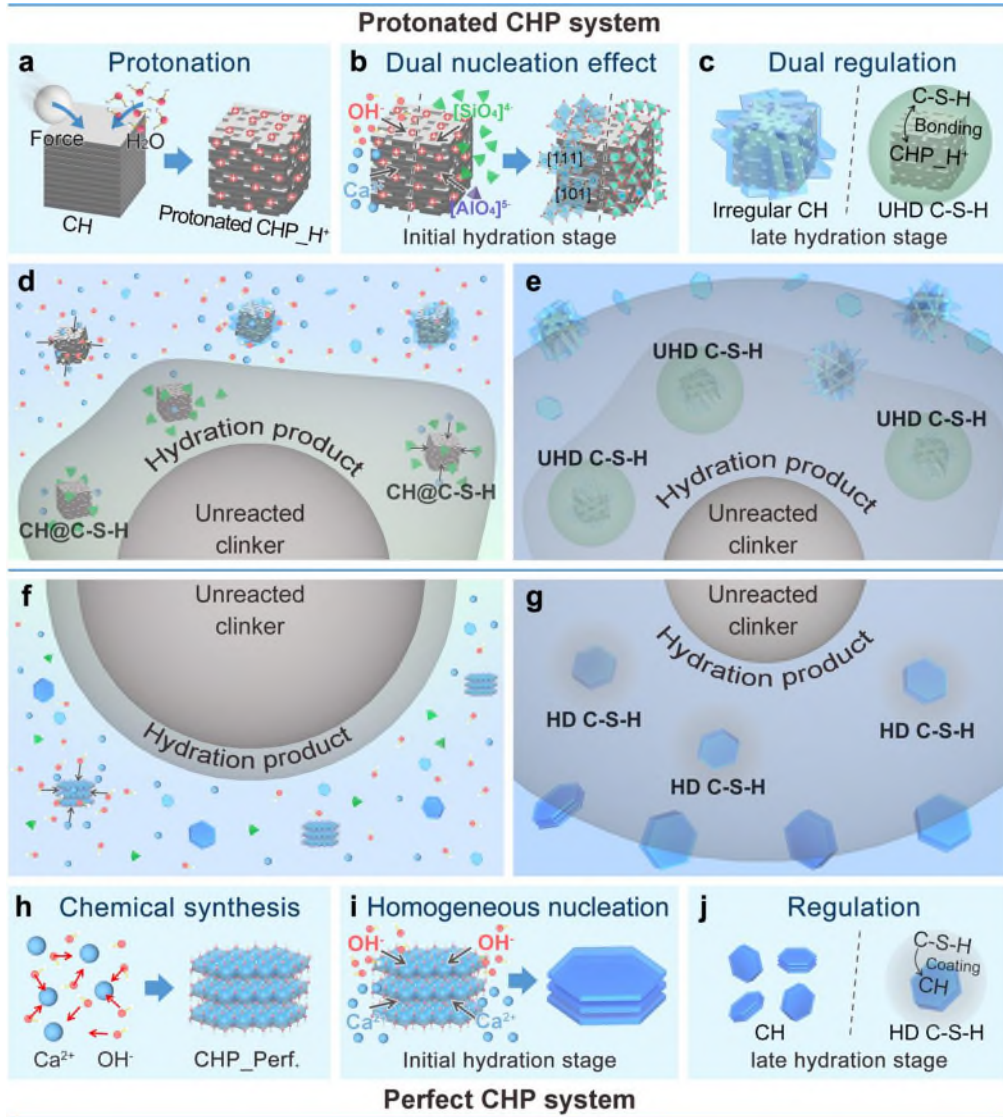


Fig. 8: Schematic showing the dual regulation of cement hydration through the super-nucleation effect of protonated CHP. **a** Protonation of CH to form CHP_H^+ with positively charged. **b** Dual nucleation effect of CHP_H^+ at the initial hydration stage. **c** Dual regulation of CHP_H^+ on the growth of CH and C-S-H at the late hydration stage. **d and e** Schematic morphological evolution of main hydration products during early (d) and late (e) hydration stages for the protonated CHP system. **f and g** Schematic morphological evolution of main hydration products during early (f) and late (g) hydration stages for the perfect CHP system. **h** Chemical synthesis of perfect CHP. **i** Homogeneous nucleation of perfect CHP at the initial hydration stage. **j** Regulation of perfect CHP on the growth of CH and C-S-H at the late hydration stage.

Response to Part (3):

Your observation that the compressive strengths of the samples were similar at 28 days is a key aspect of our experimental design. In terms of the temporal evolution

of the hydration process, the super-nucleation effect of CHP_H^+ exhibits distinct action mechanisms and manifestation characteristics at the early and late stages of hydration.

At the early hydration stage, as shown in Fig. 6a-b, the CHP_H^+ group presents a faster hydration rate, higher early-age strength, and a larger amount of hydration products compared with the other CHP groups (CHP_Perf. and CHP_OH_v). This result demonstrates that the super-nucleation effect during early hydration is driven not only by the intrinsic nucleation effect of CH itself, but also by the additional enhancement effect induced by protonation modification as a core driving factor.

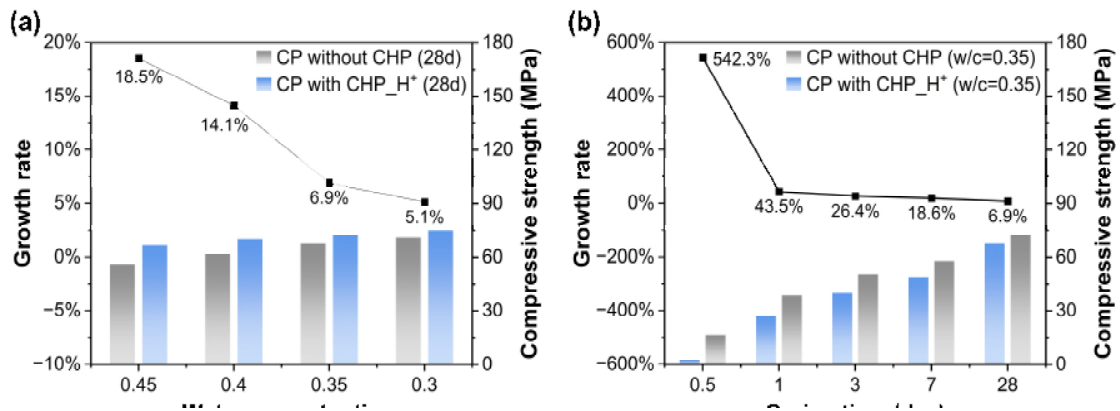
At the late hydration stage, the super-nucleation effect of CHP_H^+ shifts from enhancing macroscopic mechanical properties to strengthening the microstructure. To verify this hypothesis, it is necessary to eliminate the interference caused by differences in the hydration product content and strength, so as to accurately identify the additional improvement effects resulting from protonation. It is a well-established consensus in cement hydration research that the reaction is ultimately limited by available space and water [1, 2]. Once the space is sufficiently filled with hydration products and pore water is largely depleted, the hydration reaction enters a plateau stage, during which the increase in hydration product content and strength nearly stagnates. By adjusting the water-binder ratio and curing age, we ensured that the product content and strength of the CHP_Perf. and CHP_OH_v groups reached a level comparable to that of the CHP_H^+ group at 28 days. The results indicate that protonated CHP drives the improvement of the microstructure of the hydration products, as evidenced by the higher UHD C-S-H content, optimized pore size distribution, and increased MCL in the CHP_H^+ group (Fig. 6d-g and Fig. 7).

In summary, only protonated CHP_H^+ can exert the “super-nucleation effect” which not only greatly accelerates the hydration reaction but also markedly improves the microstructure of the hydration products. The similarity in strength at 28 days serves as further evidence that the advantages of protonation lie not only in increasing the quantity of products but also in enhancing their quality. The relevant revisions are as follows:

Page 18, line 444-455.

In this study, the water-cement ratio and curing age (28 days) were adjusted to achieve similar compressive strength and phase composition across all groups (Supplementary Fig. 22), facilitating the precise distinction between the nucleation

and filling effects of CHP and the additional improvement effect resulting from protonation. Previous studies have indicated that the restricted hydration space allows nanoscale CH to be tightly embedded within the C-S-H gel, resulting in a CH@C-S-H composite structure that contributes to the enhanced mechanical performance of the gel phase^{13, 14, 15}. The nano-micron scale of CHP_Perf. and CHP_OH_v provided the initial conditions for the formation of this composite structure, leading to a notable increase in HD C-S-H phase content compared with the group without CHP. Furthermore, the super-nucleation effect induced by protonation modification further promoted the formation of UHD C-S-H, increasing its content in the CHP_H⁺ group from 3.9% in the CHP-free group to 17.4%.



Supplementary Fig. 22. Growth rate of compressive strength. (a) Cement pastes with different water-to-cement ratios at 28 days. (b) Cement pastes at different ages of curing with w/c=0.35.

Note: The hydration reaction of cement is ultimately limited by available space and water^{5, 6}. Once the space is sufficiently filled with hydration products and pore water is largely depleted, the hydration reaction enters a plateau stage, during which the increase in hydration product content and strength nearly stagnates. Accordingly, w/c = 0.35 and curing age = 28 d were selected, as the compressive strength difference between the CHP_H⁺ group and the group without CHP was only 6.9%. Samples with w/c = 0.3 were excluded due to poor workability.

References

- [1] Scrivener, Karen, et al. *Cement and Concrete Research*, 2019, 124: 105823.
- [2] Bullard, Jeffrey W., et al. *Cement and Concrete Research*, 2011, 41(12): 1208-1223.

7. Methodological Clarifications

- (1) - Provide detailed preparation procedures for CH_Raw and CHP_Perf, including how particle size was controlled.
- (2) - Specify the CHP/water ratio used for ultrasonic dispersion and the criteria for selecting nanoindentation regions.
- (3) - Clarify the age of the samples in Fig. 7 (12 hours or 28 days).

Reply: Thanks for your detailed suggestions. We respond to each of the three methodological questions point-by-point below, with all updates reflected in the manuscript.

Response to Part (1):

We would like to clarify that CH_Raw and CHP_Perf. were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. and Hebei Yuanying New Materials Co., Ltd., respectively, as described in the Materials section. Both are commercial products and were not prepared in our laboratory. We have revised the manuscript to clarify that CH_Raw and CHP_Perf. are commercial products.

Page 3, line 79-83.

CH_Raw and CHP_Perf. were commercial products manufactured via chemical synthesis (Fig. 1a), with average particle sizes (D_{50}) of 7891.5 nm and 223.2 nm, respectively. CHP_OH_v and CHP_H⁺ were both prepared from CH_Raw via mechanical grinding (Fig. 1b), with D_{50} of 260.4 nm and 247.9 nm, respectively.

We have provided a technical document covering the key preparation details of CH_Raw and CHP_Perf. This document, obtained through consultation with the supplier, describes the preparation process in a manner that avoids potential intellectual property disputes. Their production process parameters, equipment models, and other relevant information constitute the manufacturer's trade secrets and are protected by intellectual property regulations. In addition, the supplier has provided relevant references on the laboratory preparation of CH with various particle sizes for reference [1-5]. Technical document as follows:

CH_Raw is produced from high-purity limestone, which is calcined at above 1000°C to form crude CaO. Impurity particles are removed through mechanical sorting to obtain high-purity CaO. Subsequently, under computer program control, the crushed CaO is pretreated with water, followed by primary digestion and secondary digestion in sequence. Under controlled temperature, stirring intensity and water-to-CaO ratio, CaO reacts sufficiently with water to form CH. After air

classification and residue removal, the final calcium hydroxide product is obtained. The calcium hydroxide powder is finally collected and hermetically packaged. The preparation of CHP_Perf. is similar to that of CH_Raw. The method for controlling particle size involves strictly regulating the concentration of reactants, temperature, mixing rate, and ammonia-based agents during the digestion stage, followed by sufficient ultrasonic dispersion and fractional sieving of the resulting precipitates. Finally, various size-specific products with average particle sizes of about 20 nm, 50 nm, 100 nm, 200 nm, and 500 nm are prepared.

References

- [1] Zhang, Huiying, et al. *Environmental Chemistry Letters*, 2018, 16: 1095-1100.
- [2] Cardenas-Alvarado, Aldo A., et al. *Food Chemistry*, 2025, 486: 144639.
- [3] Wang, Jian, et al. *Cement and Concrete Research*, 2020, 138: 106250.
- [4] Wang, Jian, et al. *Cement and Concrete Research*, 2022, 152: 106670.
- [5] Taglieri, Giuliana, et al. *Advances in Materials Physics and Chemistry*, 2014, 4: 50-59.

Response to Part (2):

We have provided additional details in the manuscript. The CHP/water ratio for ultrasonic dispersion was 1:7. Regions for nanoindentation were selected to avoid cracks, large pores and large cement clinker particles to ensure sufficient valid data points.

Response to Part (3):

All specimens in Fig. 7 were cured for 28 days. We have reviewed the entire manuscript to eliminate any similar issues.

Reviewer #3 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reply: We would like to express our sincere gratitude to you and the co-reviewers for your constructive comments and suggestions on the revision of our manuscript. We have made comprehensive revisions to the manuscript as suggested.

Reviewer #4 (Remarks to the Author):

The authors make a significant and deeply revision of the paper. Therefore, I accept the publication of the paper in the present form.

Reply: We greatly appreciate the reviewer's positive comments on our manuscript. Thanks again for the efforts and time spent in reviewing our research.