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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 ($Ca(NO_3)\cdot 4H_2O$), sodium silicate ($Na_2SiO_3\cdot 9H_2O$) 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.

1. Introduction

Calcium silicate ($CaSiO_3$) has gained significant attention due to its wide range of applications. It is well known that $CaSiO_3$ 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 $CaSiO_3$ 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 $CaSiO_3$ including solid-state reaction, sol–gel, hydrothermal, precipitation methods, mechanochemical and microwave-assisted methods [6,10–12]. The chemical precipitation method is the most often reported for preparing $CaSiO_3$ materials [2]. This method is low cost, simple and appropriate for industrial production but the product morphology is poor and large size crystalline particles are obtained. Recent investigations reveal that the reactivity of chemical species in solution being involved in a synthesis method can be stimulated by ultrasonic irradiation of the reaction mixture [13]. Sonochemistry shows potential for the synthesis of nanomaterials due to the ultrasonic cavitation process in an aqueous medium including formation, growth and collapse of micro bubbles. The sonochemical method has been used to produce unusual morphologies such as flower-like of monetite [14], nanorods of ZnO [15], nanosheets of SnO [16] and nanospheres of MnO_2 [17]. Recently, Zhang and Chang [7] synthesized CSH microspheres in an ultrasonic cleaning bath but other morphologies have not been well investigated. Meanwhile, the efficiency and duration of the synthesis process depend on the type of used ultrasonic device. Some literature indicate that a tip ultrasonic homogenizer is more efficient than an ultrasonic bath [13].

In the present study, we intend to synthesize calcium silicate hydrate powders by employing a tip ultrasonic irradiation in water solvent. Initially, the effect of UI time on morphology, crystallite sizes and lattice strain of the obtained powders was analyzed. The anionic surfactant SDS was then used in order to investigate the influence on the assembly of the nanosheets and crystallite sizes.

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2. Experimental

2.1. Chemicals and apparatus

All chemicals were procured from Sigma–Aldrich Ltd. and used as received. The ultrasound apparatus was a Sonic 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 ($Ca(NO_3)_2{\cdot}4H_2O$) and sodium silicate ($Na_2SiO_3{\cdot}9H_2O$). 15 ml of 0.1 ml $Ca(NO_3)_2{\cdot}4H_2O$ with a pH of 11.5, and 15 ml of 0.1 ml $Na_2SiO_3{\cdot}9H_2O$ 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 $Ca(NO_3)_2{\cdot}4H_2O$ with a pH of 11.5 and stirred for 10 min. Afterwards, 15 ml of 0.1 ml $Na_2SiO_3{\cdot}9H_2O$ 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 (CuK_α radiation on an Analytical Empyrean diffractometer) the current generated in the diffractometer was 30 mA with a voltage of 45 kV. The diffraction range was 2Θ = 20–60° at 0.1/S. The crystallite sizes and lattice strains were 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:

$$(d_{hkl}\beta_{hkl}\ cos\theta)^2 = \frac{K}{D}(d^2_{hkl}\beta_{hkl}cos\theta) + \left(\frac{\varepsilon}{2}\right)^2 \quad (1)$$

where d_{hkl} is the lattice distance between the (hkl) planes, β_{hkl} is the peak width in radian.K, D, ε and θ are the constant $(\frac{4}{3})$, crystallite size, lattice strain, and half diffraction angle, respectively.

When $(d_{hkl}\beta_{hkl}\ cos\theta)^2$ is plotted versus $(d^2_{hkl}\beta_{hkl}\ cos\theta)$ for the 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]:

$$S = \frac{m}{m_T} \times 100 \quad (2)$$

where m and m_T 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 $Ca(NO_3)_2$ and Na_2SiO_3 need to take some time until $Ca(NO_3)_2$ 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 Ca^{2+} and Sio_3^{2-} 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 1
Summary of synthesis conditions and the yields obtained.

	Sample	Ultrasonic power (%)	Time (min)	Temperature (°C)	SDS concentration (g)	Yield (%)
G1-group	S1	70	5	80	–	73
	S2	70	10	85	–	82
	S3	70	15	90	–	84
G2-group	S4	70	10	85	0.1	85
	S5	70	10	85	0.2	91
	S6	70	10	85	0.3	92