Morphogenesis of cement hydrate†

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As the most widely used synthetic material on the planet, concrete poses a serious societal concern regarding its significant environmental footprint. There is a global urgency to develop innovative strategies to develop greener concrete with improved strength and durability (to do more with less). In this context, reducing cement hydrate porosity via tuning the kinetics and morphology of its building blocks is highly desired but a fundamental challenge. Herein, we propose for the first time a unique pathway involving in situ seed generation and subsequent controlled overgrowth, demonstrating the morphogenesis of cement hydrate ranging from cubic, rhombohedral, dendritic to core–shell-like structures, which are all expressed in a single morphology diagram. Probing the mechanics of individual particles versus their assemblies at larger scales reveals that the low porosity attained by the formation of face-to-face close-packed cubic particles leads to significantly improved mechanics, opening up an entirely new phase space for bottom-up engineering of concrete while curbing its negative environmental impacts.

With more than 3 billion tons a year, cement is a key infrastructure material and the most energy intensive component of concrete. The manufacture of cement contributes to 5–10% of the total CO2 emissions worldwide. One strategy to reduce this environmental footprint is increasing the concrete’s specific strength and durability by improving the microstructure of cement hydrate, the binding phase of concrete. In this context, reducing cement hydrate porosity via tuning the kinetics and morphology of its basic building blocks, calcium–silicate–hydrate (C–S–H), is a highly desired approach but a fundamental challenge. This is because C–S–H has a variable stoichiometry and distorted layered structure with multiple defects and porosities.

As one of the most structurally complex gels, C–S–H is an important class of materials with broad applications in fields ranging from cementitious and refractory materials to bone-tissue engineering and drug delivery. Obtaining control over the morphology of C–S–H, which is known to influence the various properties of nanosystems, can be beneficial for all these applications. However, despite the significant progress achieved in shape-control of simple crystalline metallic and semi-conductor particles, controlling the nanoscale structure and the morphology of C–S–H at a single particle level has long been an engineering pursuit. Although conventional synthetic methods including pozzolanic and double decomposition reactions can generate C–S–H with controlled stoichiometry, they lack control over the product size and shape. Recently, it was shown that the chemical composition, silica polymerization, and hydration rate of C–S–H can be controlled by introducing synthetic C–S–H seeds with prescribed stoichiometries. However, size- and shape-control of C–S–H remained an essential challenge.

While researchers achieved notable progress towards the shape-control of crystalline members of the C–S–H family including wollastonite, xonotlite, and tobermorite systems, amorphous or poorly crystalline members saw only limited success. Despite the development of advanced strategies such as sol–gel, hydrothermal, microwave-assisted, reaction-rate controlled precipitation, sonochemical, and CaCO3 nanoplate network templated methods, synthesis of C–S–H only in the form of needles, hollow microspheres, hollow ellipsoidal capsules, and ultrathin sheets was possible. Moreover, many of these approaches require high temperature or pressure, prolonged reaction times, and use of organic precursors. Thus, currently there exists a knowledge-gap in developing an efficient, environmentally benign method in attaining full control over the shape and size of C–S–H particles, which govern their microstructures and properties at larger scales.
Herein, we report a comprehensive study elucidating the morphogenesis of C–S–H particles. To the best of our knowledge, this is the first report on the synthesis of cubic and rectangular C–S–H particles, illustrating the prospect of treating C–S–H on equal footing with crystalline particles in the current applications of shape-induced self-assembly mechanisms to create programmable microstructures with encoded properties. Validated by several control experiments, we propose an in situ generation of CaCO₃ seed particles and a subsequent seed-mediated growth mechanism for the shape-controlled synthesis of C–S–H. Moreover, we developed a nanoindentation-based strategy to evaluate the mechanical properties of C–S–H at the level of individual particles. This novel strategy led to interesting counterintuitive observations regarding the mechanical properties of single particle C–S–H. Together, the unique morphogenesis strategy in combination with the new property evaluation algorithm reported in this work is versatile and can be adapted to several systems beyond C–S–H.

Results

Our studies on complex metal oxide systems indicated that the amount of capping agent and solvent/metal ratio can critically influence the shapes of resulting particles. The intricate, highly non-stoichiometric structure of C–S–H makes its morphology modulation challenging and exciting. In particular, prior to this work, the synthesis of C–S–H with well-defined shapes such as cubes and rectangular prisms has never been achieved. We found that under ideal reaction conditions (0.8 mM of cetyltrimethylammonium bromide (CTAB) and Ca/Si of 1.5) in the presence of ultrasonic sound, fast reaction kinetics result in the formation of congruent, isomorphic cubic and rectangular-prismatic particles (0.4–0.8 µm in size). The kinetics of the reaction were analyzed using UV/Vis spectroscopy and it was found that most of the reaction is completed within first 25 min of reaction (Fig. 1a–c, ESI 1†). However, to establish complete reaction, the mixture was kept in the sonication bath for a minimum of 60 min. Decreasing Ca/Si ratios (Ca/Si = 1) yielded more spherical particles and smaller cubes (Fig. 1a) while increasing the ratio (Ca/Si = 2.0) resulted in highly agglomerated C–S–H spheres and cubes interdigitated with larger C–S–H cubes (Fig. 1c). This could be due to the increased supply of calcium for nucleation and overgrowth (see the mechanism, Scheme 1). Removing sonication under all conditions yielded irregular particles pointing to the importance of ultrasonic sound in attaining the optimal reaction kinetics and regular C–S–H particles (ESI 2†). The yield of cubic particles is about 60% and the non-cubic particles are mostly smaller in size, less than 100 nm. The SEM images in ESI 2† show the concentration of non-cubic products.

Evaluating the structure, chemical composition, and extent of silicon polymerization

To decode the elemental composition of cubes and to distinguish them from calcite, which are known for similar morphologies, energy dispersive X-ray spectroscopy (EDAX) was used. The EDAX spectrum and elemental mapping (Fig. 1d–h) confirmed the formation of C–S–H particles primarily composed of Ca, Si, and O (with traces of carbon). The high-resolution transmission electron microscopy (HRTEM) of the cubes demonstrated the presence of two prominent planes with interplanar distances of 3.0 and 5.2 Å corresponding to the (110) and (101) planes of the C–S–H, respectively (Fig. 1i–k). The presence of the (101) plane on the cubes again established the C–S–H formation. Selected area electron diffraction (SAED) of the cubes exhibited diffuse ring patterns characteristic of poorly crystalline C–S–H. It should be noted that due to the gel-like (water containing) interior architecture, C–S–H can undergo rapid dehydration under the exposure of an electron beam leading to material disintegration and conversion into a disordered structure (Fig. 1i, ESI 3†). As a result, analysis of the poorly crystalline C–S–H structures can be very problematic. However, on careful analysis, blurred bright spots corresponding to the (110) planes of C–S–H were also seen, indicating small crystalline islands integrated into an amorphous/semicrystalline matrix, consistent with the HRTEM images (Fig. 1j–k).

Fig. 1m illustrates the X-ray diffraction (XRD) spectrum of C–S–H cubes. The presence of intense (110) and (200) peaks at 2θ = 29.2° and 32.0° and less intense features around 16.9°, 49.8°, and 55.3° corresponding to (101), (020), and (310) planes reveals the formation of C–S–H particles (ICDD, 00-034-002). Thermogravimetric analysis (TGA) curves of the samples resemble the typical curves for C–S–H with the first peak located between ambient temperature and 250 °C (attributed to the removal of adsorbed and interlayer water), followed by a low intensity peak (240–460 °C) possibly due to the removal of constitutional water from the C–S–H, and a final minimal mass loss between 550 and 950 °C corresponding to the loss of CO₂ (Fig. 1n). The small amount of CO₂ observed in TGA analysis again confirmed that the formed particles are C–S–H and not calcite.

To probe the chemical architecture and silicon polymerization in cubic C–S–H, we used Silicon Magic-Angle Nuclear-Magnetic-Resonance (²⁹Si-MAS-NMR) and Fourier transform infrared spectroscopy (FT-IR). The ²⁹Si-MAS-NMR spectra exhibited end chain silicate (Q¹) and bridging silicate (Q²) tetrahedra at about −79.9 and −85.5 ppm for all Ca/Si ratios (Fig. 1o). Features at −92.1 ppm (a mixture of Q² and Q³ corresponding to cross-linked silicate tetrahedra) and −97.1 ppm (Q³) were also seen. Interestingly, the spectrum of C–S–H with Ca/Si = 2.0 predominantly showed Q¹ and Q² peaks with a low intensity Q³ due to the higher quantity of calcium inhibiting silicate cross-linking (Fig. 1o). It is reported that surfactants such as CTAB can enhance polymerization and significantly increase the Q³/Q¹ ratio in the C–S–H structure. Here, we suggest that while the presence of CTAB is favorable for the higher polymerization of C–S–H, other stimulants such as sonication and resultant heating of the reaction medium can increase the degree of polymerization. Thus, we postulate that the presence of the small amount of Q³ is the result of all the parameters mentioned above or the locally low Ca/Si ratio that leads to more polymerized silicate sites. The FT-IR spectrum of the cubic sample illustrated Si–O stretching vibrations (∼970 cm⁻¹), Si–O–Si bending bands (∼667 cm⁻¹), and asymmetric
Fig. 1 Characterization of cubic particles. (a–c) SEM images of C–S–H products with Ca/Si = 1.0, 1.5, and 2.0. The insets show particle size distribution histogram (bottom left), a higher magnification image (top right in (b)). Scale bar is 2 μm. (d–g) Elemental mapping of the C–S–H microstructure by SEM-EDAX. Scale bar is 1 μm in (d). (h) EDAX of the C–S–H products with a Ca/Si of 1.0, 1.5 and 2.0. (i) TEM image of the cubic particles under TEM with Ca/Si = 1.5. (j and k) HRTEM of the cubic particles with Ca/Si = 1.5. Scale bar is 3 nm in (j and k). The insets show zoom-in pictures where the interlayer distances of (101) and (110) crystalline planes are visible. (l) SAED of the cubic particles with Ca/Si = 1.5. (m) XRD pattern of the product with a Ca/Si of 1.0, 1.5 and 2.0. (n) TG analysis of the product after 2 h (blue) and 8 h (red) sonication. (o) $^{29}$Si MAS NMR of the C–S–H product with a Ca/Si of 1.0, 1.5 and 2.0.
stretching ($\nu_3$, 1420–1480 cm$^{-1}$) corresponding to the polymerized silicate chain in C–S–H,$^{46}$ in addition to the out-of-plane bending ($\nu_2$, $\sim$876 cm$^{-1}$) of the CO$_3^{2-}$ group of calcite seeds (see ESI 4† and the following nucleation mechanism).

**Particle nucleation and growth mechanism**

Nucleation is a crucial step of particle formation that influences the growth mechanism and consequently the final particle morphology. Here, the reactions were done under ambient conditions without air flow control or removing dissolved CO$_2$. Hence, the dissolution of CO$_3$ in water (solvent) introduces a third ion (CO$_3^{2-}$) into the reaction mixture in addition to Ca$^{2+}$ and SiO$_3^{2-}$ (identified by the decrease in pH from 11.5 to 11.3). We hypothesize, based on the free energy of formation and stability,$^{46}$ that Ca$^{2+}$ in the presence of CO$_3^{2-}$ and SiO$_3^{2-}$ will selectively react with CO$_3^{2-}$ and propose an *in situ* seed-mediated, surfactant assisted oriented overgrowth mechanism for the formation of C–S–H cubes (Scheme 1).

The initial reaction will generate CTAB stabilized nano-size rhombohedra/cubic calcite seeds that can undergo ordered recombination to microcubes under abundant supply of carbonate.$^{41}$ Here however, CO$_3^{2-}$ in the mixture competes with silicate anions and produces amorphous calcite (Scheme 1, Step I) which in the presence of CTAB transforms into cubic/rhombohedral seed particles via oriented growth along the (104) face (Scheme 1, Step II).$^{41,44,47}$ After the initial reaction, the concentration of CO$_3^{2-}$ drastically diminishes and the reaction between Ca$^{2+}$ and SiO$_3^{2-}$ proceeds to create C–S–H. Since the nucleation/deposition process is energetically more favorable on the surface of a seed particle,$^{47}$ C–S–H nucleation happens preferentially on the surface of calcite seeds and a surface catalyzed reaction between Ca$^{2+}$ and SiO$_3^{2-}$ results in the formation of C–S–H phases on the surface of cubic calcite seeds (Scheme 1, Step III). Then, anisotropic, surface catalyzed, semi-epitaxial growth of C–S–H in the presence of CTAB$^{48}$ leads to larger semi-crystalline C–S–H microcubes.

To substantiate the aforementioned mechanism, several control experiments were undertaken. Our control reaction in the presence of excess CO$_2$ only produced random calcite particles along with amorphous silica, justifying the proposed mechanism (ESI 5†). In this scenario, due to the continuous supply of CO$_3^{2-}$ (from CO$_2$), Ca$^{2+}$ preferentially reacts with CO$_3^{2-}$ leading to the formation of calcite and amorphous silica (from unreacted SiO$_3^{2-}$). Our control experiments with CO$_2$-free water under a N$_2$ atmosphere (to prevent the calcite seed formation) only resulted in the formation of C–S–H with a crumpled sheet-like morphology (ESI 6†), again proving the importance of CO$_2$ generated seeds in the reaction. To find more evidence of the importance of having calcite seeds in cubic particles, the particles were cut by a gallium Focused Ion Beam (FIB) in SEM, followed by elemental analysis and mapping on the cut cubes at a tilted angle in SEM (ESI 7†).

![Scheme 1](#) Schematic illustration of the proposed semi-epitaxial growth mechanism of C–S–H micro-cubes on the *in situ* generated calcium carbonate seeds.
Fig. 2a–c show a randomly chosen cubic particle cut by the FIB for elemental composition analysis in the TEM STEM mode. EDS-STEM for 10 points on the surface of a cut particle confirms the presence of Ca and Si in the particle structure (Fig. 2d–e). The elemental mapping of a cut cube with SEM shows a uniform distribution of Ca and Si on the selected cross-section (Fig. 2f–j). Although this does not support the proposed mechanism, this reveals that it is not possible to have large calcite seeds and suggests that seeds should be in nanoscale size which cannot be seen in the cross-section cut by the FIB. Furthermore, a separate reaction was performed under argon in the presence of commercial cubic calcite seeds purchased from Plasmachem to explore the possibility of C–S–H overgrowth on the surface of added seeds under sealed conditions, with no contribution of CO₂ of air. The average size of seeds was 40–60 nm and they were suspended in CO₂-free DI-water under inert gas prior to starting the reaction. The product was characterized by EDS-SEM analysis. Interestingly, large micron size C–S–H cubes were

Fig. 2 Elemental analysis on FIB cut particles. (a) A single cubic particle on the TEM grid. (b) The particle in (a) after cutting by the FIB. (c) Side view of the cut cross-section. (d and e) EDS-STEM on 10 points of the cubic particle along with the STEM image of the cross-section of the cut particle illustrating the ten selected points for the line spectrum. (f–h) Cubic particle on the SEM stub, cut by the FIB and cut particles after tilting the SEM stage. (i–k) Elemental mapping of the cut cubic particles. Scale bars show 1 μm.
observed, which were ~10 times larger than starting calcite seeds, and had Si and Ca in their structure (ESI 8†). This finding explicitly reveals that C–S–H overgrowth on top of the calcite seeds happens and strongly supports our proposed mechanism in Scheme 1.

Modulating the reaction kinetics and precursor concentrations

The versatility of our reaction allows the variation of product yield, size, and morphology by carefully modulating the precursor concentration, temperature, and duration of the reaction (Fig. 3). The intimate dependence of temperature and concentration on the shape of CaCO₃ crystals is well documented.⁴⁹,⁵⁰ Analogously in the case of C–S–H, the product structure and morphology significantly depend on both temperature and reaction concentration gradient (i.e. precursor concentration and Ca/Si).

Variation of precursor’s concentration leads to commensurate modification in particle size where an increase in the concentration leads to larger particles (Fig. 3a–f). However, this also resulted in more defects and formation of multiple twinned or ill-defined particles (Fig. 3c and f). In dilute solutions (decreased precursor concentrations), driven by the slower reaction kinetics, the smaller C–S–H nuclei formed in the reaction ensemble self-assemble to develop dendritic structures (Fig. 3h and i).⁵¹ Though heterogeneous nucleation of calcite seeds happens under these conditions, other reaction parameters including temperature, duration, and kinetics dominate the growth mechanism. Here, besides having decreased concentration (which keeps precursor concentration below supersaturation), the samples were kept in the sonication bath for a longer reaction time. This leads to an increase in the average reaction temperature (due to prolonged sonication). The increased temperature in combination with the modified concentration gradient prompt controlled diffusion of C–S–H particles. This gravitates the nucleation of seed particles below supersaturation followed by oriented stacking of particles (postulated based on the small cubes observed at the tails of the dendritic structures in the inset of Fig. 3h) at favorable sites in a diffusion-limited environment forming dendritic structures (ESI 9†). Although the dendritic shape (Fig. 3h and i) does not show a well-ordered subunit morphology, it is evident from the high magnification SEM images of samples that some of the exposed tails and edges are assembled from oriented cubic subunits (inset in Fig. 3h) pointing to a similar underlying particle nucleation mechanism.

Anionic versus cationic surfactant and influence of counterions in the precursor

Surfactants are surface active substances that chemically react with the surface of particles. To explain the role of surfactant in shape-control of C–S–H particles, we conducted the reaction in
the presence of three cationic and one anionic surfactants (ESI 10†). The importance of surfactants in the size- and/or shape-controlled synthesis of nanostructures is well known.53–55 Controlling the shape of particles has been most successfully achieved using surfactant templates. Surfactant templates provide a constrained environment during the particle growth and thus shapes will be tuned according to the surfactant template.56–57 Here, the C–S–H formation reaction was carried out in the presence of cationic surfactants namely CTAB, cetylpyridinium bromide (CPB), tetra(decyl)ammonium bromide (TDAB), and an anionic surfactant dodecyl sulfate sodium salt (SDS). These surfactants when mixed with an aqueous solution with concentrations above critical micelle concentration (CMC) form different shaped surfactant micelles with a size of a few nanometers that act as templates for growing different morphology C–S–H particles with size ranging from tens to hundreds of nanometers.58,59 Here, by controlling the nucleation and growth of surfactant-mediated nanosize C–S–H particles on micelles, through selecting different surfactant types and adjusting the kinetic conditions, we will create C–S–H particles with up to several hundreds of nanometers in size and with varying morphologies. In the presence of CTAB and CPB, the major shapes of particles were cubic, whereas TDAB produced cubic particles, rectangular prisms, and rods. However, the poor solubility of the surfactants in water caused a fraction of them to remain in the C–S–H matrix. Comparing cationic and anionic surfactants in our experiments, SDS does not appear to be an appropriate surfactant for this method, yielding highly aggregated irregular structures. We propose that the interaction of cationic surfactants with a silicate source and/or carbonate anion and their subsequent stabilization (which render the resultant structures) are the key reasons for the formation of well-defined structures. Anionic surfactants, on the other hand, could protect Ca2+, and hinder its reaction with CO3 −, thereby restricting the possibility of calcite seeds and the formation of C–S–H micro-cubes (ESI 10†).

Interestingly, changing the nature of the counter ion in the calcium precursor resulted in the metamorphosis of C–S–H. Anions are known to intimately modulate the final shape of particles in surfactant mediated synthesis.49 In the presence of nitrate in Ca(NO3)2, well-defined C–S–H nano/micro-cubic/rhombohedral particles were obtained. However, Cl− (CaCl2) and hydroxide (Ca(OH)2) counter ions resulted in mostly agglomerated irregular particles and crumpled C–S–H sheets, respectively (ESI 11†). The morphology and composition of the particles were analyzed in detail using SEM and EDAX. The analysis confirmed the presence of C–S–H with traces of carbon presumably from calcite structures or from reaction contaminants, which cannot be avoided. In the reaction using CaCl2 as the calcium source, the formed particle did not exhibit any particular preference for any shape and showed differently sized and/or shaped C–S–H structures with severe aggregation (Fig. S11a†). However, the reaction carried out using calcium hydroxide as the calcium source resulted in the formation of a sheet-like fluffy material (Fig. S11b†). This is quite similar to the formation and growth of regular C–S–H materials through reaction of pozzolans with calcium hydroxide (lime) to form C–S–H with layered structure and with a low Ca/Si ratio.

Both of these structures showed characteristic XRD patterns and IR peaks of the C–S–H phase. XRD patterns for these reactions are illustrated in Fig. S11c† which match with the C–S–H phase (ICDD, PDF # 00-034-0002). On careful examination, for the product synthesized from Ca(OH)2, we can observe less intense features around 2θ = 23.04°, 29.3°, 39.40°, 47.48° and 48.49°, due to the presence of calcite. The narrowness of the peak at 29.3° reflects the higher formation of the crystalline calcite phase in the sample due to the higher affinity of calcium hydroxide to react with carbon dioxide. This narrowness can also occur due to the effect of larger particles on sharpening the XRD peaks.48 The samples were analyzed using FT-IR spectroscopy as well (Fig. S11d†). All samples exhibited a complex ensemble of bands at ~960 cm−1, corresponding to the asymmetric and symmetric stretching vibrations of Si–O bonds, and at ~660 cm−1 corresponding to Si–O–Si bending vibrations.43 The features in the range of 1400–1500 cm−1 correspond to the asymmetric stretching of CO3 −, and the weak shoulder at ~870 cm−1 is due to the out-of-plane bending of CO3 −. CO3 − peaks have higher intensity for the C–S–H sample formed from calcium hydroxide, consistent with the XRD results pointing towards the formation of calcite in the reaction with calcium hydroxide precursors.

Morphology-mediated mechanics of particles and their assembled structures

To illustrate the beneficial effects of controlling shape on the properties of C–S–H, we probed its mechanical properties as an example. The morphology of individual C–S–H particles, the building blocks of cementitious materials, has a profound impact on the integrity and mechanical properties of the system at larger scales. Here, we investigated the mechanical properties both at the single particle level and its pressure-induced (compacted) assembled superstructure. First, we describe the mechanics of individual C–S–H particles. The mechanical properties of C–S–H particles are generally extrapolated from their bulk compacted samples via nanoindentation61–63 and atomic force microscopy.64,65 However, as can be expected, such extrapolations can only give approximate data, and there is currently no direct method for probing the mechanics of “individual” C–S–H particles and/or the effect of the shape. For example, the latest state-of-the-art approaches indent the microstructure of C–S–H at different porosities and then extrapolate the results to zero porosity, approximating the mechanical data for individual particles.66 But this method is neither able to directly probe individual particles nor unravel the effect of shape and size on their mechanical properties.

Here, we developed a de novo matrix-based algorithm to conduct hundreds of indentations on sparse particles using a flat-end tip to directly obtain the mechanics of individual particles isolated from their bulk phases. To investigate the unique mechanical behavior of cubic C–S–H particles, we employed a flat-end indentation probe with a diameter of 20 μm (from Anton Paar) to compress the individual particles against
a glass substrate and measure their hardness and elastic modulus (Fig. 4a–c). Nanoindentation was performed on a grid of 10 × 10 points with a spacing of 30 µm. After nanoindentation, a clear breakdown of individual particles occurred resulting in the formation of debris on the substrate. Fig. 4a shows SEM images of an individual cubic C–S–H particle before and after indentation when the particle is crushed. Fig. 4b shows the schematic of cubic particles crushed by the flat-end tip. Fig. 4c shows the schematic of the indentation tip while indenting a single cubic particle. The average values of hardness and elastic moduli are shown in Fig. 4d which indicate that the hardness and stiffness values of individual cubic particles were improved by ~650% and ~300% respectively, compared to those of the individual non-cubical control particles. Since the regular C–S–H materials have unknown morphology and it is impractical to prepare an individual regular C–S–H particle, synthetic C–S–H particles with irregular shapes were used as the control particles in this study to investigate the effect of morphology on the mechanics of the individual particles. We utilized these particles because they were the most equivalent particles to regular C–S–H particles. These findings clearly demonstrate the impact of shape on the mechanical properties of individual particles. To our knowledge, this study for the first time measured directly the mechanical properties of C–S–H at the level of the individual particles.

In view of our flat-tip indentations on individual particles, the physical origin of the shape-induced mediated mechanical properties is as follows: in the case of cubic particles in contact with the flat-tip (Fig. 4c), the critical surface area of the sample subject to fracture is uniform throughout the thickness and is simply the cross-section of the cube (flat tip is larger than the cube surface area). However, in the case of a non-cubic particle (for example a spherical particle), the critical surface area in contact with the flat tip is not uniform throughout the thickness and is lower towards the particle boundary. This lower surface area creates larger stress and given that the inherent strength of the material is constant, the non-cubical particle tends to fracture with a smaller load, resulting in poorer mechanical properties. A similar physical phenomenon is valid when the particles are assembled into a microstructure (Fig. 4e–f). In the latter case, the flat tip is indeed replaced by another cubic particle; thus face-to-face attachment of two cubic particles creates uniform (delocalized) stress in both particles (Fig. 4e). In contrast, microstructures that have particles with random shapes tend to have non-uniform stresses along the thickness of their particles and thus fail under lower external load (Fig. 4f). For example, consider two spheres in a particulate microstructure that are pushed against each other. The fracture will happen close to the surface of one (or both) sphere(s) because of higher localized stresses in those areas. This finding on the effect of shape on the mechanics of single C–S–H particles and C–S–H microstructures is original in cementitious materials and a significant result of this paper.

To validate the above observation, we measured the mechanical properties of pressure-induced assembled C–S–H particles via nanoindentation testing by using a Berkovich tip as well as by conventional compressive tests. Note that while the use of a flat-tip is ideal for probing individual particles, it is established that the use of a Berkovitch tip is more appropriate for compacted samples (half infinite media). For nanoindentation on compacted samples, we compressed the as-synthesized cubic and control C–S–H particles inside a pressing die with a pressure of 193 MPa into pellet form samples. The SEM image in Fig. 4g shows the cross-section of a broken pellet created by compaction and assembly of the cubic particles. Next, we measured the pellets’ mechanics by forming a grid of 10 × 10 indents on the surface of each compacted sample with a spacing of 3 µm and a maximum force of 50 mN (Fig. 4h). Fig. 4i shows that the average values of the hardness and elastic modulus of the pellets were improved by ~83% and ~30%, respectively, compared to those of control compacted samples. These lower mechanical properties of the control sample are due to the irregular morphology of the non-cubical particles that tend to form an inefficient assembly, leading to more nanoscale pores and lower mechanical properties of the pellet. However, the somewhat face-to-face contact and assembly of the cubic particles results in a more packed structure with less porosity along with higher frictional bonding, exhibiting improved mechanical properties. Fig. 4j shows all nanoindentation load–displacement curves of cubic C–S–H particles and control particles where the thick black lines correspond to the average plot. From this figure, one can readily realize that for a constant load (50 mN), the average displacement in the control samples is larger, suggesting that the control (non-cubical) particles have inferior mechanical properties compared to the cubic particles. This result clearly shows the impact of shape on the mechanical properties of C–S–H microstructures, another significant result of this paper.

For the conventional compression tests, we used a similar technique to compact the synthesized cubic C–S–H particles into pellet forms and then measured the porosity as well as the mechanical properties of the bulk C–S–H pellet (see Methods). We created two C–S–H pellets, namely Cubic (I) and Cubic (II), with porosities of ~26% and ~17%, that were compacted with a pressure of 198 and 330 MPa, respectively. Fig. 4k illustrates the stress–strain plot of these pellets, along with that of the control pellet, which was created in a similar manner with a compacting pressure of 330 MPa. The compressive strength generally increases from Cubic (I) to Cubic (II) samples, correlating well with the reduction in the porosity (Fig. S15†). Although the compaction pressure of both the control and Cubic II samples was identical, the Cubic (II) pellet exhibited ~36% higher compressive strength and ~18% more elastic modulus, again suggesting that the cubic C–S–H particles are compacted more efficiently than the irregular control particles due to their well-defined surface structure and morphology. As stated before, the compacted samples of the irregular control particles exhibit a porosity of ~34%. This higher porosity is due to the formation of higher numbers of interparticle nanoscale pores. Furthermore, the toughness and ductility of the Cubic (II) sample are ~300% and ~77% larger than those of the control sample, respectively (see Methods and Fig. 4l). This is mainly
because the cubic samples are devoid of significant nano/micropores, which are present in the control sample as evidenced by the microstructural characterization of the pellets through cross-sectional SEM images (Fig. 4h and S16†). The homogenous composition of both individual particles achieved from elemental analysis further demonstrates the individual particles’ morphology-dependent mechanics of the compacted pellets.

Discussion

The key novelties of this work lie in (i) the shape-controlled synthesis of complex semi-crystalline calcium–silicate–hydrate (C–S–H) with a variety of particle morphologies and sizes via an in situ generated seed-mediated growth protocol, (ii) elucidating the significance of controlling the shape of the C–S–H particles in the mechanics of both individual particles as well as their
assemblies at larger scales, and (iii) isolation and direct measurement of mechanical properties of individual C-S-H particles for the first time. Together, these novel findings have a profound impact on engineering cementitious materials. Our results demonstrate how the complexity of the shape-controlled gelatinous C-S-H particles can be condensed into a few (four) critical parameters, i.e. Ca/Si ratio, surfactant type, mixing techniques, and nature of counter-ions in the precipitant, and a valid path to optimize the regulated reaction kinetics and C-S-H growth to derive the desired morphology. This is a significant result of this paper. The versatility and ease of our method in using inexpensive precursors and ambient conditions overcome the existing limitations of other engineering strategies, as it requires no changes in reaction temperature, pH, or solvent. This novel protocol allows for a variety of morphologies, which can be categorized into a single morphology diagram containing three main classes according to their morphological features: cubic, core/shell-like and dendritic shapes (Fig. 5). This morphology diagram provides an important guideline on how modulating the reaction parameters can lead to C-S-H particles with desired shape and size. In particular, we reported the first synthesis of cubic C-S-H particles via in situ seed-mediated nucleation and overgrowth where the seed calcite particles form naturally in situ via the available CO₂ in the air. Our control experiments in the presence of excess CO₂ resulted in calcite particles only, and under a N₂ atmosphere irregular shapes were produced, thus confirming the proposed mechanism.

Our investigation of the mechanics of the individual C-S-H particles and their pressure-induced microstructure assemblies via nanoindentation revealed that the particle shape has a critical role in mechanical properties. In the case of individual particles, we found that the hardness and stiffness of cubic C-S-H particles were on average ~650% and ~300% higher than those of the control sample, respectively. For assembled structures, although these improvements drop, they are still significantly (around 83% and 30%) larger than those of assembled control samples. The latter results are consistent with the strength and stiffness data of the compacted cubic particles measured by conventional compressive tests, which showed ~18%, 36%, 77% and 300% improved stiffness, compressive strength, ductility, and toughness compared to those of the control particle assemblies, respectively. This is because of the tendency of the system to form more closely-packed microstructures induced by the energetically favorable face-to-face attachments of the cubic particles, resulting in ~32% lower porosity and thus improved structural integrity. Although this close-packing of the cubes reduces the porosity of the structure and thus results in smaller capillary forces (due to less water in the pores), the higher specific contact area of the particles gives rise to higher van der Waals forces and also an enhanced frictional bonding. Our work suggests that besides chemical composition and particle size, the morphology of the C-S-H particles, which dictates the architecture and packing of the microstructure, has a significant impact on the mechanical properties and durability of the bulk materials. The benefits of this strategy can be readily realized when considering conventional assembly and growth of cement hydrate microstructures, which are based on irregularly shaped C-S-H particles, leaving multiple levels of porosities in the final structure. From this perspective, our novel results pave the path towards an entirely new manufacturing method for high performance cementitious and concrete materials while curbing their negative energy and environmental impacts. The latter is possible through two routes: (1) increasing the average strength of cement hydrate allows reducing its structural dimensions and thus its weight and associated CO₂ emissions and energy consumption. For instance, increasing the average strength of concrete by a factor of x mitigates its environmental footprint to 1/x for columns and 1/x^{0.66} for beams,4 and (2) improving the packing of cement hydrate results in more concrete durability since higher packing makes concrete less vulnerable to various deleterious ion penetrations (known as chemical attacks) and thus increases its durability. Consequently, higher durability directly translates into less maintenance and replacement cost, which entails environmental benefits. For example, a concrete with 3× more durability can reduce the concrete manufacturing energy and its associated CO₂ emissions to one-third.

Adapting our lab-scale findings to hydration of cement is the natural extension of this work for future studies. The following two key strategies are possible practical pathways in making cementitious materials with cubic C-S-H particles: (1) synthesis of cubic C-S-H particles in an industrial ultrasound-equipped reactor. The starting point is the hydration of individual components of Portland cement (PC) (alite, belite, etc.) in the presence of the right surfactants (as suggested in our work), followed by optimization of the mixture when all PC components are present (clinker phase). The separate refinement and control of defects of the individual components of PC prior to mixing the components and final optimization allows to adjust the particle morphology independent of the possible impurities that may hinder the direct growth and development of C-S-H particles with specific morphologies. A key advantage

Fig. 5 Morphology diagram of C-S-H obtained via in situ seed generation and seed mediated overgrowth. The particles are drawn in scale. The error bars indicate upper and lower particle sizes.
of our protocol is that CO₂ in the air will naturally dissolve in the water and react favorably with Ca²⁺ ions to form what we call in situ calcite seeds. This novel process eliminates the use and manual addition of seed particles like the ones by BASF, etc. Note that although one may expect that a softer and conventional irregular structure of C–S–H may serve as an efficient matrix between various hydration products of clinkers, we suggest that the cubic C–S–H particles may serve as excellent seeds for the rest of the system such that they impart semi-epitaxial growth of other products (e.g. hydration of aluminate) on the surface of cubic C–S–H. In such cases, the poor interfacial contacts, which are usually the bottlenecks in adhesion between the matrix/inclusions, are minimized, and in case the process in (1) may not lead to setting of a hard solid cement hydrate product, one can collect the cubic C–S–H deposits and compact them as a “Precast cement product”. This process is very similar to the compaction technique we have adopted in this work. As an example of commercial realization of this compaction technique, continuous manufacturing of precast cement products composed of cubic C–S–H particles, which entails improved mechanics and durability and thus less environmental footprint.

Although using relatively expensive surfactants at the first glance does not sound a cost-effective and efficient method for adjusting the shape and size of C–S–H materials at larger scales, the improved properties and added benefits of the final cementitious materials such as higher strength, lower maintenance cost, and less adverse environmental impacts significantly justify the use of surfactant templates and in general the efficiency of our method.

In conclusion, this work developed a unified protocol elucidating the morphogenesis of the complex cement hydrate into a simple morphology diagram (Fig. 5). Such a fine-control over morphology and the associated nucleation and growth mechanisms will not only impact tuning properties of individual cement hydrate particles, but will lay the foundation for de novo concepts and strategies for shape-regulated self-assembly of cementitious microstructures, opening up an entirely new phase space for bottom-up engineering of concrete materials with ultra-high strength and durability while curbing their negative environmental impacts. Broadly, the innovative concepts, strategies, and techniques of this work can have important implications for other applications of C–S–H in bone-tissue engineering, drug delivery and refractory materials, and can also impact other complex systems such as ceramics and complex colloids, which are made of analogous elements but grow epitaxially on/around different primary seed nuclei. Moreover, our novel algorithm developed to measure single-particle level properties is amenable to other systems and can potentially replace atomic force microscope-based techniques to alleviate the composition variability and reproducibility problems in complex systems. Together, our results demonstrate the first report on morphogenesis of cement hydrate, and illustrate the prospect of treating concrete and similar complex materials on equal footing with metallic and semiconductor particles in the current applications of shape-induced self-assembly mechanisms to create programmable microstructures with ultra-high performance and low environmental footprints.

**Methods**

**Materials**

Sodium metasilicate pentahydrate (99%) was bought from Strem Chemicals. Calcium nitrate tetrahydrate was purchased from Alfa Aesar. CTAB (95%). CPB and calcium hydroxide and chloride were obtained from Sigma-Aldrich. SDS (99%) was acquired from Fischer Scientific. TDAB (>98%) was purchased from Fischer Scientific. All the chemicals were used as received without further purification.

**Synthesis methods**

C–S–H samples with Ca/Si ratios of 1.0, 1.5, and 2.0 were prepared using stoichiometric amounts of Ca(NO₃)₂·4H₂O and sodium metasilicate pentahydrate. For example, for the model reaction of C–S–H with Ca/Si = 1.5 and [CTAB] = 0.8 mM, first 0.03 g of CTAB was dissolved in a 100 mL Na₂SiO₃·5H₂O aqueous solution (5 mM) to form a homogeneous solution. The resulting solution was transferred to a commercial ultrasonic cleaning bath (40 kHz, 130 W, Branson, 3510) and sonicated for 20 minutes. Subsequently, Ca(NO₃)₂·4H₂O powder was gradually added into the beaker while the solution was continuously sonicated for 90 min until the powders were completely converted to C–S–H. Time-dependent spectroscopic monitoring of the reaction implied that the reaction kinetics are relatively fast in the first 25 min and after 1 h negligible reaction occurred (ESI 1†). As the reaction proceeded, a white precipitate formed.

The precipitate was collected by centrifuging with 2 mM calcium hydroxide (CH) solution (3 × 20 mL) and ethanol (2 × 10 mL) respectively. Other controlled reactions followed a similar procedure except that the stoichiometry of raw materials (Ca/Si ratio of 1 and 2), surfactant (CPB, TDAB or SDS of 0.4, and 1.6 mM), calcium salt [Ca(OH)₂, CaCl₂] and volume (25, 50 and 200 mL) were different.

**Characterization**

Powder X-ray diffraction (XRD) data were obtained with a Rigaku D/Max-2100 PC powder diffractometer using unfiltered Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA and a step size of 0.02°. The contribution from Kα₂ radiation was removed using the Rachinger algorithm. Goniometer alignment was performed regularly with the use of a SiO₂ reference standard. Post-acquisition XRD data processing was carried out using MDI’s Jade 2010. Powder diffraction files (PDF) from the ICDD were used as references for phase identification. Fourier transform infrared spectroscopy (FT-IR) data were recorded on a Perkin-Elmer spectrometer with two spectrophotometers using attenuated total reflectance. Transmission electron microscopy (TEM) experiments were performed by depositing a drop of a suspension of the particles diluted in EtOH onto a carbon-coated copper grid. The solvent was evaporated, and the sample
was analyzed using a JEOL 2100 Field Emission Gun Transmission Electron Microscope. Scanning electron microscopy (SEM) experiments on samples were carried out by depositing a drop of a diluted EtOH suspension of the sample on an aluminum stub or a silicon wafer or glass slides. The solvent was evaporated, and the stub was coated with a thin layer of gold in a CRC-150 sputter coater in the case of using glass. Energy dispersive X-ray spectroscopy (EDAX) analyses were carried out on a JEOL FEI Quanta 400 ESEM FEG on C–S–H particles. Measurements were performed at 20 kV and with a measured beam current of 1 nA. The aluminum stub covered with carbon tape was used for elemental analysis of samples. The focused ion beam (FIB) method was done in a FEI Helios NanoLab 660 DualBeam system using the gallium ion beam. Solid state Magic Angle spectra (29Si MAS NMR) were collected on a Bruker Advance 200 spectrometer at 39.76 MHz. The samples were measured using a 7 mm extended VT MAS probe with 7 mm long barrel ZrO2 rotors and plugs and Kel-F fluoropolymer caps. Chemical shifts were referenced to hexamethyldisiloxane (δ = −9.66 ppm) by sample replacement. All spectra were collected at a Magic-Angle Spinning speed of 6.00 kHz without high-power 1H decoupling. Spectra were acquired for signal saturation using a 90°-29Si pulse of 5.75 μs with ~20 s recycle delay and a spectral width of 14 750 Hz. Data were collected and analyzed with TopSpin v.1.3 and Dmfit 2011.75 Thermal analyses on powder samples (~3 mg) were carried out using a Q-600 Simultaneous TGA/DSC from TA Instruments at 20 °C min⁻¹ from room temperature (RT) to 1000 °C under an argon atmosphere using a flow rate of 60 mL min⁻¹.

Nanoindentation tests

Nanoindentation was carried out using an Anton-Paar Nanoindentation Tester (NHT2) of the Laboratory of C-Crete Technologies LLC (Fig. S17a and b†). Specimens were created by depositing a drop of a diluted EtOH suspension of the sample on a glass slide. The sample was first suspended for half an hour in ethanol in an ultrasonic bath to prevent the self-agglomeration of particles. A flat-end tip with a diameter of 20 micrometer was used to indent individual sparse particles using a grid of 10 × 10 points. We used a force-controlled mode with the maximum applied force of 10 mN. A trapezoidal loading program was used which consists of the loading to maximum force, holding for 5 seconds at the peak load, and unloading periods. From load–displacement, P–h, curves, we calculated Young’s modulus, $E = \frac{0.5\pi S/\sqrt{a}}{1 - p^2}$, and hardness, $H \equiv P_{\max}/a$, where a is the contact area at $P_{\max}$ and S is the slope of the unloading curve.86

Mechanical and porosity measurements

C–S–H powdered particles were compacted in a cylindrical pellet pressing die consisting of a hardened stainless steel (S.S.) base with a vacuum outlet, the main cylindrical body with an internal diameter of 13 mm, two anvils, a plunger, and a pellet extractor. The surfaces of the anvils that contact and press powdered particles were highly polished. Pellet preparation involved placement of the cylindrical body on the top of the S.S. base and the anvil inside the cylindrical body and then covering it up with the pre-measured weight of powdered particles. The powdered sample was then covered with the second anvil, and the plunger was inserted into the cylindrical body on the top of the second anvil. The entire assembly was placed in a hydraulic pressing machine (Fig. S17c–e†) where the pressure was increased gradually to the point where the porosity of the compacted samples was within the desired limit, akin to the porosity of naturally hydrated cement. The relevance of comparison of compressed C–S–H particles and naturally set C–S–H is an established subject. It has been demonstrated that the compacted samples of hydrated Portland cement particles exhibit similar Young modulus and hardness properties to hardened Portland cement paste.76–79 The amount of C–S–H particles was selected such that the thickness of all compacted samples was ~2.5 mm. Next, an Instron machine (model 4505) with a 100 kN load cell was used to measure the compressive strength, axial deformation, and elastic modulus. Toughness was defined as the amount of energy a material absorbs before failure (representing the work-of-fracture),80,81 which is different from the classical “fracture toughness” with the unit of Pa√m. The work-of-fracture is the area under the stress–strain curve, which is deeply affected by gradual, graceful fracture, whereas the “fracture toughness” does not include this entire process.82–85 The control sample was prepared by fully hydrating tricalcium silicates (Ca₃SiO₅) in excess amounts of water and collecting and compacting the deposits under identical conditions to those of the cubic C–S–H particles. The porosities of both cubic and control samples were calculated by using the dimensions of the compacted samples and the density of the powder which was determined via a micrometrics AccuPyc II 1340 helium pycnometer.

Authors’ contributions

R. S. designed and directed the research; S. E. M., V. H., S. M., T. S. S., J. M., B. S., S. Z., and R. S. performed the research; S. E. M.,

Competing financial interest

The authors declare no competing financial interest.

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