Hydrophobic calcium carbonate with hierarchical micro-/nanostructure for improving foaming capacity

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Abstract
In this paper, a strategy for synthesizing hierarchical calcite calcium carbonate (CaCO3) microspheres was developed. The material was characterized by SEM, TEM, EDS, FT-IR and XRD. The synthetic CaCO3 has an excellent micro-/nano self-assembled structure, which changes the surface wettability. And the contact angle of CaCO3 with water as high as 130.9°, which has a great change compared with the ordinary CaCO3. At the same time, the product has good foaming properties (increase by 17%) and high adhesion. Novelly, the topographical hydrophobic particles are applied to stabilize the foam.

1. Introduction
Calcium carbonate (CaCO3) because of its prominent environment friendly, biodegradability and bio-compatibility, is one of the most broadly used carbonates in various industries [1, 2]. Besides the wide application in the areas of food, paints, plastics, battery and medicine, CaCO3 is one of the most widely existing in the petroleum industry latterly because of the highest output and lowest cost of commercial materials [3–8].

There are mainly two synthesis methods of CaCO3 particles: CO2 bubbling methods and biomimetic synthesis. The reverse emulsion method and the precipitation method are the main methods of the biomimetic synthesis CaCO3 method. There are four main polymorphs of CaCO3: vaterite, aragonite, calcite and amorphous CaCO3, and calcite is the most thermodynamic stable phase [2].

The surface of CaCO3 contains a large amount of free energy, making it more hydrophilic. Since the hydrophilic nature of CaCO3 nanoparticles limits its application and development, the modification of CaCO3 nanoparticles is particularly important. Many scholars have used surface modification of silane coupling agents [9, 10], titanate coupling agents [11], fatty acid (sodium stearate) [12], palmitic acid [13], polyphosphate [14], oleic acid [15], alkyl benzene sulfonic acid [16], and achieve a hydrophobic effect. There are two main factors affecting the wettability of solid surfaces. In addition to the surface free energy, the surface microstructure plays a very important role [17, 18]. Jiang Lei et al proposed that the surface microstructure can be changed simply to change the hydrophobicity [19, 20], and the micro-/nano hierarchical structure has good hydrophobicity. Arbatan et al synthesized oleophilic and superhydrophobic CaCO3 particles with a water contact angle of 152° [21]. Nosonovsky et al discusse the roughness-induced superhydrophobicity theory using the Wenzel and Casey-Baxter equations [22]. It is reported that Rajakumar Ananthakrishnan adopt the method to synthesize oleophilic and superhydrophobic CaCO3 (needle-shaped) with a water contact angle of 166.1°, among them, palmitic acid is used as a surface modifying agent [23].

In this letter, we present a novel hydrothermal method for CaCO3 micro-/nanostructured materials from precipitation reaction of CaCl2 with Na2CO3 in the solvent mixture of Polyethylene glycol (PEG), Sodium dodecyl sulfate (SDS) and H2O at room temperature. Measurements of XRD, FT-IR, TEM, SEM and EDS are used to characterize the morphology and structure. Besides, a rational explanation is used to demonstrate the applications of hydrophobicity for foamability and foam stability.
2. Experimental

2.1. Chemicals and materials
Polyethylene glycol 10000 (PEG 10000), Sodium dodecyl sulfate (SDS), Betaine, Sodium carbonate (Na$_2$CO$_3$) and calcium chloride (CaCl$_2$) were purchased from Aladdin Chemical Reagent Corporation. Anhydrous ethyl alcohol, Methylene blue, Kerosene oil, distilled water. All of the reagents were used directly.

2.2. Synthesis of calcium carbonate microspheres
All the CaCO$_3$ were prepared by hydrothermal method. Direct preparation of CaCO$_3$ was as follows: 0.2 g of PEG 10 000 and 0.2 g of SDS were mixed with 100 ml of distilled water, and disperse the liquid evenly with high frequency ultrasound. Then 0.1 M CaCl$_2$ and 0.1 M Na$_2$CO$_3$ were added in this solution. The mixture was stirred at room temperature for 2 min. Then the formed solution was transferred into a 90 ml Teflon-lined stainless-steel autoclave and maintained at 120 °C for 12 h. The final CaCO$_3$ was finished after centrifugation, washing with absolute ethyl alcohol and drying under 60 °C for 12 h.

2.3. Characterization techniques
Scanning electron microscopic (SEM) and Energy deprivatives spectrometry (EDS) analyses were performed using SIGMA (Zeiss German) acceleration voltage of 5 kV. TEM images of the samples were obtained using JEM-2100 TEM machine at 200 kV an accelerating voltage to characterize their dispersion and morphology. The phase of the CaCO$_3$ was characterized by x-ray diffraction (XRD), Target source: Cu-Ka target, Power:16 kW, Rated tube pressure—Tube flow: 40 kv–40 mA, Scanning range:5°–90°) and Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700).The wettability tests were measured by JY-PHb Automated Goniometer.

2.4. Preparation and characterization of aqueous foams
1 wt% CaCO$_3$ nanoparticles was initially dispersed in SDS solution and the solution was dispersed with ultrasonic waves. Then 100 cm$^3$ of dispersion was transferred to a 800 cm$^3$ stirring cup. The stirring cup was stirred with high speed mixer for 2 min. The volume of foam produced was transferred to a 1000 cm$^3$ cylinder and recorded. The initial foam volume was taken as the measures of foamability. Take the foam half-decay times and liquid half-decay times as a measure of foam stability [24].

3. Results and discussion
A novel sample is synthesized with the in situ reaction of CaCl$_2$ and Na$_2$CO$_3$ in PEG/SDS mixed solvent at 120 °C for 12 h. The morphology and structure of the CaCO$_3$ are shown in figure 1. In the above method, CaCl$_2$ is added to the Na$_2$CO$_3$ solution, and the appearance of the product is as shown in figure 1(a), which is a larger square CaCO$_3$ crystal. The order of addition of the solution is changed. When Na$_2$CO$_3$ is added to the CaCl$_2$ solution, the formed micro-spherical shape of CaCO$_3$ is as shown in figure 1(b). CaCO$_3$ is deposited into a sphere from small square crystals to form a micro-/nanostructure with good hydrophobicity. Some researchers [25, 26] reported that the mixed mode and added order of this reaction affect the distribution, size and morphology of the particles. Actually, when the Ca$^{2+}$ solution is added into the CO$_3^{2-}$ solution, the PH of solution is high due to initial introduction of Ca$^{2+}$, and uniformity of the particles is partially lost with more free Ca$^{2+}$ ions growing onto nuclei. So the particles become bigger and widely distributed, but the opposite process produces smaller particles of uniform in size. Therefore, in this paper, Na$_2$CO$_3$ is added to CaCl$_2$ to synthesize a hydrophobic CaCO$_3$ micro-/nanostructured sphere.

The reaction is carried out under conditions of low-frequency ultrasonic (3 000r min$^{-1}$) and high-frequency ultrasonic (1200 kr min$^{-1}$) respectively, and the resulting product morphology is shown in figures 1(c) and (d). It can be seen that in the case of high-speed stirring, it is advantageous to form smaller crystals, and it is easy to self-assemble to form micro-/nanostructured sphere products after aging. TEM images (figures 1(e) and (f)) show that the Sunken district is submicron-sized, and the nanoparticle subunit is 5–10 nm in diameter. The final product of CaCO$_3$ is a three-dimensional nanostructure with good hydrophobicity.

From the results of the EDS in table 1, the synthetic product contain only C, O and Ca elements. Figure 2(a) shows the typical XRD pattern of CaCO$_3$ microspheres further. Sharp reflections of x-ray diffraction pattern consistent with the (116), (018), (202), (113), (110), (104) and (012) reflections. Obviously, all reflections can be easily pointed to the pure calcite phase in accordance with the space group [24]. As far as we know, calcite is the most stable among many kinds of CaCO$_3$ polymorphs [2]. The nanoparticles exhibit characteristics peaks at 2511, 1756, 1432, 876 and 724 cm$^{-1}$ in the infrared spectra (figure 2(b)). The appearance of peaks around 1756, 1432, 876 and 724 cm$^{-1}$ in all of these four spectra are relevant to C–O stretching vibration, C–O asymmetric stretching vibration, CO$_3^{2-}$ external deformation vibration, and C–O internal deformation vibration.
Glass slides were successively immersed in the 30% H₂O₂ and 4% HCl solution for 1 h. Then they were rinsed with a copious amount of water and dried in an oven at 60 °C. Finally, Place an appropriate amount of calcium carbonate on the glass slide and compact it with another slide until the surface is uniform before measuring the contact angle. The general CaCO₃ is hydrophilic and its contact angle is shown in figure 2(c1). The CaCO₃ synthesized by the method has strong hydrophobicity due to its nano multi-scale structure on the surface, and its contact angle can reach 130.9° (figure 2(c2)) [27, 28]. As can be seen from figure 2(d), CaCO₃ should sink to the bottom of the water after adsorption of Methyl blue. However, in the test of adding kerosene to the upper layer, CaCO₃ does not sink to the bottom after adsorbing Methylene blue, but between oil and water, which fully shows the lipophilicity and hydrophobicity of CaCO₃. The CaCO₃ is not only hydrophobic, but also does not roll off even if it is inverted on the surface, as shown in figures 2(c3), (c4). Because of the quasi-continuous and the generation of discontinuous at the nano-microscale, the CaCO₃ exhibits petal state—the water droplet can be hung when the surface is erected or inverted, hydrophobicity and high adhesion [29].

The volume of foam in the graduated cylinder is measured with 1 wt% CaCO₃ nanoparticles [24] dispersed in different concentrations of anionic surfactant SDS solution and compared to the solution containing no particles (figure 3(a)). It can be seen that when the SDS concentration is less than 1 mM, a stable foam is not produced. Above this concentration, the foam volume increases steadily as the concentration of SDS increases and 0.1 M 1 SDS become the optimum foaming agent concentration. The foam volume of solution with CaCO₃ particles is increasing compared with the pure SDS solution. Because the adsorption of SDS molecules at the micro-/nano CaCO₃ particle/water interface produces a synergistic effect.

At this concentration, different amounts of kerosene are added for the foaming test, and the foaming volume and half-decay times of the final foam are shown in figure 3(b). Adding synthetic 1 Wt% micro-/nano CaCO₃ to the foaming system (oil-water ratio is 3:10), it can be clearly seen that CaCO₃ is added at the same SDS concentration as compared with the non-granular foaming system (figure 3(c)). The foam volume of the foaming system of the particles is significantly increased with and without kerosene from figures 3(a), (c), and the liquid half-decay times is also increasing. Although there was no significant increase in the foam half-decay times, the foam volume is increased by 17% and the liquid half-decay times is increased by 13.8%.

| Table 1. Energy spectra of CaCO₃. |
|-----------------------------------|
| Element  | Weight % | Atom % |
| C        | 22.23    | 33.04  |
| O        | 48.22    | 53.80  |
| Ca       | 29.54    | 13.16  |

Figure 1. (a)–(d) SEM images of CaCO₃. (a) CaCl₂ was added in Na₂CO₃ solution; (b) Na₂CO₃ was added in CaCl₂ solution; The stirring rate: (c) 3 000r min⁻¹; (d) 1200r min⁻¹. (e) and (f) TEM images of the hierarchical micro-/nanostructure calcite CaCO₃.
The main reasons are as follows: on the one hand, solid particles can be adsorbed to the oil/water interface under certain wettability, rearranged by certain interactions, forming a three-dimensional barrier between the droplets and obstructing the liquid. It has the effect of pickering emulsion lotion. On the other hand, the positively charged CaCO₃ particles attract the negatively charged SDS molecules in the aqueous phase to the interface, increasing the amount of surfactant adsorbed at the interface, which is beneficial to reducing oil and water interfacial tension. Due to the bio-compatibility and environment friendly, the foaming capacity of as-prepared CaCO₃ is superior to some nanomaterials, such as SiO₂ and CaCO₃ modified by a chemical modifier [24, 30].

4. Conclusion

In summary, we developed a one-pot method for synthesizing hierarchical calcite CaCO₃ microspheres with hydrophobicity and oleophilicity. When Na₂CO₃ is added to CaCl₂ at high stirring rate, the formation of hydrophobic CaCO₃ can be formed. The synthetic CaCO₃ has an excellent micro-/nano self-assembled
structure, which changes the surface wettability. And the contact angle of CaCO₃ with water as high as 130.9°, which has a great change compared with the ordinary CaCO₃. At the same time, the product has good foaming properties, so that the system of adding particles increases the foaming volume by 17% and liquid half-decay times compared to the surfactant-only system. Simultaneously, it becomes a promising material for stabilization foam to enhance oil recover because of bio-compatibility and environment friendly.

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**References**

[1] Ma X et al 2016 Tunable construction of multi-shelled hollow carbonate nanospheres and their potential applications Nanoscale 8 8687–95
[2] Boyjoo Y, Pareek V K and Liu J 2014 Synthesis of micro and nano-sized carbonate particles and their applications J. Mater. Chem. A 2 14270–88
[3] Naka K and Chuojo Y 2001 Control of crystal nucleation and growth of carbonate by synthetic substrates Chem. Mater. 13 3245–59
[4] Stupp S I 1997 Molecular manipulation of microstructures: biomaterials, ceramics, and semiconductors Science 277 1242–8
[5] Wang L and Nancollas G H 2008 Calcium orthophosphates: crystallization and dissolution Chem. Rev. 108 6628–69
[6] Yang L et al 2013 Morphology and size control of nano calcium carbonate crystallized in reverse micelle system with cationic surfactant cetyltrimethylammonium bromide Micro. Nano Lett. 8 94–8
[7] Stanley M S 2008 Effects of global seawater chemistry on biomineralization: past, present, and future Chem Rev 108 4483–98
[8] Cui Z G, Cui Y Z, Cui cf, Chen Z and Binks B P 2010 Aqueous foams stabilized by in situ surface activation of CaCO₃ nanoparticles via adsorption of anionic surfactant Langmuir 26 12567–74
[9] Yang Z Y, Tang Y J and Zhang J H 2013 Surface modification of CaCO₃ nanoparticles with silane coupling agent for improvement of the interfacial compatibility with styrene–butadiene rubber latex Chalcogen, Lett. 14 41–41
[10] Gupta S, Ramamurthy P C and Madras G 2011 Covalent grafting of polydimethylsiloxane over surface-modified alumina nanoparticles Ind. Eng. Chem. Res. 50 6585–93
[11] Liu W, Xie Z P and Jia C 2012 Surface modification of ceramic powders by titanate coupling agent for injection molding using partially water soluble bindersystem J. Eur. Ceram. Soc. 32 1001–6
[12] Tran H V, Tran L D, Vu H D and Thai H 2010 Facile surface modification of nanoprecipitated calcium carbonate by adsorption of sodium stearate in aqueous solution Colloid Surface A 366 93–103
[13] Jiang J, Zhang Y, Yang X, He X, Tang X and Liu J 2014 Assemblement of nano–calcium carbonate particles on palmitic acid template Adv. Powder Technol. 25 615–20
[14] Penczek S, Pretula J G and Kaluzynski K 2005 Synthesis of a triblock copolymer: poly(ethylene glycol)–poly(alkylene phosphate)–poly (ethylene glycol) as a modifier of caco₃, crystallization J. Polym. Sci. Pol. Chem. 43 630–7
[15] Jin K, Iba S K, Kim Y H, Kim D W, Lee K Y and Lee C M 2015 Improved suspension stability of calcium carbonate nanoparticles by surface modification with oleic acid and phospholipid Biotechnol BioProc E 20 794–9
[16] Song E M, Kim D W, Kim B W and Lim J C 2014 Surface modification of caco₃ nanoparticles by alkylbenzene sulfonic acid surfactant Colloid Surface A 461 11–10
[17] Li H L et al 2018 Strain–tuning atomic substitution in two-dimensional atomic crystals ACS Nano 12 4853–60
[18] Li H L, Wang X, Zhu X L, Duan X F and Pan A L 2018 Composition modulation in one-dimensional and two-dimensional chalcogenide semiconductor nanostructures Chem. Soc. Rev. 47 7504–21
[19] Lei J and Lin F 2007 Bionic Intelligent nano Interface Material (Beijing, China: Chemical Industry Press)
[20] Wen L, Tian Y and Jiang L 2015 Bioinspired super–wettability from fundamental research to practical applications Angew. Chem. Int. Edit. 54 3387–99
[21] Suni S et al 2008 Use of a by-product of peat excavation, cotton grass fibre, as a sorbent for oil-spills Mar. Pollut. Bull. 49 916–21
[22] Nosonovsky M and Bhushan B 2008 Roughness-induced superhydrophobicity: a way to design non-adhesive surfaces J. Phys. Condens. Matter 20 225009–38
[23] Patowary M, Pathak K and Ananthakrishnan R 2015 A facile preparation of superhydrophobic and oleophobic precipitated calcium carbonate sorbent powder for oil spill clean-ups from water and land surfaces RSC Adv. 5 79852–9
[24] Cui Z et al 2010 Aqueous foams stabilized by in situ surface activation of CaCO₃ nanoparticles via adsorption of anionic surfactant Langmuir 26 12567–74
[25] Afsah A et al 2010 Fracture behavior dependence on load-bearing capacity of filler in nano- and microcomposites of polypyrrole containing calcium carbonate Mater Design 31 802–7
[26] Li S et al 2010 Facile preparation of diversified patterns of calcium carbonate in the presence of DTAB J. Cryst. Growth 312 1766–73
[27] Zhang X, Jarm M, Peltonen J, Vor E, Vuorinen T, Levonen E and Mantyla T 2008 Analysis of roughness parameters to specify superhydro–phobic antireflective boehmite films made by the sol–gel process Eur. Ceram. Soc. 28 2177–81
[28] Guan B Y, Lu Y, Wang Y and Lou X W 2018 Porous iron–cobalt alloy/nitrogen-doped carbon cages synthesized via pyrolysis of complex metal–organic framework hybrids for oxygen reduction Adv. Funct. Mater. 28 1708738
[29] Wang S T, Liu K S, Yao X and Jiang L 2015 Bioinspired surfaces with superwettability: new insight on theory, design, and applications Chem. Rev. 115 8230–93
[30] Vatanparast H, Samiee A and Bahramian A 2017 Surface behavior of hydrophilic silica nanoparticle-SDS surfactant solutions: I. Effect of nanoparticle concentration on foamability and foam stability *Colloids & Surfaces A Physicochemical & Engineering Aspects* **513** 430–41