Simple preparation and initial characterization of semi-amorphous hollow calcium silicate hydrate nanoparticles by ammonia-hydrothermal-template techniques

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Article note:

Abstract

Semi-amorphous hollow calcium silicate hydrate nanoparticles (CS10d120Hac) were successfully synthesized via simple ammonia-hydrothermal template approach (AHT) followed by acid treatment. Results revealed that the newly synthesized samples had homogenous hollow nano-interior wherein the shell-wall contained semi-amorphous calcium silicate hydrate. The AHT intensified the formation of a stronger electrostatic interaction (Si-O-Ca) from the weaker electrostatic contact composed of silicate wall-calcium hydroxide interaction (Si-OH-Ca) forming a thin semi-amorphous calcium silicate hydrate shell wall. This is also a convenient way for structural stability of the hollow calcium silicate hydrate nanoparticle (CS10d120Hac). The CS10d120Hac showed a relatively higher surface area, which is uniquely rare especially if compared with bulk calcium silicate particles. This CS10d120Hac can be selectively functionalized with multiple organic and inorganic groups. Hence, this work may open a new route for the formation of hybrid hollow bio-active particles.

Keywords Calcium silicate hydrate, Hollow nanoparticles, Colloidal, Hydrothermal-template synthesis

Introduction

Recently, nanosize calcium silicate hydrate (CSH) materials have been increasingly significant because of its potential function in the field of nano-medicine and cement science applications (Gandolfi et al. 2010; Wu et al. 2010; Chen et al. 2011). CSH possesses a remarkable level of structural stability, which is about more than 30 crystalline CSH excluding the amorphous CSH, and are described as generic term CSH (Taylor 1986). The composition varies with no specific range and is usually prepared by hydrothermal process (HP), wherein the structures can be in a range of semi-crystalline to nearly amorphous structure. The synthesis of CSH microfibers via HP, subjected to high temperature reaction at 180 to 350 ^{o}C, was successfully done (Mitsuda et al. 1986; Udawatte et al. 2000; Watanabe et al. 2001; Rios et al. 2009; Nicoleau 2010). Moreover, some researchers also attempted to form a bone-like CSH-apatite-like material with hollow microspheres for drug delivery applications (DDA) (Li et al. 2005; Gandolfi et al. 2010; Wu et al. 2010; Zhang et al. 2010) but the synthesized CSH particles were too large, hierarchically not well defined, unstable, of non-uniform particle size, and were produced in low quantity from a technically complicated process. Accordingly, in order to maximize the full potential of CSH materials for bio-activity and DDA, a large specific surface area with a relatively higher pore volume, lower density, and well-defined interconnected pore networks are desired and precisely significant (Okada et al. 1994; Huang et al. 2002; Saravanapavan et al. 2003; Gou et al. 2004; Allen et al. 2007; Coleman et al. 2007; Pei et al. 2010). One strategy is to produce nanosize CSH phase material with porous shell wall and hollow interior structures that could lead to superior nano-bio-active material or nano-cement applications. This type of CSH nano-material is usually difficult to prepare using the most common processes (such as nano-emulsion, sono-

chemical, etc). For this reason, the development of a general and simple method for the preparation of hollow CSH nanoparticles is needed so that the surfaces can be easily modified and can be used for practical-novel applications. Up to now, the attempt to fabricate semi-amorphous hollow CSH nanoparticles (CS10d120Hac) is still a challenge and this new type of CSH nanoparticles has not yet been fully reported.

To address this issue we used our previous research on colloidal core-shell $CaCO_3$@SiO_2 (calcium-silicate system) nanoparticles (Shin et al. 2003; Fuji et al. 2007; Virtudazo et al. 2010) followed by aging by solvothermal concept (SC) to form CSH phase nano-materials (Chippindale et al. 1996; Devaraju et al. 2009; Chang et al. 2010; Blakely et al. 2011). Fabricating the nano-CSH shell structure via SC is a convenient method to produce this type of materials (Udawatte et al. 2000; Takagi et al. 2009; Nicoleau 2010). The SC process is done by heating the solution (sample with solvent) above its boiling point contained in a sealed vessel (such as an autoclave container) wherein the pressure autogenously far exceeds the ambient pressure. In this process, the autoclave in an aqueous ammonia solution with core-shell particles designate as the ammonia-hydrothermal template method (AHT) (Lin et al. 1999, 2000, 2001). This process exploits the measurable solubility and reactivity of the inorganic substances in the solvent at elevated temperature and pressure. Moreover, it permits subsequent partial crystallization of the dissolve precursor ions during the AHT process. Hence, complex structures (such as CSH) may occur in AHT. Generally, the reaction temperature, solvent and concentration are some of the parameters that can be readily altered in AHT. In this paper, we report a novel type, eco-friendly, surfactant-free and non-toxic method to fabricate semi-amorphous CS10d120Hac via AHT followed by dissolution of $CaCO_3$ core-nanoparticles from the colloidal solution composed of

composite core-shell ($CaCO_3$@SiO_2) nanoparticles. The CS10d120Hac produced is a relatively uniform nanosize hollow particles ranging from (60 to100) nm with a stable surface morphology, composed of ultra microporous shell wall. It contains an external and internal surface that can be selectively functionalized with multiple organic and inorganic groups. Henceforth, this work may open a new route to prepare hybrid hollow bio-active particles.

Experimental

Materials

Nanocube 60 calcium carbonate ($CaCO_3$, Nittetsu Mining Co., Ltd Japan), tetraethoxysilane (TEOS, Wako Pure Chemical Industries, Ltd., > 95 %), ammonia water (NH_4OH, Wako Pure Chemical Industries, Ltd., >28 %) and ethanol (EtOH (CH_3CH_2OH), Wako Pure Chemical Industries, Ltd.,> 99.8 %) were used as received.

Synthesis of core-shell CSH nanoparticles

The synthesis was based on our previous works (Virtudazo et al. 2010; Fuji et al. 2011; Takai et al. 2011) with the addition of AHT during the reaction. In this procedure, 3.29 g of $CaCO_3$ nanocube particles was dispersed in 15.52 mL of EtOH and continuously stirred for 10 min at room temperature (RT) using an ultrasonic. Then 1 mL of TEOS was slowly added to the solution, followed by 1 mL of NH_4OH_{aq}. The white slurry was continuously stirred for 2 h, then obtained a composite core-shell $CaCO_3$@SiO_2 nanoparticles with a typical molar ratio of 7.3:58.9:1:7.8:3.4 ($CaCO_3$: EtOH: TEOS: H_2O:NH_3). After 2 h, the slurry was transferred to a 50 mL-autoclaveable, Teflon-lined stainless steel with an estimated pressure of 50 kg cm^{-2}. This was heated to 120 ^oC for 10 d. After 10 d

aging, the vessel was cooled to RT and then synthesized product was filtered and washed several times with EtOH/H_2O mixture until neutral. The composite core-shell calcium silicate hydrate nanoparticles (CSH nanoparticles) were then dried in a vacuum oven at 90 ^{o}C for 5 h.

(*Note* During AHT, the temperature reactions were varied from RT (no hydrothermal; HS0dAH0ac), 90 ^{o}C for 10 d (HS10d90Hac), and 120 ^{o}C for 10 d (CS10d120Hac)).

Fabrication of hollow CSH nanoparticles

To obtain hollow particles, 0.7 g of dried powder sample (all as-synthesized dried core-shell nanoparticles) was subjected to acid treatment using 15 mL of 3 mol L^{-1} HCl with continuous stirring for 8 h at RT. The mixture was then filtered and washed several times (until neutral) with EtOH/H_2O mixture. The obtained glassy gel solid (hollow) was vacuum dried at 90 ^{o}C for 1 d. The hollow nano-size particles obtained were named as follows: HS0dAHOac, HS10d90Hac and CS10d120Hac. The process flow for the formation of (CS10d120Hac) hollow CSH nanoparticles is illustrated in Fig. 1.

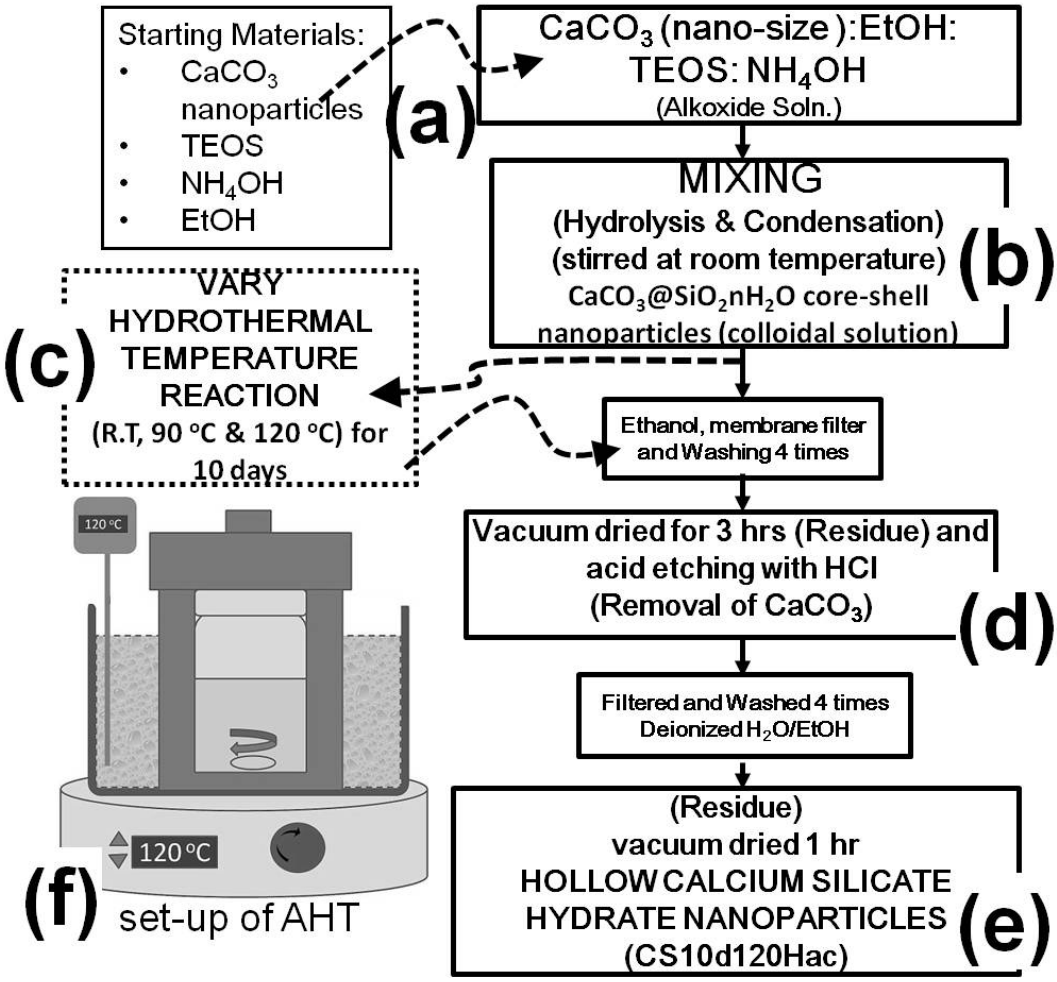

Fig. 1 Process flow with an illustration of the simple set-up of AHT (**f**) during the synthesis of CS10d120Hac: **a** proportioning; **b** mixing for hydrolysis and condensation to form core-shell nanoparticles ($CaCO_3$@SiO_2.nH_2O); **c** subjected to AHT at varying temperature for 10 days; **d** Dried and acid etched to remove $CaCO_3$ nanoparticles templates; **e** then obtain CS10d120Hac

Characterization

The products were characterized by X-ray Diffraction (XRD, Model RINT 1100, Rigaku) with Cu Kα radiation (λ= 1.54056 Å) at a scanning rate of 0.02 ^{o} s^{-1} (5 ^{o}-60 ^{o}, 2θ) with an operating voltage of 40 kV and emission current 40 mA. The thermal property of the sample was investigated using thermogravimetry (TG, TG-8120, Rigaku, Japan) under oxygen atmosphere. The temperature was increased at a rate of 10 ^{o}C min^{-1} from 22 to 1000 ^{o}C. Morphology and microstructure of the hollow particles were examined using scanning electron

microscopy (SEM; JSM-7000F, JEOL) and transmission electron microscopy (TEM, 2000EXII). The specific surface area and cavity-pore size distribution of the hollow samples were determined by Brunauer-Emmett-Tellers (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively via the automatic surface area analyzer (BELSORP-max) using Nitrogen gas (N_2) adsorption desorption isotherm recorded at 77 K.

Results and discussions

Figure 1 illustrates the process for producing CS10d120Hac via AHT. Core-shell nanoparticles were formed during hydrolysis of TEOS (a siloxane) followed by condensation of silicate which coated the core-$CaCO_3$ nanoparticles. The colloidal solution was then subjected to AHT with aging and followed by acid-etching.

Crystallographic properties

Using the x-ray diffraction patterns (XRD), the results showed a diffraction angle identified as calcite (core nanoparticles $CaCO_3$) (Hoshino, et al. 2006; Fuji, et al. 2007). This was clearly shown for the samples such as the raw-$CaCO_3$ nanoparticles (Fig. 2a), samples synthesized at RT (Fig. 2b) and samples synthesized by AHT at 90 ^{o}C for 10 d (Fig. 2c) before acid treatment. This verifies that the core nanoparticle ($CaCO_3$) was coated by amorphous silicate (schematically shown in Fig. 1, 5).

But the AHT as-synthesized samples treated at 120 ^{o}C and aged for 10 d (Fig. 2d), formed an additional sharp peak at ~18.1 (2θ). This peak corresponds to an overlap diffraction peak of $Ca(OH)_2$ (Wang et al. 1997; Hong et al. 1999; Chen et al. 2004; Kim et al. 2004; Qing et al. 2007) and is denoted as the low crystalline phase of CSH, see Fig. S5 (Ishida et al. 1992b; Wang et al. 1997; Chen et al. 2004; Yanagisawa et al. 2006; Baltakys et al. 2007; Qing et al. 2007).

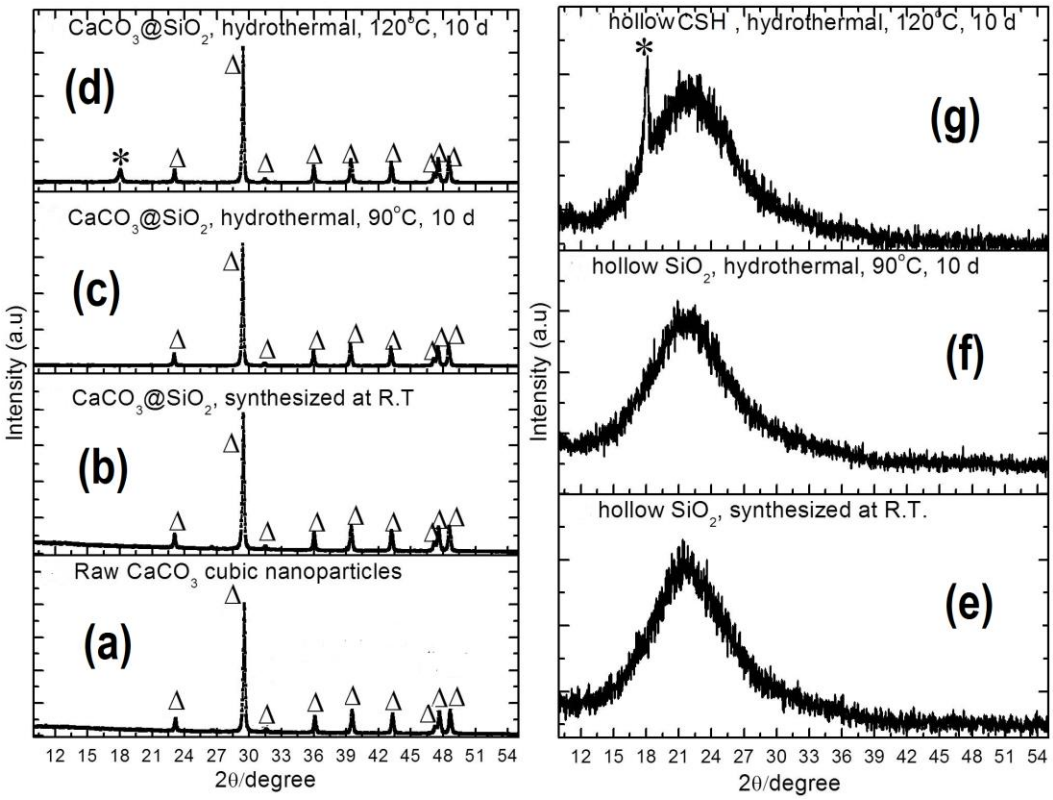

Fig. 2 XRD pattern of $CaCO_3$ (raw) nanoparticles (**a**), as synthesized samples at RT (**b**) and samples AHT aged for 10 d at 90 ^oC (**c**) and 120 ^oC (**d**). Then after acid treatment, formed an amorphous phase hollow samples (HS0dAH0ac (**e**) and HS10d90Hac (**f**)) except for sample CS10d120Hac (**g**). The (Δ) indicates the cubic calcite while (*) is the overlapped $Ca(OH)_2$ and semi-amorphous CSH phase , see Fig. S5

To confirm the formation of $Ca(OH)_2$ - SiO_{2-X} - H_2O system within the amorphous silicate-surface shell wall, an acid treatment was done for all the experimental samples for the dissolution of the $CaCO_3$ core-template nanoparticles. After acid etching, the reflection peak at ~18.1 (2θ) still existed for CS10d120Hac sample (see Fig. 2g, S5, S6), while no visual peaks (no other crystalline phases) were observed for the other samples such as the HS0dAH0ac (Fig.2e) and HS10d90Hac (Fig. 2f). Therefore, semi-amorphous CSH was contained in the shell wall of CS10d120Hac.

Thermal analysis and nitrogen adsorption-desorption isotherm

For confirmation, all synthesized hollow samples were subjected to thermogravimetric analysis (TG). As shown in Fig. 3a, a large gap of weight loss was detected between non-hydrothermal (HS0dAH0ac [■]) and AHT-treated hollow nanoparticles (HS10d90Hac [●] & CS10d120Hac [▲]). This was due to the removal of organic solvent and OH- groups (Kim et al. 2000; Li et al.2004). A slight drop in percentage weight loss at temperature (500 -600) ^{o}C was monitored for CS10d120Hac [▲] sample. This is due to the formation of new phase CSH during the synthesis of semi-amorphous CS10d120Hac (Ishida et al. 1992a, 1993; Saravanapavan et al. 2003; Brunner et al. 2006). These results are in-agreement with the XRD data obtained. In addition, the removal of organic solvent and OH groups accelerated during the AHT reaction. Structural re-arrangement within the amorphous silica shell occurred and led to the formation of (CS10d120Hac) hollow CSH with $Ca(OH)_2$ that was deposited onto the shell walls composed of silicate networks (Li et al. 1999,2002, 2004).

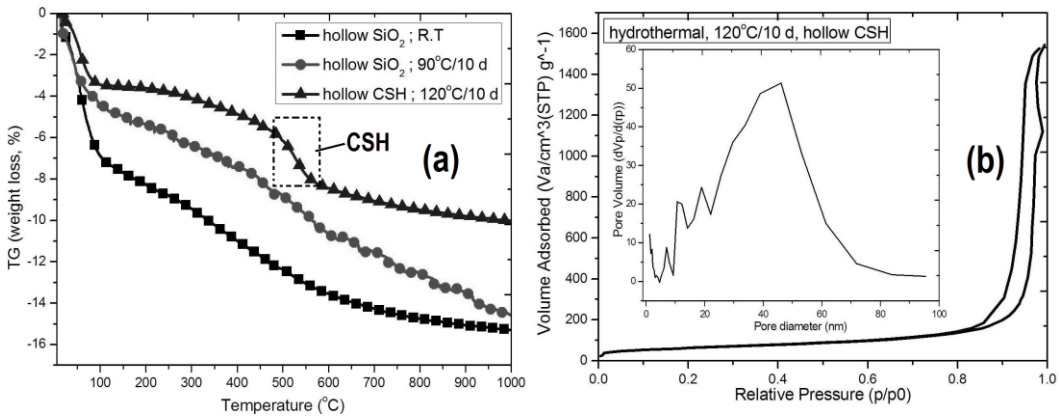

Fig. 3 Thermogravimetric analysis (TG) (**a**) of the hollow samples namely HS0dAH0ac (■), HS10d90Hac (●) and CS10d120Hac (▲). Then in (**b**), N_2 adsorption desorption isotherm with inset pore (macro-pore) size distribution of CS10d120Hac particles (samples)

For the surface area properties of the synthesized CS10d120Hac nanoparticles, N_2 adsorption-desorption isotherm (77 K, Fig.3b) was used. Based from the isotherm

pattern, CS10d120Hac is classified as type II isotherm - adsorption-desorption hysteresis with no plateau at high p/p_o (Sing et al. 1985). The steep increase at p/p_o (0.9-1.0) denotes the macropore space in between the CS10d120Hac nanoparticles or the macro-hole within the shell wall. The macropore space was measured using Barrett-Joyner-Halenda (BJH) method ranging from (30 to 60) nm based from the pore-space-size distribution curve pattern as shown in inset Fig. 3b. Then using Brunauer-Emmett-Tellers (BET) method, the specific surface area of the CS10d120Hac samples was measured as 215.21 $m^2 g^{-1}$. A slight difference is observed, as compared to the HS0dAH0ac samples (358.08 $m^2 g^{-1}$, see Fig. S4). The decrease in surface area of CS10d120Hac could be due to the thickening of the silanol groups, which were developed during the formation of semi-amorphous CSH phase framework with $Ca(OH)_2$ that was present within the shell wall (Lin et al. 1999; Wei et al. 2008). This improved the structural stability of the nano-size CS10d120Hac particles within the shell wall which was composed of ultra-fine micropores (Shin et al. 2003; Fuji et al. 2006, 2007).

Structural and surface morphology

The morphological profiles of the synthesized samples were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 4, no major alteration was detected in terms of shape and size of nanoparticles.

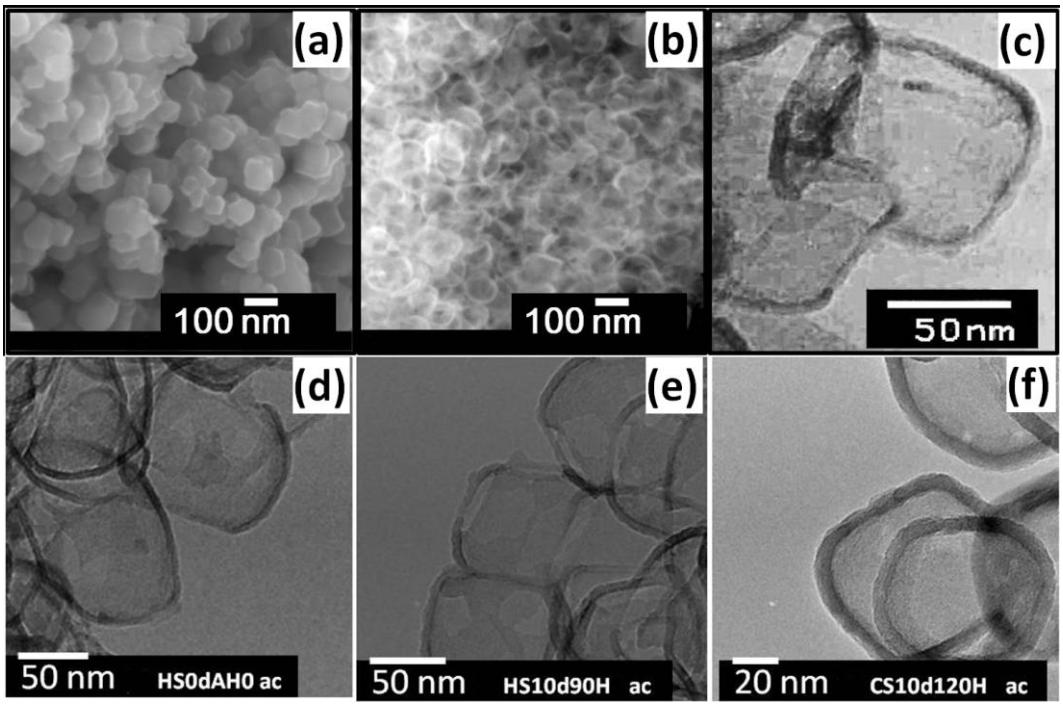

Fig. 4 SEM images of AHT synthesized sample at 120 ^{o}C for 10 d before (**a**) and after acid etch produced CS10d120Hac (**b**) with TEM images of CS10d120Hac (**c, f**), HS0dAH0ac (**d**) and HS10d90Hac (**e**)

The morphological shape of the samples was visibly preserved even after aging at ~120 ^{o}C for 10 d, as shown in Fig. 4a. After acid treatment, the hollow interior was clearly observed with hollow cavity size ranging from 60-100 nm and the uniform shell wall thickness approximately around ~10 nm as shown in SEM (Fig. 4b) and TEM images (Fig. 4c, 4f) for sample CS10d120Hac. These results were almost likely the same for the samples HS0dAH0ac (Fig. 4d) and HS10d90Hac (Fig. 4e) (see also Fig. S1, S2, S3).

Possible mechanism for the formation of semi-amorphous hollow calcium silicate hydrate nanoparticles via AHT method

The formation of unique CS10d120Hac was attained by AHT at relatively low temperature reaction (i.e. 120 ^{o}C for 10 d) wherein the shell wall network structure of the synthesized hollow particles were composed of $Ca(OH)_2$ and low

crystalline CSH (Wang et al. 1997; Chen et al. 2004; Yanagisawa et al. 2006; Baltakys et al. 2007). Figure 5 illustrates the basic schematic plausible mechanism for the formation of semi-amorphous hollow CSH nanoparticles by AHT with aging. Upon increasing the reaction temperature of the AHT, the less-condensed silicate species (Si-OH groups) can be subsequently re-arranged. Stabilization of Si-OH groups occurred at this stage of the reaction. The $Ca(OH)_2$ present on the surfaces of $CaCO_3$ nanoparticles attached onto the exposed hydroxyl groups of the silicate chains. At this critical point, the interaction between silicate (Si-OH) and calcium hydroxide (Ca-OH) were transformed from a weaker electrostatic interface (Si-OH-Ca) to a stronger electrostatic interaction (Si-O-Ca). A stable phase of amorphous CSH systems was formed from AHT aging by deprotonation caused by high pH (high alkaline) and high temperature (see Fig. S6). After acid etching, hollow nanoparticles were produced wherein the thin-shell wall is composed of semi-amorphous CSH (CS10d120Hac).

This process not only re-structures the silicate networks (ultra-microporous structures) that led to the formation of semi-amorphous CSH with $Ca(OH)_2$, but also increased the thermal and hydrothermal stability of the nanostructure shell wall (Lin et al. 1999, 2002; Park et al. 2001; Parfenov et al. 2003; Virtudazo et al. 2010). The nano-structural features of CS10d120Hac are highly desirable in understanding the theoretical aspect of CSH nano-structure. The new synthesized material exhibits a higher specific surface area and interconnected micropore channels, which makes it worthy for drug loading and release applications. Typically, the inner diameter and morphology of the unique CS10d120Hac can be controlled by adopting varying sizes of $CaCO_3$ particles. In addition, further characterization and experiment have been continuously done such as adjusting

the shell to mesoporous dimensions, varying the thickness, and incorporating other bio-active materials to the network.

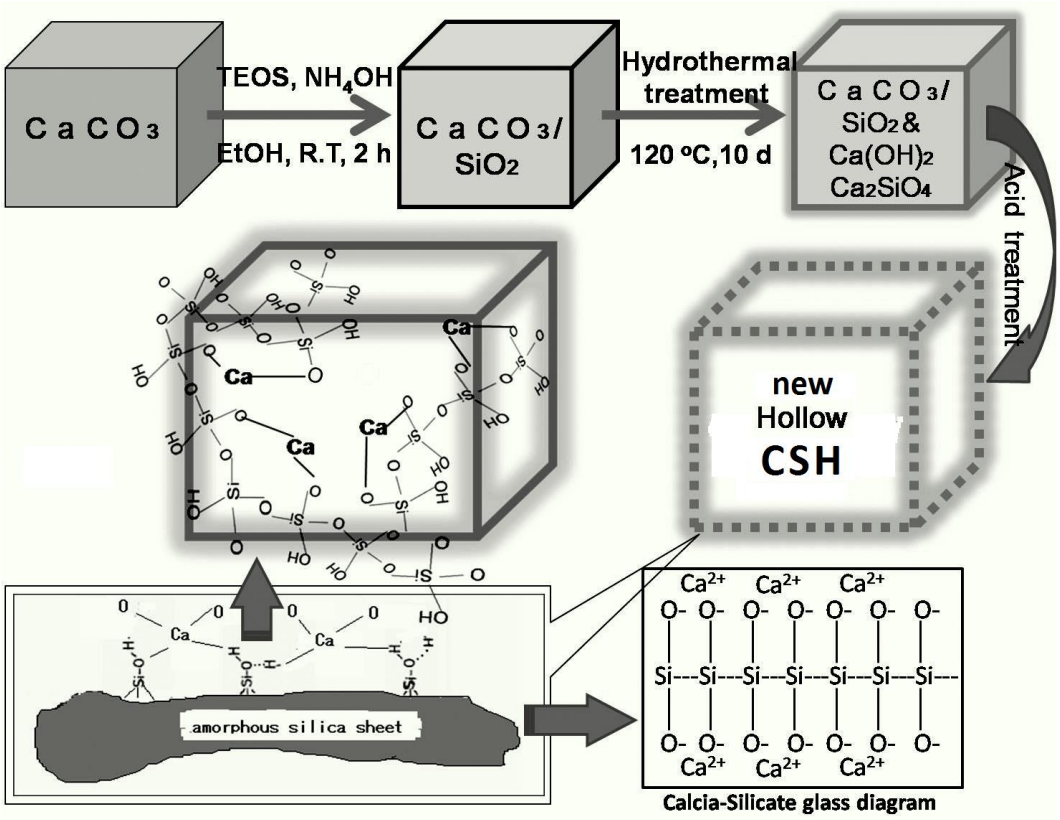

Fig. 5 Schematic illustration and chemical reaction for the possible mechanism for the formation of hollow CSH nanoparticles (CS10d120Hac), see also Fig. S6

Conclusion

In this article, we demonstrated a simple method for the fabrication of semi-amorphous, nanosize CS10d120Hac ranging from 60-100 nm via AHT-aging process followed by acid treatment. The nanostructure shell stability of CS10d120Hac was dependent on the AHT reaction temperature and aging time. In future work, this material can be functionalized to form more dispersed particles and produce hollow hybrid bio-glass particles. Moreover, due to its exceptional specific surface area, porosity, and nanostructure, these may find wide use for varied applications such as in nano-cement, nano-biomedicine, and coating additives for thermal insulating materials.

Conflict of interest

The author declares that they have no competing interest.

Authors Contributions

RVRV carried out the experimentation, characterization and preparation of the manuscripts. M.F and H.W guided the study, participated in the design, coordination and preparation of the manuscripts. M.F and T.S assisted in guiding the experiment and coordinating and monitoring the equipments during the research work. All the authors approved the final manuscript.

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Supplementary materials

Supplementary materials (the abbreviation and further characterization details of the results on SEM/TEM images, XRD analysis, Nitrogen adsorption desorption isotherms, detailed schematic possible reactions of CS10d120Hac) is available in the online version of this article.

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Simple preparation and initial characterization of semi-amorphous hollow calcium silicate hydrate nanoparticles by ammonia-hydrothermal-template techniques

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FIGURE CAPTIONS

Fig. 1 Process flow with an illustration of the simple set-up of AHT (**f**) during the synthesis of CS10d120Hac: **a** proportioning; **b** mixing for hydrolysis and condensation to form core-shell nanoparticles ($CaCO_3$@$SiO_2.nH_2O$); **c** subjected to AHT at varying temperature for 10 days; **d** Dried and acid etched to remove $CaCO_3$ nanoparticles templates; **e** then obtain CS10d120Hac

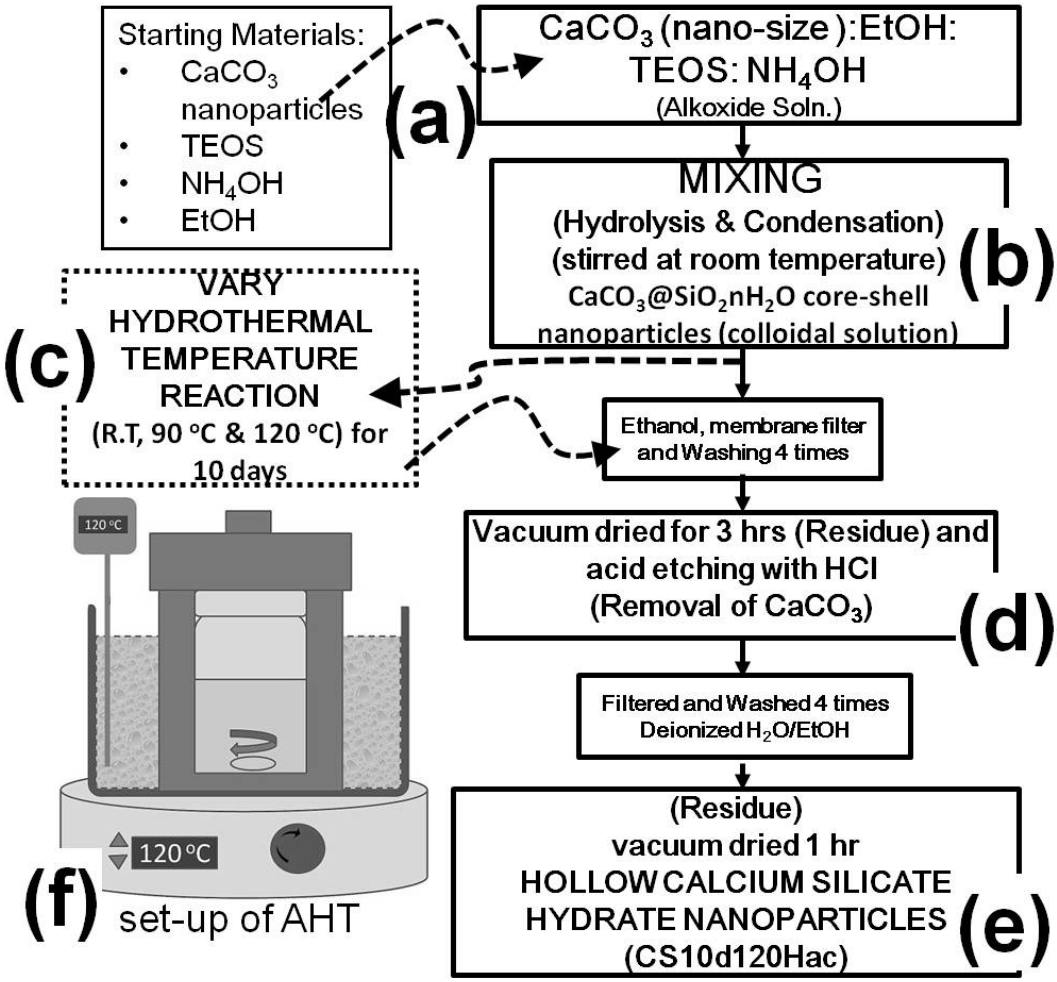
Fig. 2 XRD pattern of $CaCO_3$ (raw) nanoparticles (**a**), as synthesized samples at RT (**b**) and samples AHT aged for 10 d at 90 ^oC (**c**) and 120 ^oC (**d**). Then after acid treatment, formed an amorphous phase hollow samples (HS0dAH0ac (**e**) and HS10d90Hac (**f**)) except for sample CS10d120Hac (**g**). The (Δ) indicates the cubic calcite while (*) is the overlapped $Ca(OH)_2$ and semi-amorphous CSH phase, see Fig. S5

Fig. 3 Thermogravimetric analysis (TG) (**a**) of the hollow samples namely HS0dAH0ac (■), HS10d90Hac (●) and CS10d120Hac (▲). Then in (**b**), N_2 adsorption desorption isotherm with inset pore (macro-pore) size distribution of CS10d120Hac particles (samples)

Fig. 4 SEM images of AHT synthesized sample at 120 ^oC for 10 d before (**a**) and after acid etch produced CS10d120Hac (**b**) with TEM images of CS10d120Hac (**c, f**), HS0dAH0ac (**d**) and HS10d90Hac (**e**)

Fig. 5 Schematic illustration and chemical reaction for the possible mechanism for the formation of hollow CSH nanoparticles (CS10d120Hac), see also Fig. S6

FIGURES



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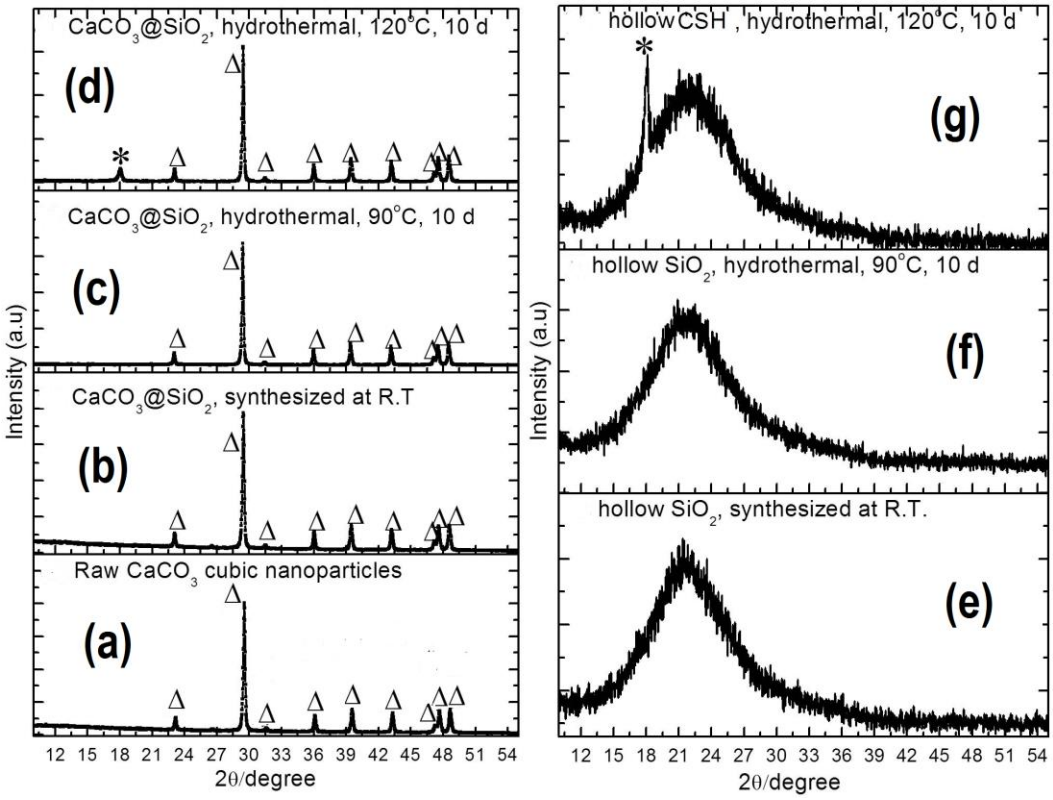

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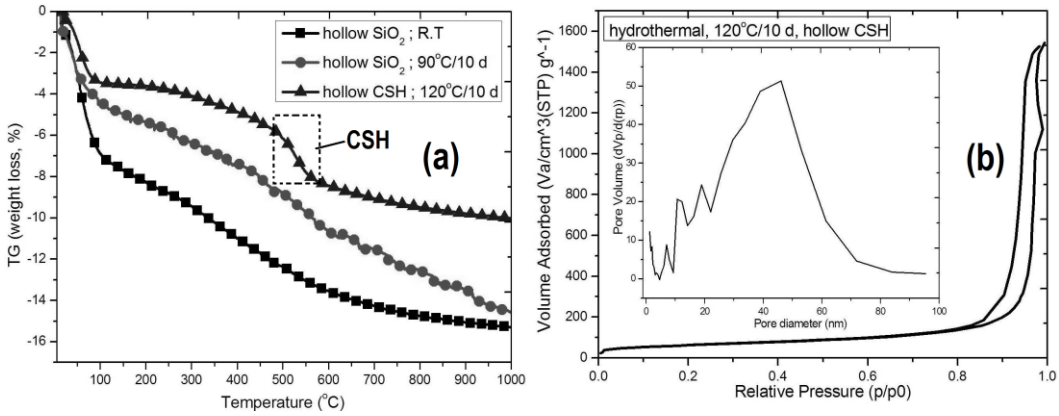

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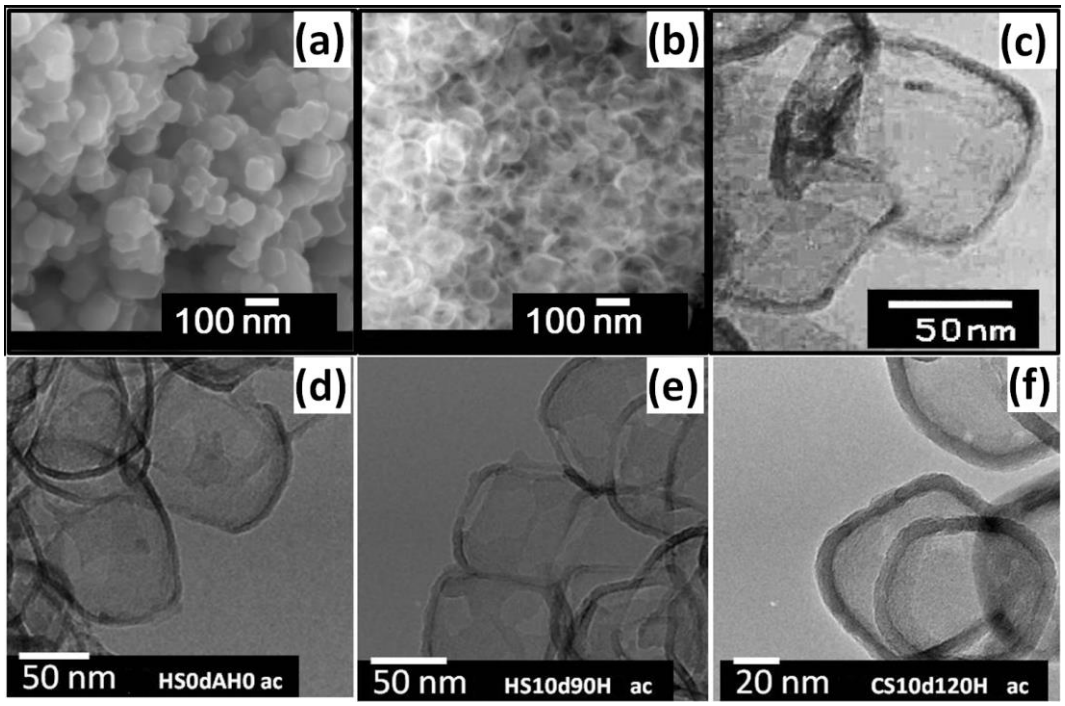
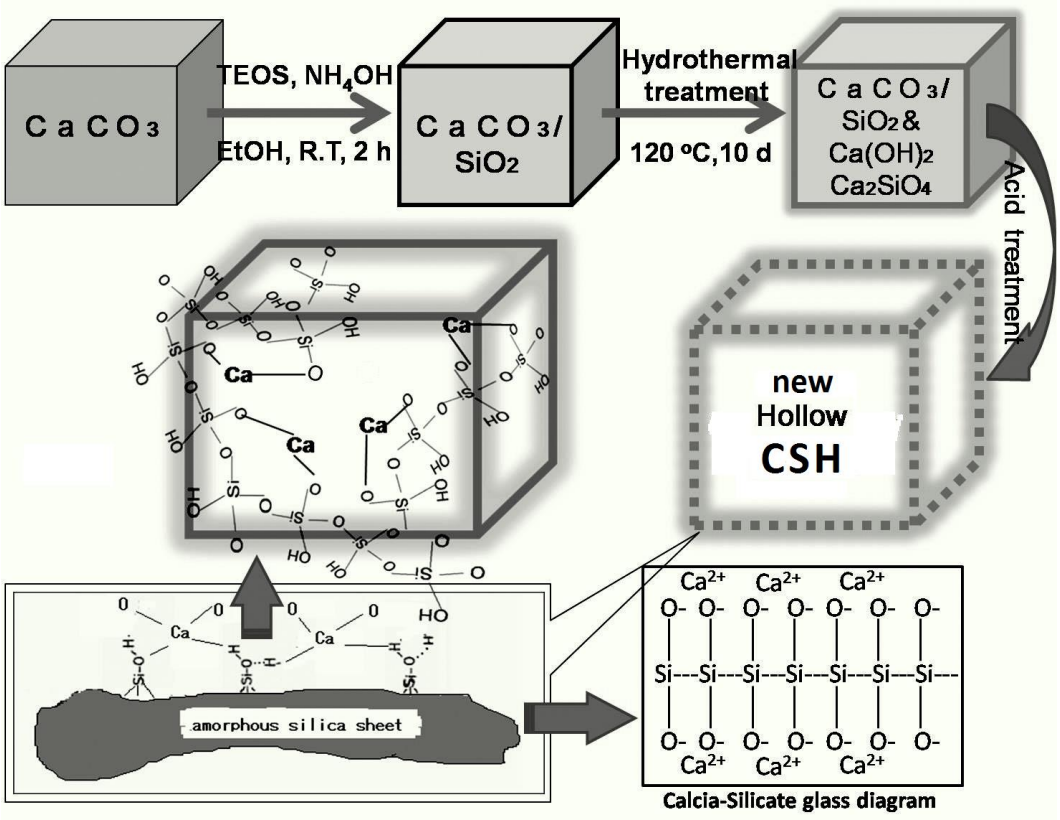


Fig. 4 SEM images of AHT synthesized sample at 120 ^{o}C for 10 d before (**a**) and after acid etch produced CS10d120Hac (**b**) with TEM images of CS10d120Hac (**c, f**), HS0dAH0ac (**d**) and HS10d90Hac (**e**)



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Supporting information

Simple preparation and initial characterization of semi-amorphous hollow calcium silicate hydrate nanoparticles by ammonia-hydrothermal-template techniques

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ABBREVIATIONS

CSH, CC calcium silicate hydrates; RT, CC room temperature; HP, CC hydrothermal process; DDA, CC drug delivery application; CS10d120Hac, CC hollow CSH nanoparticles; $CaCO_3$@SiO_2, CC calcium carbonate & silicate core-shell; SC, CC solvothermal concept; EtOH, CC ethanol; AHT, CC ammonia-hydrothermal technique; $Ca(OH)_2$, CC calcium hydroxide; $CaCO_3$, CC calcium carbonate, SiO_2, CC silica, silicate; TEOS, CC tetraethyl orthosilicate; XRD, CC x-ray diffraction; NH_4 (aq), ammonia solution; HS0DAHac, CC hollow SiO_2 nanoparticles non-AHT treatment; HS10d90Hac, CC hollow SiO_2 nanoparticles AHT treated for 10 d at 90°C; SEM, CC scanning electron microscopy; TEM, CC transmission electron microscope; TG, CC thermogravimetric analysis; BJH, CC Barrett-Joyner-Halenda method; BET, CC Brunauer-Emmett-Tellers Method.

Results

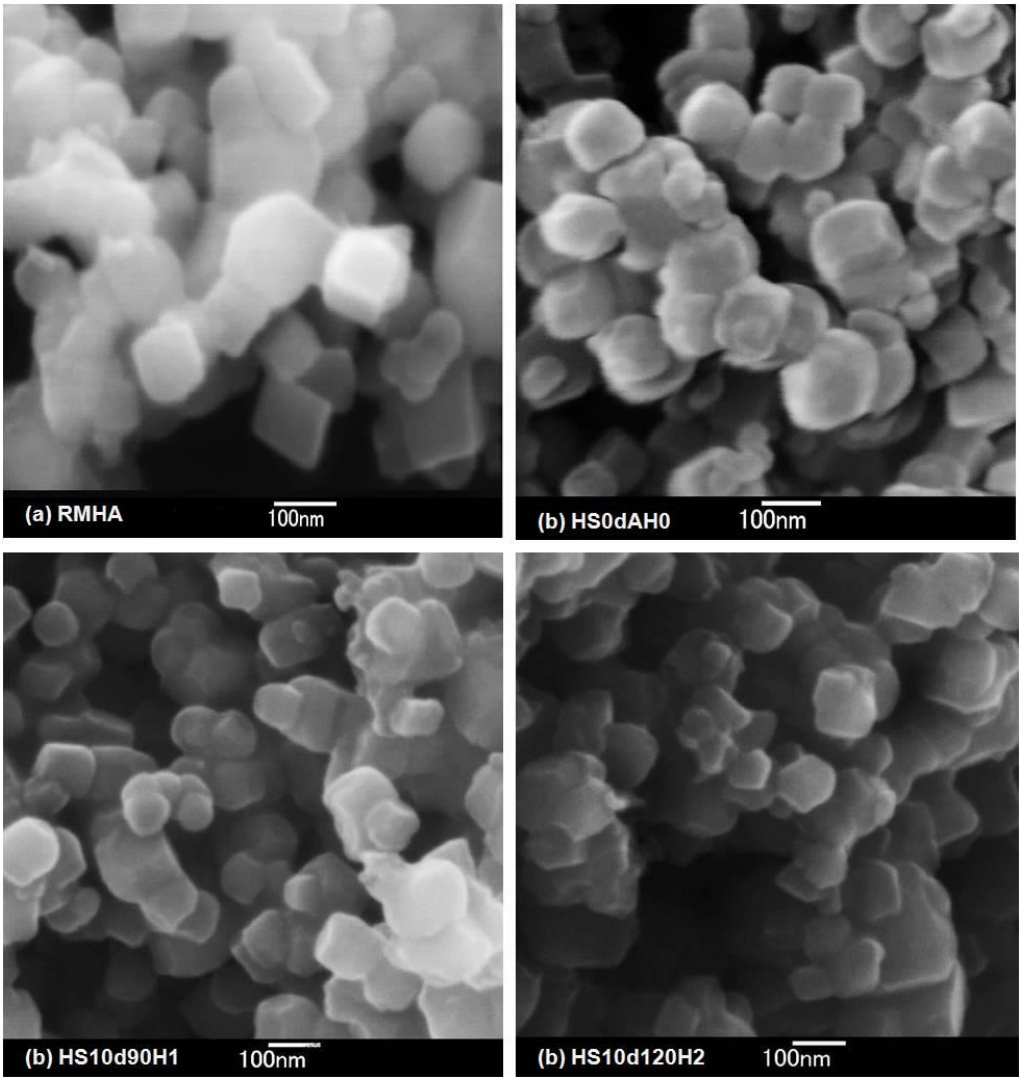

Fig. S1 SEM images of before acid treatment : (a) $CaCO_3$ raw (RMHA) , (b) $CaCO_3$ coated with SiO_2 without hydrothermal (HS0dAH0) , (c) $CaCO_3$ coated with SiO_2 by hydrothermal at 90 ^{o}C for 10 d (HS10d90H1), (d) $CaCO_3$ coated with SiO_2 by hydrothermal at 120 ^{o}C for 10 d (CS10d120H2).

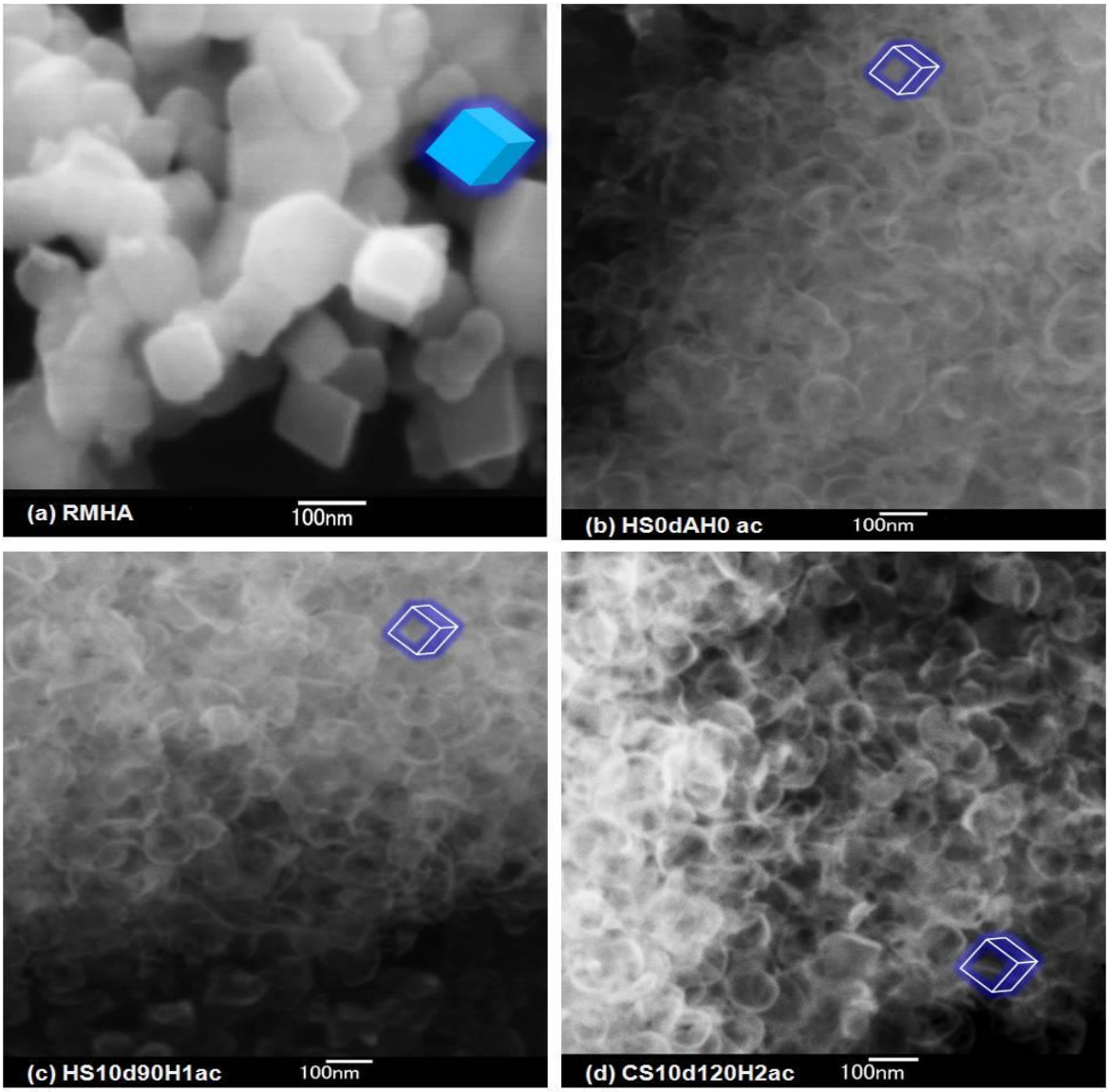

Fig. S2 SEM images: (a) [RMHA] $CaCO_3$ raw; after acid treated samples (b) (HS0dAH0ac) nano-size hollow SiO_2 without hydrothermal, (c) (HS10d90H1ac) nano-size hollow SiO_2 by hydrothermal at 90 ^{o}C for 10 d (d) (CS10d120Hac) nano-size hollow CSH with hydrothermal at 120 ^{o}C for 10 d.

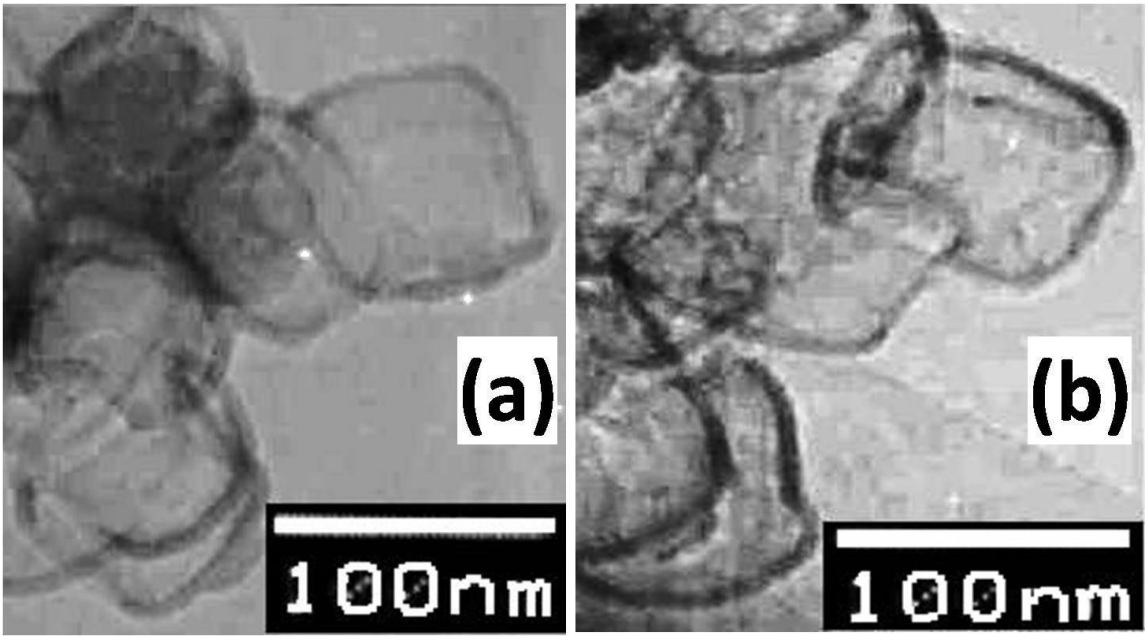

Fig. S3 TEM images: Acid treated samples (a) (HS0dAH0ac) nano-size hollow SiO_2 without hydrothermal, (b) (CS10d120Hac) nano-size hollow CSH with hydrothermal at 120 ^{o}C for 10 d.

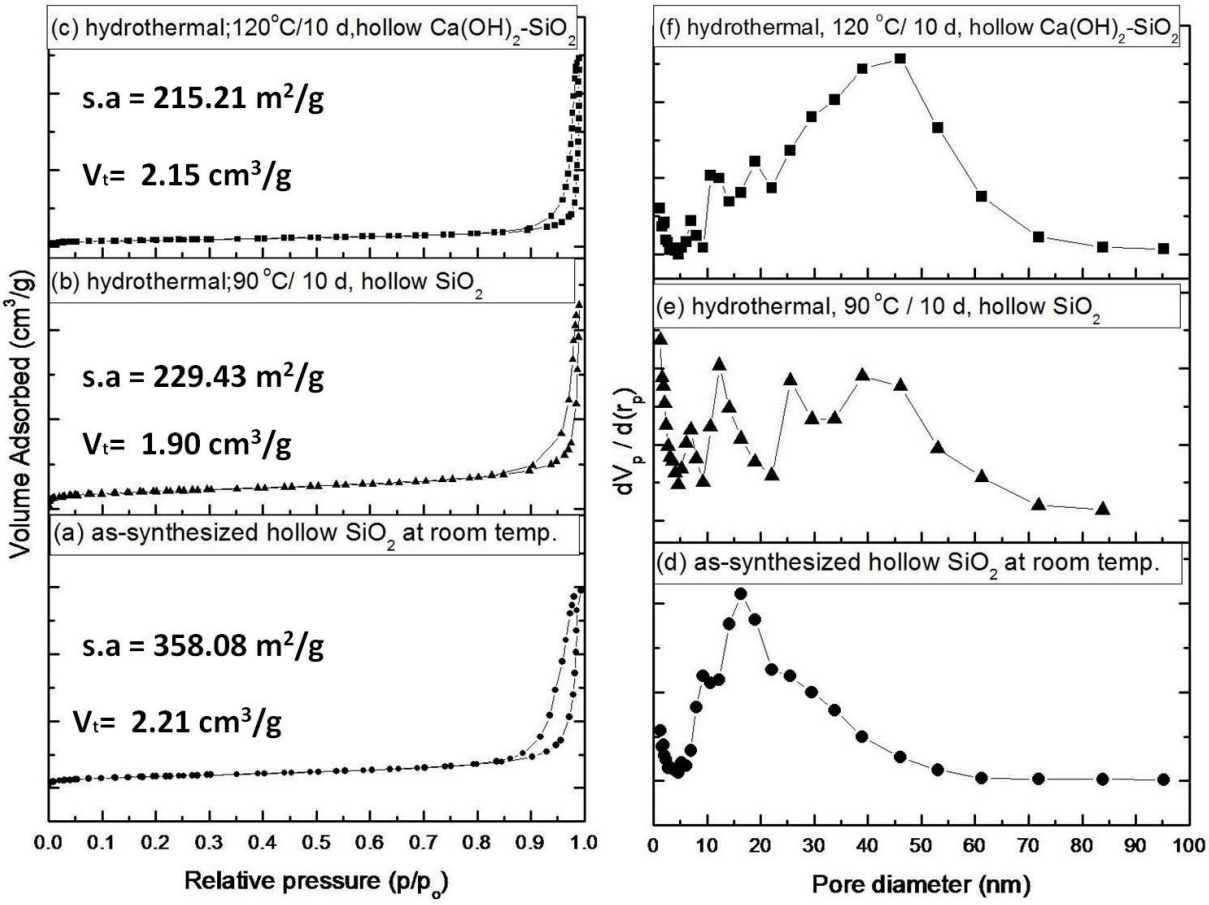

Fig. S4 Nitrogen adsorption-desorption isotherms (a to c) and BJH differential pore size distribution (d to f) of hollow particles synthesized at ambient temperature (HS0dAH0ac), hollow particles hydrothermally treated at 90 ^{o}C for 10 d (HS10d90Hac) and hollow calcia-silicate nano particles hydrothermally treated at 120 ^{o}C for 10 d (CS10d120Hac).

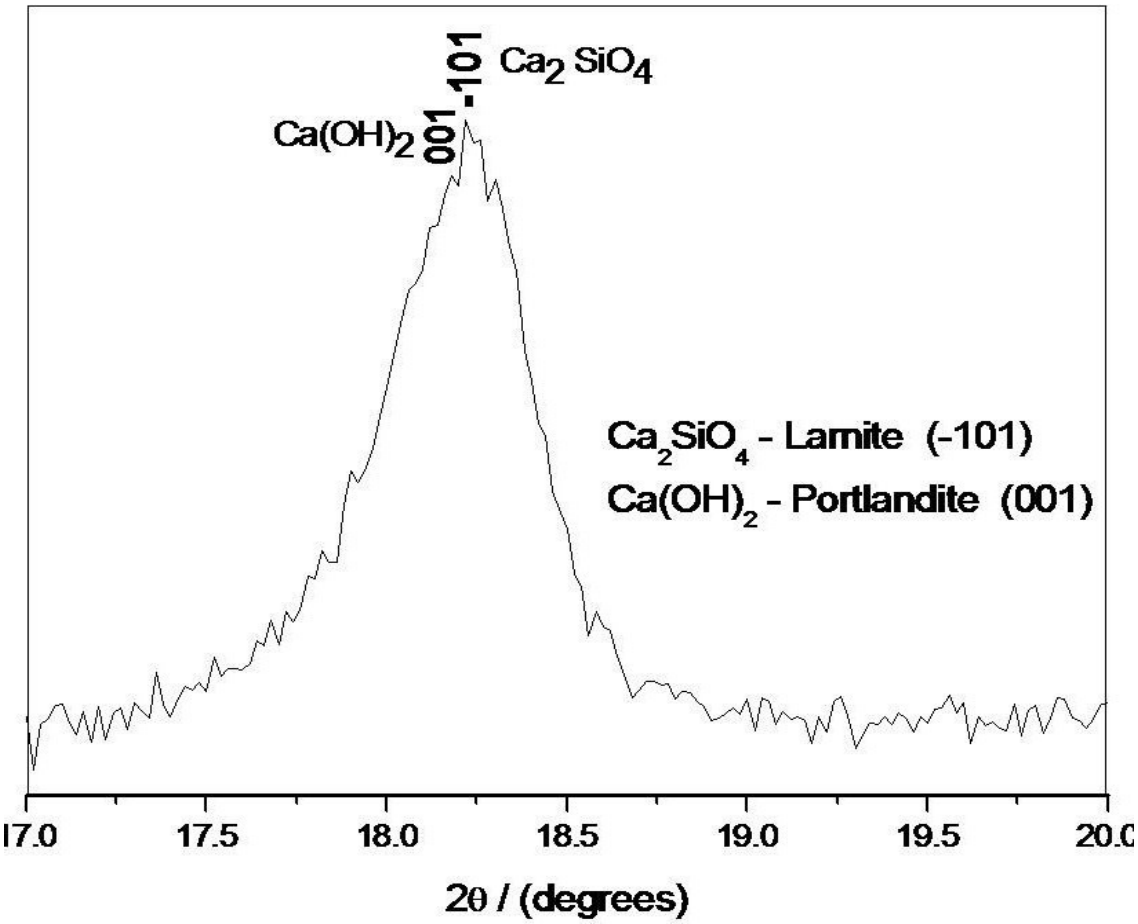

Fig. S5 Enlarge XRD of (CS10d120Hac) hollow CSH nanoparticles hydrothermally treated at 120 ^{o}C for 10 d ranging from (17.0 to 20.0) 2θ. [1-3]

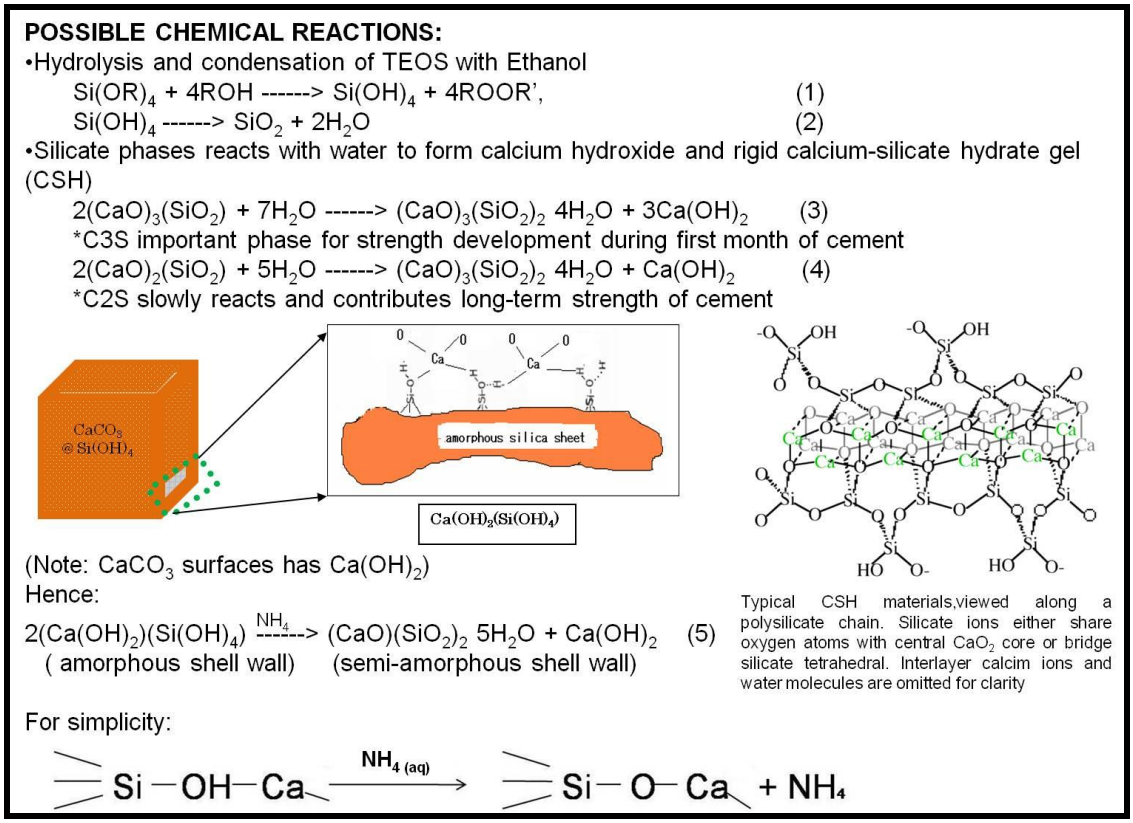

Fig. S6 Possible chemical scheme for the formation of hollow CSH nanoparticles

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