Facile synthesis of calcium silicate hydrate using sodium dodecyl sulfate as a surfactant assisted by ultrasonic irradiation

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ABSTRACT

Calcium silicate hydrate (CSH) consisting of nanosheets has been successfully synthesized assisted by a tip ultrasonic irradiation (UI) method using calcium nitrate (Ca(NO3)2 4H2O), sodium silicate (Na2SiO3 9H2O) and sodium dodecyl sulfate (SDS) in water. Systematic studies found that reaction time of ultrasonic irradiation and concentrations of surfactant (SDS) in the system were important factors to control the crystallite size and morphologies. The products were characterized by X-ray power diffraction (XRD), field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectrometry (FTIR). The size–strain plot (SSP) method was used to study the individual contributions of crystallite sizes and lattice strain on the peak broadening of the CSH. These characterization techniques revealed the successful formation of a crystalline phase with an average crystallite size of about 13 nm and nanosheet morphology at a reaction time of 10 min UI with 0.2 g SDS in solvent which were found to be optimum time and concentrations of SDS for the synthesis of CSH powders.

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1. Introduction

Calcium silicate (CaSiO3) has gained significant attention due to its wide range of applications. It is well known that CaSiO3 has excellent bioactivity, degradability, biocompatibility, and thus can be used as a substitute material for damaged teeth or bones and drug delivery [1–3]. Some studies have shown that calcium silicate hydrate (CSH) can induce formation of a bone-like apatite layer on their surface after soaking in simulated body fluid (SBF) [4]. The biocompatibility, stability, heat-insulating ability, low dielectric loss at high frequency and mechanical properties of calcium silicates are determined by their morphology, crystal size, composition and structure. Hence, the control over the morphology of calcium silicate and CSH is of great importance for biomedical and industrial applications [5–8]. Many efforts have been made to synthesize CaSiO3 and CSH of different morphologies such as nanowires, nanobelts and hollow microspheres with varying diameters [2,6,7,9,10]. Many methods have been also used for synthesizing CaSiO3 including solid-state reaction, sol–gel, hydrothermal, precipitation methods, mecha-nochemical and microwave-assisted methods [6,10–12]. The chemical precipitation method is the most often reported for preparing CaSiO3 materi-
2. Experimental

2.1. Chemicals and apparatus

All chemicals were procured from Sigma–Aldrich Ltd. and used as received. The ultrasound apparatus was a Sonics Vibra Cell KS-1220 model (20 kHz, 1200 W) using a direct immersion titanium horn.

2.2. Synthesis of calcium silicate hydrate by sonication at different times

The calcium silicate hydrate for the present study were synthesized by the reaction of calcium nitrate (Ca(NO₃)₂·4H₂O) and sodium silicate (Na₂SiO₃·9H₂O). 15 ml of 0.1 ml Ca(NO₃)₂·4H₂O with a pH of 11.5, and 15 ml of 0.1 ml Na₂SiO₃·9H₂O were mixed and the solution was stirred at room temperature for 10 min. Then, the sonic horn was dipped into the solution in order to initiate ultrasonic irradiation at different sonication times (5, 10, and 15 min) under ambient conditions. Finally, the product was separated from the solution by centrifuging at 6000 rpm washed with DI water and ethanol and dried in a controlled humidity chamber at 80 °C for 24 h. For comparison, a parallel experiment was also performed by mechanical stirring at the same condition such as temperature, pH, etc., in the absence of ultrasonic irradiation.

2.3. Synthesis of calcium silicate hydrate by ultrasonication with different concentrations of SDS

In a typical experiment, different amounts of SDS (0.1, 0.2 and 0.3 g) were added in 25 ml of 0.1 ml Ca(NO₃)₂·4H₂O with a pH of 11.5 and stirred for 10 min. Afterwards, 15 ml of 0.1 ml Na₂SiO₃·9H₂O was slowly added into the same beaker. The solution was sonicated for 10 min at room temperature. For comparison, detailed information for each prepared powder is given in Table 1.

2.4. Characterization

X-ray diffactometry (CuKα radiation on an Analytical Empyrean diffractometer) the current generated in the diffractometer was determined using the size–strain plot (SSP) method. In cases of isotropic line broadening, size–strain plot method (SSP) formula, is one of the equations used for determining average crystallite size and lattice strain [18]. This method has the advantage of giving less weight to data from reflections at high angles, where the precision is generally lower [19]. The size–strain plot equation that determines crystal size and lattice strain is:

\[ (d_{hkl}/hkl \cos \theta)^2 = \frac{K}{D} (d_{hkl}/hkl \cos \theta) + \left( \frac{\varepsilon}{2} \right)^2 \]

where \(d_{hkl}\) is the lattice distance between the \((hkl)\) planes, \(\theta_{hkl}\) is the peak width in radian, \(K\), \(D\), \(\varepsilon\) and \(\theta\) are the constant (\(\frac{1}{4}\)), crystallite size, lattice strain, and half diffraction angle, respectively.

When \((d_{hkl}/hkl \cos \theta)^2\) is plotted versus \((d_{hkl}/hkl \cos \theta)\) for all orientation peaks of CSH, the crystallite size is determined from the slope of the linearly fitted data, and the root of the y-intercept gives the strain.

The yield \((s)\) of the CSH powders after drying was calculated by the following equation [20]:

\[ S = \frac{m}{m_1} \times 100 \]

where \(m\) and \(m_1\) are the practical and theoretical quantity (g) of the obtained CSH powders. The characteristic peaks of CSH powders were obtained on a Fourier Transformation Infrared (Perkin Elmer-spectrum100 model FTIR) spectrometer in the wave range of 4000–400 cm⁻¹. The morphology of the synthesized powders was studied by means of field emission scanning electron microscopy (FESEM, CARL ZEISS-AURIGA 60).

3. Results and discussion

As shown in Table 1, it was found that the yield of CSH increased when the sonication time was extended from 5 to 15 min at the same UI condition. The UI wave is not enough to blend the solution and precipitant uniformly within a short period of time, therefore the yield of CSH powders increased at longer times of insonation.

Fig. 1 shows the X-ray Diffraction (XRD) patterns of G1-Group obtained at different sonication time and in non-sonicated sample, which coincided with the calcium silicate hydrate in the JCPDS card 03-0606. No other diffraction peaks were observed other than the main peaks that corresponded to the CSH structure. This result illustrates that the ultrasonic irradiation is very effective to obtain CSH as the main phase and could promote the crystallization of CSH in a short period of time. On the other hand, in our experimental results show that CSH cannot be synthesized at same condition by mechanical stirrer in the absence of ultrasonic irradiation. Due to the CSH powders synthesized by chemical precipitation method, the reaction between Ca(NO₃)₂ and Na₂SiO₃ need to take some time until Ca(NO₃)₂ powders are completely converted to the CSH. Also, the CSH produced with UI samples show rapid synthesis and suitable yield. This is surprising, because apparently most of the Ca²⁺ and SiO₃²⁻ ions present in the solution reacted to form CSH. In the presence of UI, the ultrasonic irradiation effect on nucleation is the reduction in the elapsed time between the establishment of supersaturation and the onset of nucleation and crystallization. All of the effects are because of the pressure created by bubble collapse, temperature and the highly spatially concentrated regions of extreme energetic agitation and following the release of shock waves. An additional, significant factor associated with UI is reaction kinetics. Since the collapse of the microbubbles is the event during which energy is released in the form of a shock wave this is the moment when the activation energy barrier is surmounted [21]. Simultaneously, since the collapse of the bubble arises over a very short time the nuclei created around this event, while numerous, have their growth confined by the short period of time during which the collapse occurs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ultrasonic power (%)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>SDS concentration (g)</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>G1-group</td>
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<td></td>
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</tr>
<tr>
<td>S1</td>
<td>70</td>
<td>5</td>
<td>80</td>
<td>–</td>
<td>73</td>
</tr>
<tr>
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<td>70</td>
<td>10</td>
<td>85</td>
<td>–</td>
<td>82</td>
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<tr>
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<td>15</td>
<td>90</td>
<td>–</td>
<td>84</td>
</tr>
<tr>
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<td>85</td>
<td>0.1</td>
<td>85</td>
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<tr>
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<td>10</td>
<td>85</td>
<td>0.2</td>
<td>91</td>
</tr>
<tr>
<td>S6</td>
<td>70</td>
<td>10</td>
<td>85</td>
<td>0.3</td>
<td>92</td>
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<tr>
<td>G2-group</td>
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Table 1

Summary of synthesis conditions and the yields obtained.
It was found that sonication time also influenced the average crystallite size and lattice strain. The crystallite size and lattice strain is estimated from the peak broadening of XRD reflection according to the SSP formula (Eq. (1)). The results obtained are in Fig. 2 and listed in Table 2.

According to the data presented in Table 2, the crystallite size and the lattice strain initially decrease with time from 5 to 10 min sonication; and later both crystallite size and lattice strain increases from 10 to 15 min. These results suggested that it is possible to tailor crystallite size by UI duration alone. Moreover, the decrease of CSH crystallite size compared to the increase of sonication time is not linear. The reaction media of CSH by chemical precipitation method from these sources is an exothermic reaction [22], in our experimental was shown that temperature increased to 90 °C after 15 min sonication while the changes in pH of our irradiated samples were negligible. The temperature of solution rapidly increased from 32 °C to 80 °C within 5 min UI and then the temperature was rising with a rate of = 1 °C/min from 5 to 15 min. Therefore, the results indicated that long irradiation times increased the temperature of the reaction media. The researcher reported that increasing the temperature in UI can be effective in growth of crystallinity [14,23]. By comparing the X-ray diffraction (XRD) patterns presented in Fig. 1, can be observed that the crystallinities of the resultant CSH increased with increasing the synthesis temperature and sonication time and that the improved crystallinity degree may be due to raised temperature and irradiation time in the aqueous solution during UI.

Fig. 3 illustrates the FTIR spectra of the CSH samples synthesized at three different times 5, 10 and 15 min. The formation of CSH is indicated by a complex group of bands in the range of 800–1200 cm⁻¹ [24,25]. The sharp band at 980 cm⁻¹ is characteristic for the Si–OH vibration [25,26]. The band at 1086 cm⁻¹ can be attributed to Si–O stretching vibrations, and the group of bands between 670 and 744 cm⁻¹ can be attributed to Si–O–Si bending vibration. These two groups of bands are features of silicate chains (SiO₃) [24]. Moreover, the characteristic bands for the CO₂⁻ group occur in the spectrum at 1500 cm⁻¹ (ν₂, asymmetric stretch.
vibration) and at 856 (ν2, out-of-plane bend vibration). All the experimental conditions by UI were carried out in air; therefore it is not possible to prevent incorporation of CO2 if the sample is exposed to air [24]. The broad band at 2800–3700 cm⁻¹ is due to stretching vibrations of O–H groups in H₂O or hydroxyls with a wide range of hydrogen bond strengths. In order to form calcium silicate hydrate, more H₂O molecules become coordinated in the produced CSH structure, participating with Si–O groups to form an intricate network of hydrogen bonds. These results are in good agreement with the X-ray diffraction analysis.

The morphological features of the CSH samples at different times by UI are given in the FESEM images (Fig. 4). By comparing the micrographs of the obtained powders by UI, it can be shown that UI duration affected morphologic features. The FESEM micrograph of CSH derived at 5 min shown in Fig. 4 (S1) suggests that the sample consists of agglomerated nano particles. When the ultrasonication time was increased to 10 min, the needle-like shape morphology dominated, where diameter and length of the CSH varies in the range of 20–30 and 300–500 nm, respectively, as measured by internally supported software (Fig. 4 (S2)). In addition, when the sonication time was increased to 15 min, the concentration of the needle-like morphology is further increased (Fig. 4 (S3)).

Prolonged reaction time of 15 min showed the formation of large number of needle-like shape with well-defined morphology with typical widths of 30–50 nm and lengths in the range of

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Fig. 3. FT-IR spectra of G1-group prepared using different UI times.

Fig. 4. FESEM micrographs of the G1-group (S1, S2, S3) and G2-group (S4, S5, S6).
100–200 nm. There are two regions of sonochemical activity: one is between the cavitation bubble and the surrounding bulk solution, and the other is inside the collapsing bubbles [27]. If the reaction takes place inside the bubble, the powders are amorphous, and if it takes place in the surrounding region, it is supposed to be that the products are nanocrystalline. In our present case, crystalline powders with needle-like morphology were obtained, it is to be expected that the formation of the CSH probably occurs in the interfacial region. The formation mechanism of the needle-like morphology is based on the electrostatic interaction between Ca$^{2+}$ and SiO$_3^{2-}$ ions at first and then followed by their assembly on the surface of micelles. In the early stage, the examination of intermediate products shows the coexistence of agglomerated nano particles and then needle like formed with increasing irradiation time. The formation process of needle-like can be schematically illustrated in Fig. 5.

The FESEM results demonstrated the deagglomeration abilities of the UI process. Incorporation of ultrasound as a reaction aid to promote deagglomeration has been studied [28,29] and established and the present results further support potential uses of sonochemistry in synthesis.

The results above show that CSH with different crystallite sizes and morphologies have been prepared successfully at different sonication times and 10 min UI was the optimal time for CSH synthesis by ultrasonication technique.

In the present study, SDS was used as a surfactant to modify and control the morphology and size of the CSH. In the absence of SDS, the morphologies of CSH were needle-like and not uniform. Therefore, the influence of various concentrations of SDS at 10 min UI on the structure of the final products and the growth-orientation processes were examined.

A significant effect of SDS was observed on the yield of CSH (Table 1), where the yield percentage increased when concentration of SDS was increased. Fig. 6 shows the XRD patterns of samples obtained from varying concentrations of SDS. The resulting diffractogram demonstrates that the sonochemically synthesized product at different amounts of SDS is CSH (JCPDS 03-0606). It was found that sample G2 (added SDS) has higher XRD diffraction intensity and sharper XRD peaks than that of sample G1 (no SDS). Hence, the intensification of XRD peaks would result in improved CSH intensity due to the increase of crystallinity. In addition, the peak intensity decreases when the concentration of SDS is increased. According to data presented in Fig. 7 and Table 2, the crystallite size and lattice strain of the CSH synthesis powders at various SDS concentrations which were measured by the SSP formula (Eq. (1)) using the profile of the main peaks of the XRD pattern. It is evident that the crystallite size and lattice strain between different surfactant concentrations is not linear. The crystallite size of CSH powders without the addition of SDS was 9 nm at 10 min by UI, while the sizes in the presence of SDS ranged between 13 and 24.7 nm as the SDS content rises from 0.1 to 0.3 g at 10 min by UI. The rise of crystallite size and reduction of lattice strain with the addition of SDS suggests that SDS may encourage particle growth.

Based on these results, the smallest crystallite size with maximum lattice strain obtained was about 13 nm from 0.2 g SDS in 10 min UI. The characteristic peaks for SDS (C–H) stretching and bending
bands in 2853–2965 cm\(^{-1}\) and \(-\text{OSO}_3^–\) bending band at 720 cm\(^{-1}\) were found, identifying that the precipitated CSH was covered with template SDS [30] and is very weak. The FTIR also identifies the functional groups of CSH samples that are comparable with G1-group (no SDS) as explained above. On the basis of XRD and FTIR results, one concludes that samples obtained in the different SDS concentrations are CSH.

Fig. 4 (G2-group) presents the effect of different concentrations of SDS on the morphology of the CSH powder synthesized with 10 min of ultrasonic irradiation time. In the absence of SDS, the morphologies of CSH were needle-like and not uniform. No nanosheet morphology was obtained. However, the uniform needle-like and nanosheet morphologies were formed in the presence of SDS. As shown in Fig. 4 (S4), by comparing the micrographs of the obtained powders with 0.1 g SDS (S4) and without SDS (S2) were ultrasonicated for 10 min, it can be seen that SDS improved the morphology by increasing the diameter and length of the CSH needle-like particles variably in the range 100–200 nm and 1–2 \(\mu\)m, respectively. When concentration of SDS was increased to 0.2 g, the highly oriented needle-like particles were assembled to form the bundles of nanosheet morphology. As shown in Fig. 4 (S5), a smooth surface is observed on the solid nanosheets of CSH. The width and length of the nanosheets are 300–500 nm and 2–3 \(\mu\)m, respectively. When the amount of SDS increased to 0.3 g in the solution, it had a direct destructive effect on the morphology and irregular morphologies without bundles of nanosheets and needle-like particles were observed (Fig. 4 (S6)).

Considering all factors, as also schematically illustrated in Fig. 9. The assembled process of CSH nanosheets under the effects of SDS and ultrasound is proposed as follows: First, due to the electrostatic interaction and stereochemical matching with Ca\(^{2+}\) ions, the negatively charged SDS polar groups acted as active sites for nucleation of CSH. Then, Ca\(^{2+}\) ions strongly absorbed on the micellar surface of the opposite charge, leading to a much faster nucleation rate on the surface of the SDS micelles and calcium ions can then react with the SiO\(^2–\) groups. However, with the work done by ultrasonic radiation, the CSH nanosheets arranged and formed an orderly assembled structure along the direction of flow with low energy. Consequently, both SDS and ultrasound had an impact on the orderly layered assembly of CSH nanosheets: SDS as a template made sure the formation and stability of CSH nanosheets, and the ultrasound provided the necessary work and driving force for assembly of CSH nanosheets. These results confirm that different amounts of SDS are favorable for the synthesis of CSH with various types of morphologies.

4. Conclusion

The main contribution of this study is that the synthesis of calcium silicate hydrate with appropriate quality and different morphologies is successfully performed via ultrasonic irradiation method. The following conclusions are drawn: (i) The output data from XRD and FESEM indicated that needle-like morphology with average crystallite size of 9 nm have been successfully obtained by using calcium nitrate (Ca (NO\(_3\))\(_4\)H\(_2\)O) and sodium silicate (Na\(_2\)SiO\(_3\)·9H\(_2\)O) in distilled water via Ul. Moreover, the reaction time

Fig. 7. The SSP plot of CSH samples G2-group with different concentrations of SDS at 10 min Ul. The particle size is achieved from the slope of the line fitted data, and the root of y-intercept gives the strain.

Fig. 8. FT-IR spectra of G2-group prepared using different concentrations of SDS at 10 min Ul.
has a significant effect on the size and morphology of CSH. (ii) The results show that the SDS anionic surfactant has a significant effect on the assembly of CSH with the assistance of ultrasonication. SDS molecules can help the formation and stabilization of CSH bundles into nanosheets because of the charge and stereochemistry matching. (iii) The results indicate that the optimum crystallite size is about 13 nm after 10 min of sonication time with 0.2 g SDS in mixed solvent and demonstrates bundles of nanosheets morphology with an average diameter and nanosheets length 300–500 nm and 2–3 μm, respectively. (iv) The results confirm that this CSH production method is simple, reduces the preparation time, and low-cost with a range of different morphologies and size.

Fig. 9. Schematic diagram of the formation process of CSH nanosheets with the effect of SDS and ultrasonic radiation.
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