

Article

Controllable Synthesis of Nano-Micro Calcium Carbonate Mediated by Additive Engineering

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Abstract: Nano-micro calcium carbonate has a small particle size, uniform distribution, and good dispersion performance, offering great research value and development prospects. It has been widely used as a filler material for rubber, paper, ink, pigments, and coatings. Developing an efficient and controllable approach to preparing nano-micro calcium carbonate with adjustable morphology and controllable size has significant economic and environmental benefits. This study reports the controllable synthesis of nano-micro calcium carbonate mediated by additive engineering. The effects of various additives including inorganic acids, organic acids, alcohol, and surfactants on the particle size and morphology of the prepared materials were investigated. SEM, FT-IR and other characterization methods were used to analyze the prepared nano-micro calcium carbonate particle size, dispersion, and uniformity. The results showed that the particle size of calcium carbonate was 4–7 μm with a cubic structure. The particle size of calcium carbonate prepared by adding surfactant additives is in the range of 1–4 μm , and the crystal shape of calcium carbonate changes from calcite to vaterite after adding sodium dodecyl benzene sulfonate. With the aid of additives, the calcium carbonate particles dispersed more evenly. The mechanism of the controllable synthesis of nano-micro calcium carbonate mediated by additive engineering is elucidated and discussed. SDBS was found to be the best additive for preparing nano-micro calcium carbonate, and the synthesis conditions were explored and optimized.

Keywords: calcium carbonate; additive; particle size and morphology; energy conservation



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1. Introduction

Calcium carbonate (CaCO_3) is an abundant mineral in nature and has unique physical and chemical properties [1–3]. There are three crystal forms of CaCO_3 : calcite, aragonite, and vaterite [4–6]. Among those, calcite is the most stable polycrystalline form, with a tripartite rhombohedral crystal structure. Aragonite is a metastable polycrystalline type with an orthogonal structure. As for vaterite, it is another metastable form of calcium carbonate with a hexagonal crystal structure [7]. Under typical conditions, the first stage of CaCO_3 crystallization is the formation of amorphous CaCO_3 [8]. The lack of thermodynamic stability of this form causes it to rapidly transform into vaterite and then into calcite at room temperature.

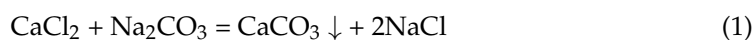
Calcium carbonate is an important industrial product [9–12]. It has been widely used as a filler material for rubber [13], paper [14], ink [15], pigments [16], and coatings [17]. In addition, calcium carbonate shows good biocompatibility, making it an ideal material for biomedical applications [18,19] such as antacid tablets, bone regeneration [20], and drug delivery systems [21]. However, the larger particle size of CaCO_3 leads to rough surface of the product, poor outlook, and poor colorability. In recent years, the design and development of nano-micro calcium carbonates have drawn wide attention. Liu et al. [22]

modified cement-based materials by using nano- CaCO_3 and modified polypropylene (PP) fiber, which significantly improved the printing and hardening properties of the materials. Phuhiangpa et al. [23] studied the effect of nano-micro CaCO_3 on the properties of non-crosslinked rubber composites and improved the properties and processing properties of natural rubber composites. Feng et al. [24] coated nano-calcium carbonate on the surface of polypropylene to accelerate the autonomous healing of gelled composites. Popova et al. [25] synthesized a monodisperse inorganic nanoparticle based on calcium carbonate, which can be combined with anti-cancer drugs to improve the effectiveness of treatment. Nano-micro calcium carbonate has a wide range of applications, so it is important to develop simple and effective synthesis methods to achieve the control of different sizes, crystal forms, and morphologies on an industrial scale.

The development of synthesis routes of CaCO_3 particles at nano- and micrometer scales is challenging yet practically important [26,27]. The ball-milling approach can obtain CaCO_3 particles at about a hundred micrometer scale. Other approaches include the precipitation method, CO_2 bubbling method, and emulsion method. The precipitation method is one of the simplest methods to synthesize CaCO_3 nano- and microparticles [28]. Volodkin et al. [29] obtained spherical particles by using saturated solution and high speed rotation without additives, but with the extension of reaction time, the particle diameter can be increased to 15–20 μm . Wei et al. [30] compared the effects of three surfactants (sodium dodecylsulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), and sodium dodecylsulfonate (DDS)) on the crystal form of calcium carbonate. They found that DDS did not greatly affect CaCO_3 morphology. However, SDS can prepare monodisperse calcite hollow spheres, and SDBS can prepare monodisperse vaterite microspheres. Atchudan et al. [31] reported the synthesis of monodisperse CaCO_3 nanoparticles having either a cubic or spherical structure in the presence of cetyltrimethylammonium bromide (CTAB) via the sonication method, but this approach is complicated. The carbon dioxide (CO_2) bubbling method is also used for the production of CaCO_3 particles [32]. It uses limestone to produce hydrated lime and then sends carbon dioxide CO_2 bubbles through calcium hydroxide to form CaCO_3 particles [33]. However, the agglomeration of particles prepared by this method is relatively common [34,35]. The emulsion method is a type of controlled precipitation reaction frequently used to synthesize micro- and nanosized particles [36]. However, the emulsion method needs a high amount of co-surfactant and surfactant to stabilize the droplets, and it also limits the phase separation and suffers from a lack of homogeneity [28]. In general, various methods are investigated to control the crystal type.

Calcium carbide slag is a by-product produced in the process of calcium carbide production of polyvinyl chloride (PVC). The content of the major component $\text{Ca}(\text{OH})_2$ is as high as 70–80% [37]. At present, there are two main techniques for preparing nanometer calcium carbonate from calcium carbide slag: the decomposition carbonization method and the carbon dioxide carbonization method [38]. However, the carbon dioxide carbonization method requires a low reaction temperature and $\text{Ca}(\text{OH})_2$ concentration, complex operation, large energy consumption, and high investment. The decomposition method does not need to undergo calcination, is low in energy consumption, and is simple and more suitable for industrial production.

To solve the problems of high cost and high energy consumption in the method of preparing nanometer calcium carbonate by using calcium carbide slag, this study proposed a route to use chlor-alkali industrial by-products as raw materials to prepare calcium carbonate, and the method was the decomposition carbonization method:



The route is energy saving with a low production cost, allows industrial solid waste calcium carbide slag to be used effectively, is more energy saving and environmentally benign, and is conducive to industrial production. To control the morphology and particle size of nano-micro CaCO_3 , a simple and environmentally friendly method using additive engineering was proposed. Specifically, organic acids, inorganic acids, alcohol, and surfac-

tants were tested in the process of preparing nano-micro CaCO_3 to tune the size and shape of CaCO_3 crystals. After adding the additive, the calcium carbonate was uniformly dispersed, and the morphology could transform from cubic to spherical. When organic acids, inorganic acids, and alcohol were added, the particles have a cubic structure, and when surfactants are added, cubic and spherical particles can be obtained. Importantly, after the addition of SDBS, the particles of CaCO_3 are spherical, and the particle size is significantly reduced to about 3 μm or less. This work provides a simple and environmentally friendly method for preparing nano-sized calcium carbonate particles.

2. Materials and Methods

2.1. Materials

Calcium chloride (CaCl_2 , AR grade), sodium carbonate (Na_2CO_3 , GR grade), dipentaerythritol (90%), and polyethylene glycol (PEG, average Mn 6000) were purchased from Aladdin. Sulfuric acid (H_2SO_4 , AR grade), hydrochloric acid (HCl , AR grade), acetic acid (AR grade), and ethylene diamine tetraacetic acid (EDTA, AR grade) were purchased from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). Salicylic acid (AR Grade) was purchased from Macklin. Sodium dodecyl benzene sulfonate (SDBS, AR Grade) was purchased from Meryer. Dishwashing liquid was purchased from Guangzhou Libai Enterprise Group Co., Ltd. (Guangzhou, China). Hexadecyl trimethyl ammonium Bromide (CTAB, 98%) was purchased from Heowns. All solutions were prepared using deionized water produced by an ultrapure water machine.

2.2. Synthesis of Calcium Carbonate

At first, aqueous stock solutions of Na_2CO_3 (0.005 M) and CaCl_2 (0.1 M) were configured. Then, 100 mL of the Na_2CO_3 (0.005 M) solution and specific amounts of additives were added to the beaker to form a mixed solution. The solution was then placed on a stirring table at a stirring speed of 300 r/min and a temperature of 30 $^\circ\text{C}$. Next, 6 mL of CaCl_2 (0.1 M) solution was added drop by drop to the beaker during stirring, and stirring continued for 30 min. After this, the beaker was sealed and aged for a certain time. Next, the aged mixture was filtered and rinsed with water repeatedly to collect the solid powder. The solid powder was finally dried in the oven at a temperature of 60 $^\circ\text{C}$ for ten minutes to obtain nano-micro CaCO_3 . The synthetic route is shown in Figure 1. The specific amount of additives is shown in Table 1.

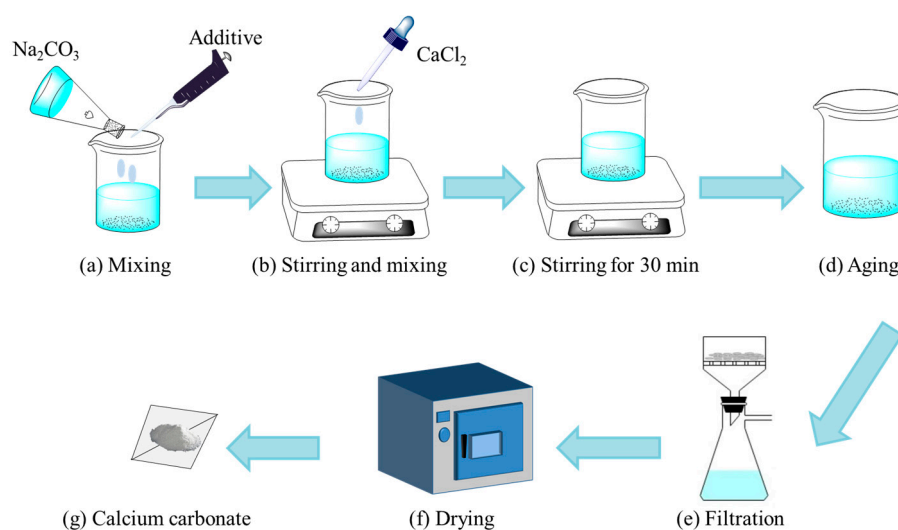


Figure 1. The scheme of synthesis of CaCO_3 .

Table 1. Different types of additives and amount used.

Name	Additive Type	n (Additives) (mmol)	Aging Time (h)
CaCO ₃ -5 AA-24	acetic acid	0.025	24
CaCO ₃ -3 SA-24	salicylic acid	0.015	24
CaCO ₃ -10 H ₂ SO ₄ -24	H ₂ SO ₄	0.05	24
CaCO ₃ -20 H ₂ SO ₄ -24	H ₂ SO ₄	0.1	24
CaCO ₃ -10 HCl-24	HCl	0.05	24
CaCO ₃ -3 EDTA-24	EDTA	0.015	24
CaCO ₃ -3 Dipe-24	Dipentaerythritol	0.015	24
CaCO ₃ -HD-24	Household detergent	2.90 (g)	24
CaCO ₃ -20 SDBS-12	SDBS	0.1	12
CaCO ₃ -20 SDBS-6	SDBS	0.1	6
CaCO ₃ -10 SDBS-12	SDBS	0.05	12
CaCO ₃ -10 SDBS-6	SDBS	0.05	6
CaCO ₃ -0.5 PEG-24	PEG	0.0025	24
CaCO ₃ -10 CTAB-24	CTAB	0.05	24

2.3. Characterizations

The morphologies of the prepared samples were observed by field-emission scanning electron microscope (FE-SEM, Phenom Pharos) (Eindhoven, The Netherlands y). X-ray diffraction (XRD, Thermo Scientific ARL EQUINOX 1000) (Brno, Czech Republic) was measured using a Cu K α radiation source operated at 40 kV and 30 mA. The Fourier transform infrared spectroscopy (FT-IR) was tested in a Thermo Scientific Nicolet iS5 spectrometer. The product was mixed with dry potassium bromide and ground and pressed into pieces for FT-IR determination. The scanning range was 400–4000 cm^{−1}.

3. Results and Discussion

3.1. Effect of Additives for Tuning the Morphology of Nano-Micro CaCO₃

Figure 2 shows the morphology of CaCO₃ particles prepared with Na₂CO₃ and CaCl₂ without additives. According to Figure 2a, the particle size distribution of CaCO₃ is very uneven, and the agglomeration phenomenon is relatively serious. From Figure 2b, the particle size of CaCO₃ is 7–10 μ m, but there is debris on the surface of the particle, which may be caused by the particle breaking and then the debris adhering to other particles. To explore the effect of additives on the particle size and morphology of CaCO₃, different types of additives were tested in the process of preparing CaCO₃. The CaCO₃ was characterized by using SEM, FT-IR, and XRD.

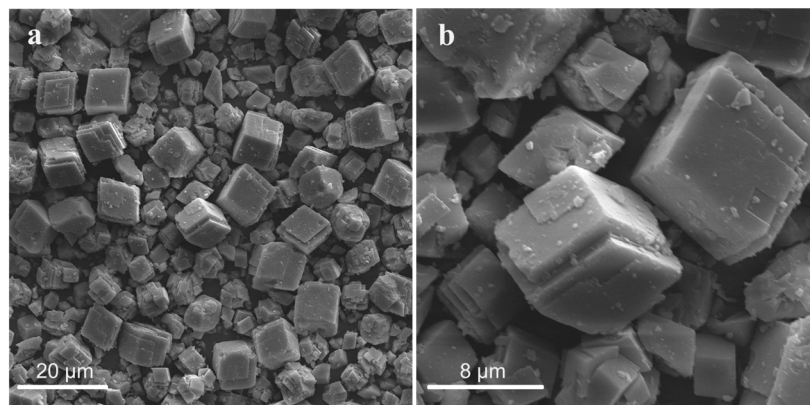


Figure 2. SEM images of CaCO₃ prepared from Na₂CO₃ and CaCl₂ without additives at (a) low and (b) high magnifications.

3.1.1. Effect of Acids on Particle Size and Morphology of CaCO_3

Firstly, the effects of organic acids on the particle size and morphology of CaCO_3 were studied. The adsorption effect of CaCO_3 on carboxylate is stronger than that of carboxylic acid on free calcium ions. During crystal growth, carboxylic acid is adsorbed on CaCO_3 particles, which influences the crystal growth [39,40]. Acetic acid, salicylic acid, and EDTA were used in this experiment.

It can be seen from Figure 3a,c that after acetic acid and salicylic acid are added, CaCO_3 particles disperse, and most show a cubic structure. The particle size of CaCO_3 prepared by adding acetic acid is about 4~5 μm (Figure 3b), and the particle size of CaCO_3 prepared by adding salicylic acid is about 5~7 μm (Figure 3d). As can be seen from Figure 4, the CaCO_3 particles prepared by adding EDTA also show a cubic structure, with a particle size of about 5~7 μm . This also shows that the CaCO_3 prepared by adding acetic acid, salicylic acid, and EDTA has a cube structure with a particle size of about 4~7 μm .

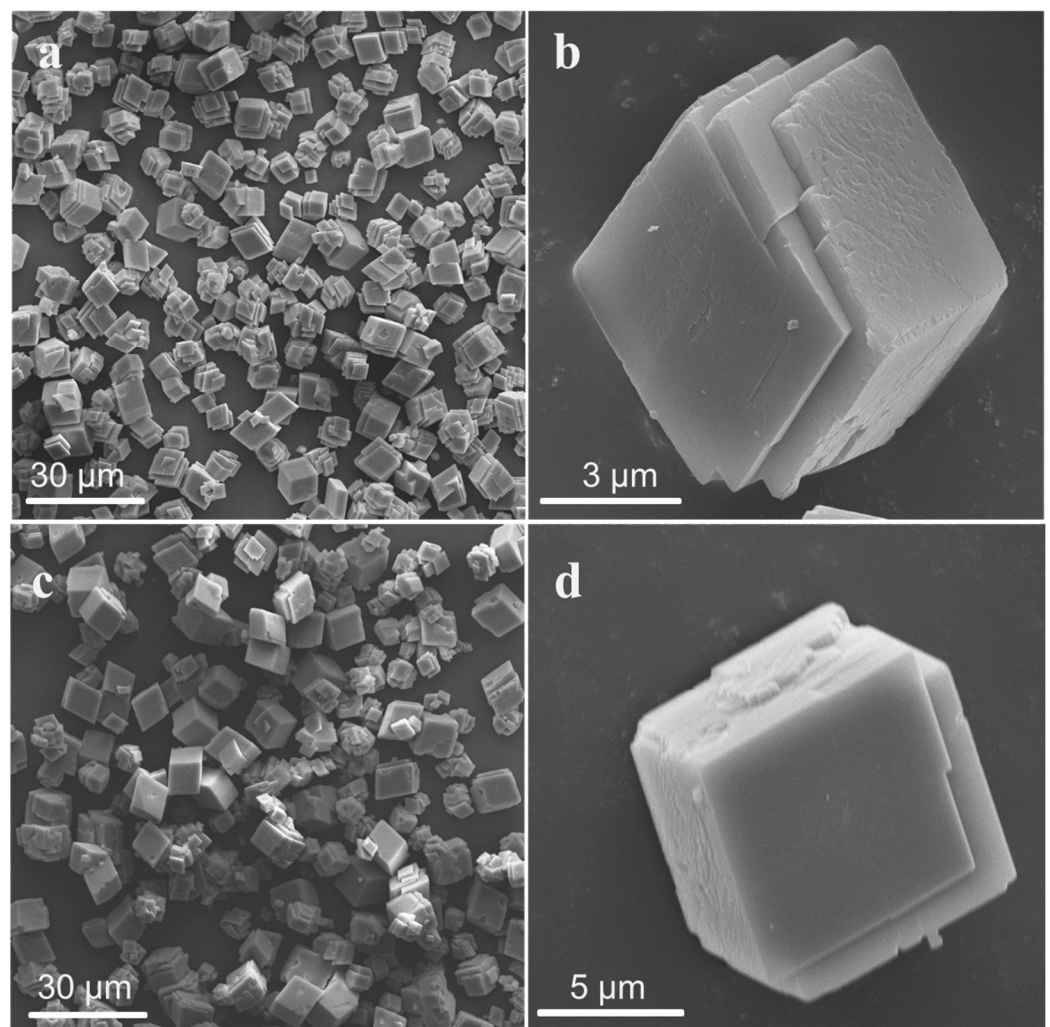


Figure 3. SEM images of CaCO_3 -5 AA-24 (a,b); CaCO_3 -3 SA-24 (c,d).

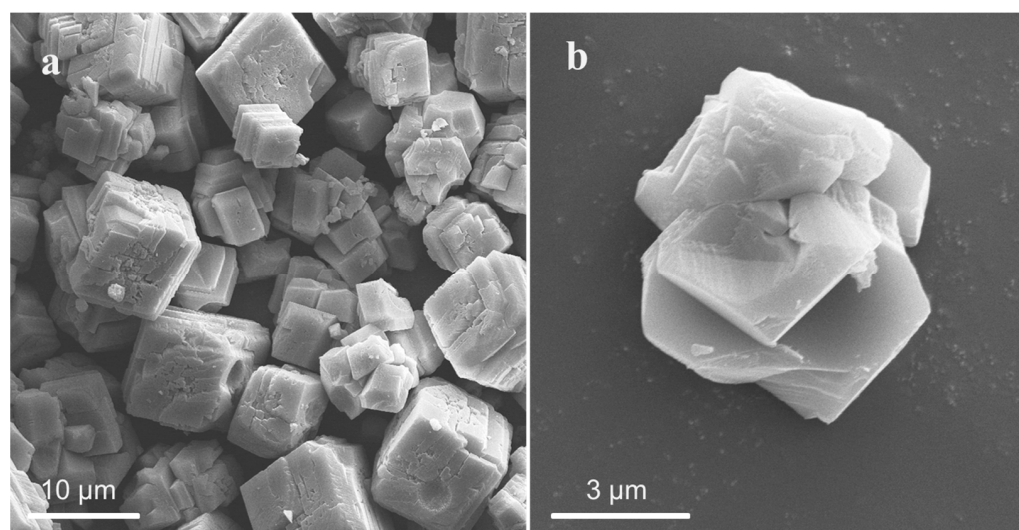


Figure 4. SEM images of CaCO_3 -3 EDTA-24 at (a) low and (b) high magnifications.

Two inorganic acids were also tested as an additive. The most commonly used sulfuric acid was chosen as an additive for preparing nano-micro CaCO_3 . As SO_4^{2-} and Ca^{2+} form CaSO_4 crystal medium, it is easy for calcium carbonate particles to grow directionally and form a chain structure. SO_4^{2-} has strong adsorbability, so that the generated CaCO_3 molecules are selectively adsorbed on the grain with a relatively high interface energy; such conditions lead to the formation of a specific shape of calcium carbonate particles. In addition to sulfuric acid, hydrochloric acid was also chosen as an additive.

Figure 5 contains the SEM images of CaCO_3 prepared with the addition of different amounts of sulfuric acid. Both CaCO_3 -10 H_2SO_4 -24 and CaCO_3 -20 H_2SO_4 -24 show similar cubic structures. CaCO_3 particles prepared by adding 0.05 mmol H_2SO_4 were uniformly dispersed with a particle size of about 4~6 μm (Figure 5a,b). The CaCO_3 particles prepared by adding 0.1 mmol H_2SO_4 were uniformly dispersed with a particle size of about 3~4 μm (Figure 5c,d). Figure 6 shows the SEM images of CaCO_3 prepared by adding 0.05 mmol of HCl. It can be seen from Figure 4 that CaCO_3 after adding HCl presents a cubic structure similar to H_2SO_4 . The particle size of CaCO_3 is approximately distributed in the range of 4~6 μm , with uniform particle distribution and a regular shape. Strong and medium inorganic acids such as sulfuric acid and hydrochloric acid could interfere with the formation of the CaCO_3 crystals by continuing the etching of the crystals. This is consistent with the results in that polycrystalline structures were observed in both cases. It was found that CaCO_3 prepared by adding H_2SO_4 and HCl has a similar morphology and polycrystalline cubic structure. The particle size is also similar and roughly in the range of 4~6 μm . Information on samples prepared by adding different acids is shown in Table 2.

Table 2. Information on different samples prepared by adding different acids as additives.

Name	Morphology	Particle Size (μm)
CaCO_3 -5 AA-24	cube	4~5
CaCO_3 -3 SA-24	cube	5~7
CaCO_3 -3 EDTA-24	cube	5~7
CaCO_3 -10 H_2SO_4 -24	cube	4~6
CaCO_3 -20 H_2SO_4 -24	cube	3~4
CaCO_3 -10HCl-24	cube	4~6

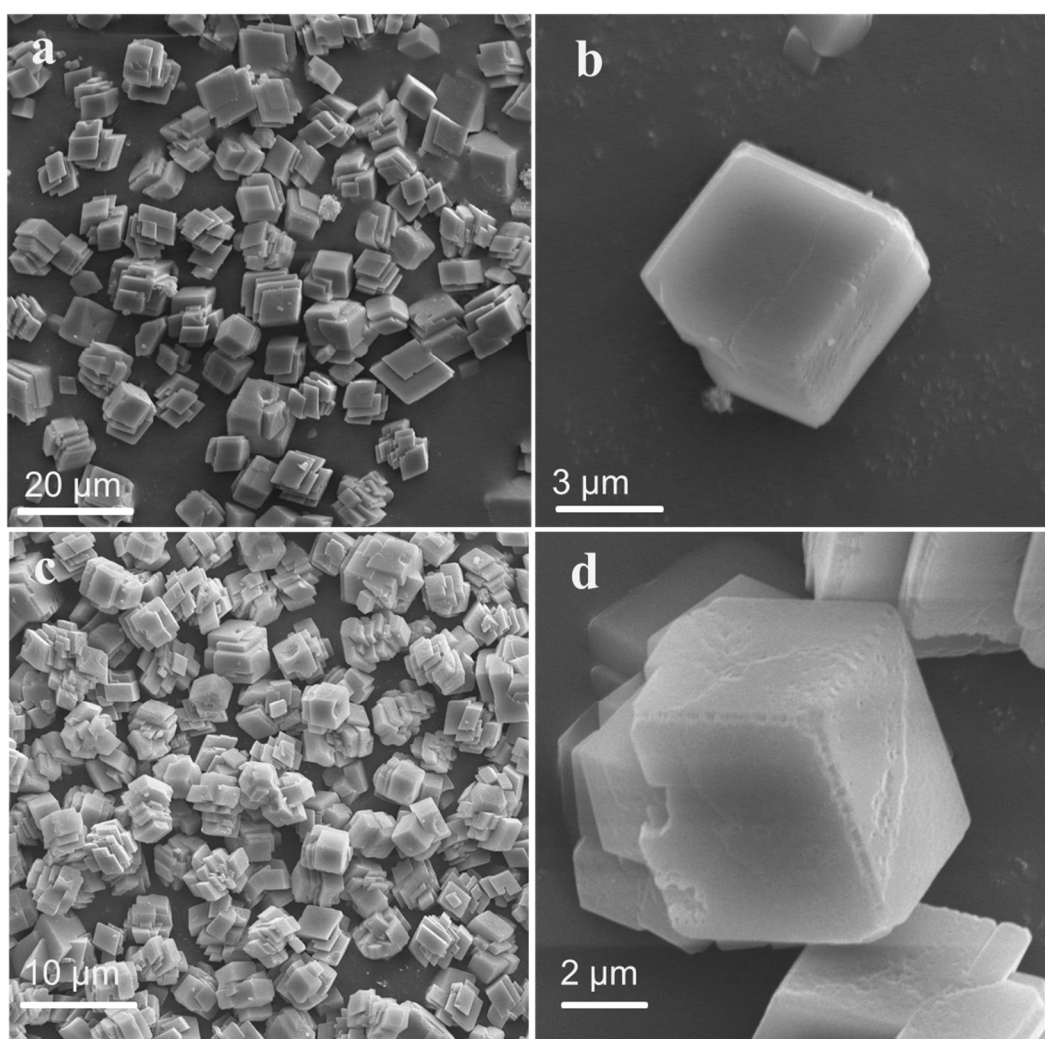


Figure 5. SEM images of CaCO_3 -10 H_2SO_4 -24 (a,b); CaCO_3 -20 H_2SO_4 -24 (c,d).

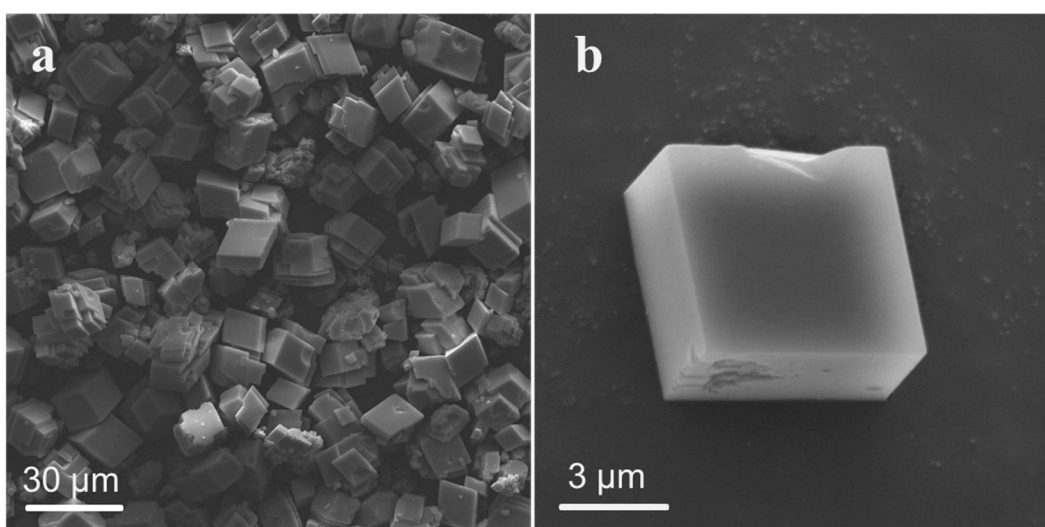


Figure 6. SEM images of CaCO_3 -10HCl-24 at (a) low and (b) high magnifications.

3.1.2. Effect of Alcohol on Particle Size and Morphology of CaCO_3

The addition of alcohol additives can change the interaction between the solvent and the solute in the solution. Due to the electrostatic matching effect between the hydroxyl group contained in the dipentaerythritol and Ca^{2+} in the solution, it may affect the morphology and particle size of CaCO_3 particles. From this perspective, alcohols are also selected and tested as additives [41]. In this experiment, dipentaerythritol was selected.

Figure 7 shows the morphology of CaCO_3 particles prepared by adding dipentaerythritol. As one can see in Figure 7, CaCO_3 particles formed in a square shape with a particle size of 5–7 μm upon addition of 0.015 mmol of dipentaerythritol. The dispersion of CaCO_3 particles was rather uniform, but some of the particles were irregular in shape and agglomerates appeared.

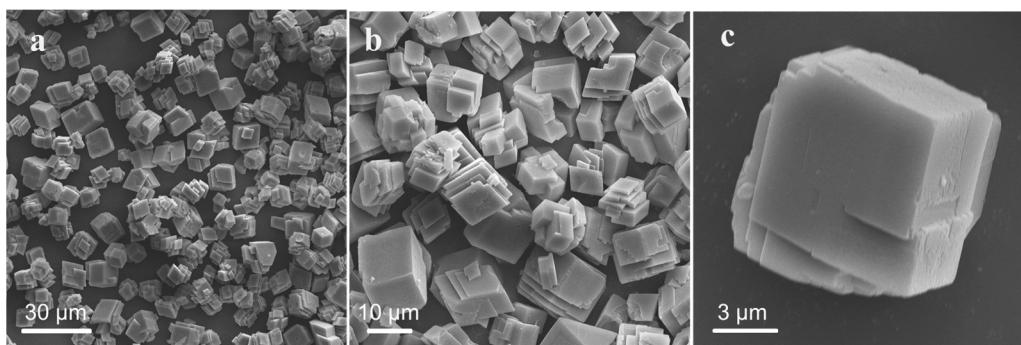


Figure 7. SEM images of CaCO_3 -3 Dipe-24 at (a) low and (b,c) high magnifications.

3.1.3. Effect of Surfactants on Particle Size and Morphology of CaCO_3

In addition to acid and alcohol additives, different types of surfactants were also studied as additives to adjust the morphology and size of nano-micro CaCO_3 during the preparation process. Surfactants can selectively adsorb on different crystal faces, which participate in the growth of some crystal faces and can change the relative growth rate of the crystals, thus controlling the shape and size of the formed crystals [30].

PEG and CTAB were selected as additives first. Figure 8 shows the morphology of CaCO_3 particles prepared by adding non-ionic surfactant PEG. In Figure 8, a layered cube can be obtained with a particle size of about 1–2 μm . Figure 9 shows the morphology of CaCO_3 particles prepared by adding the cationic surfactant CTAB. In Figure 9, after adding CTAB, a similar cube structure but with a larger particle size of 5–7 μm is observed.

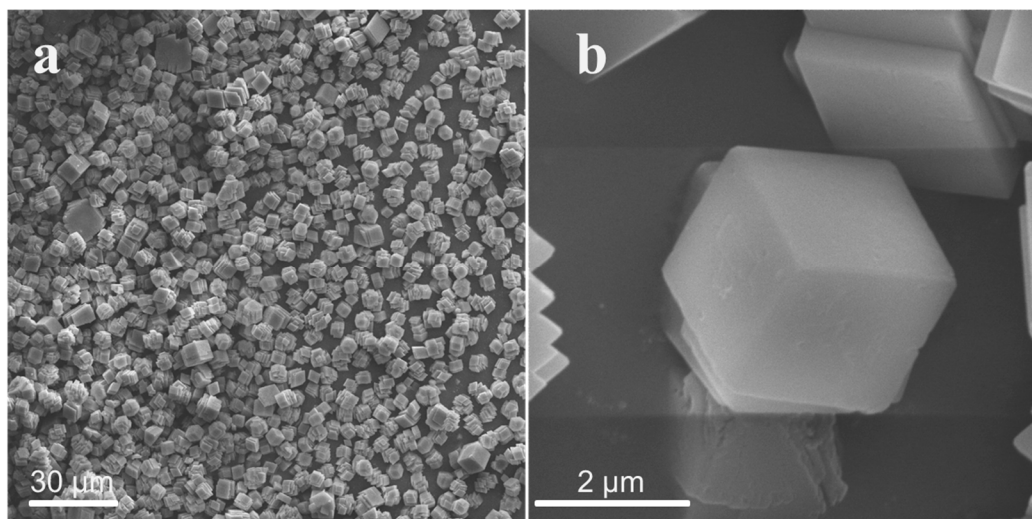


Figure 8. SEM images of CaCO_3 -0.5 PEG-24 at (a) low and (b) high magnifications.

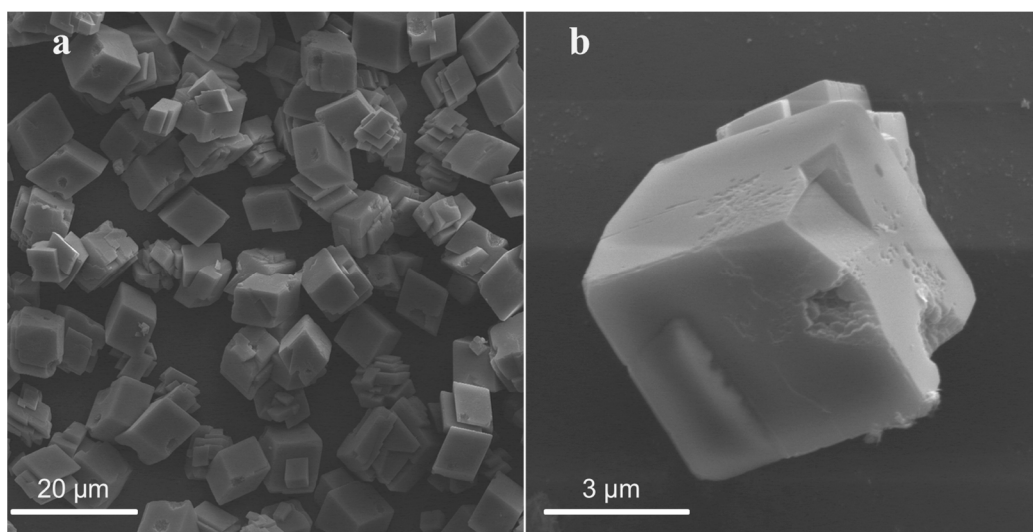


Figure 9. SEM images of CaCO_3 -10 CTAB-24 at (a) low and (b) high magnifications.

In addition to the above tested surfactants, anionic surfactants were also chosen as additives to regulate the morphology and particle size of CaCO_3 . Since household detergent is a very common product and its main component is an anionic surfactant, it was tested as an additive to tune the morphology and size of CaCO_3 . Figure 10 shows CaCO_3 particles prepared by adding household detergent. As can be seen from the figure, the obtained particles were relatively in spherical shape, with a particle size of 6–14 μm . Obviously, the morphology of CaCO_3 particles changed by adding household detergent. Since household detergent is a complex mixture, the key single component surfactant, SDBS, was used as an additive.

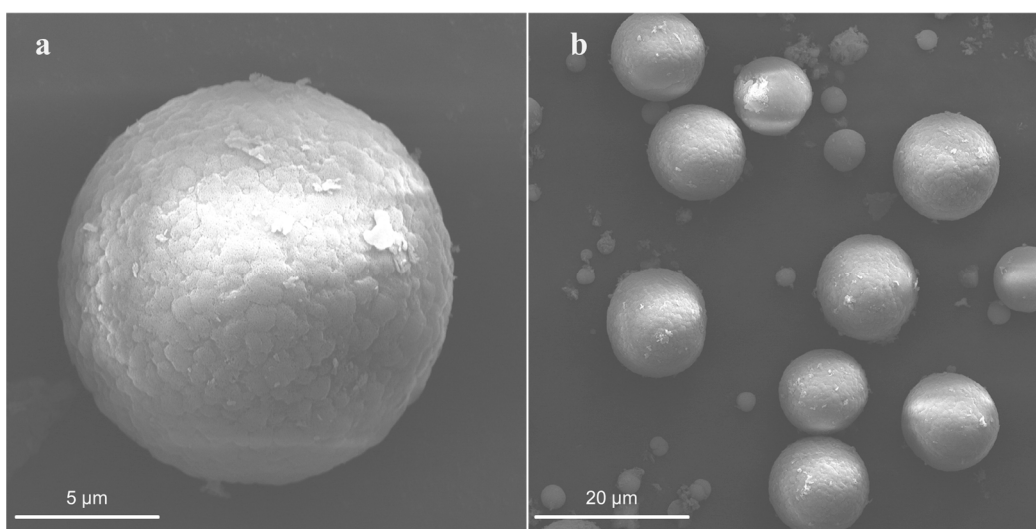


Figure 10. SEM images of CaCO_3 -HD-24 at (a) high and (b) low magnifications.

Figures 11 and 12 show the morphology and size of CaCO_3 particles prepared with different amounts of the anionic surfactant SDBS and different aging times. As shown in Figure 11, the sample sizes of the CaCO_3 -20 SDBS-12 and CaCO_3 -20 SDBS-6 are not uniformly distributed, and their particle sizes are larger than 10 μm . According to Figure 11a,b, when the aging time is 12 h, the agglomeration of CaCO_3 particles is quite serious. In contrast, CaCO_3 particles prepared with the addition of 0.05 mmol SDBS are rather evenly distributed and have a relatively smaller particle size of about 2–3 μm (Figure 12). Results showed that the CaCO_3 prepared by adding SDBS is spherical. When the addition amount

is 0.05 mmol, the distribution of spherical particles is very uniform, and the particle size is approximately in the range of 2~3 μm .

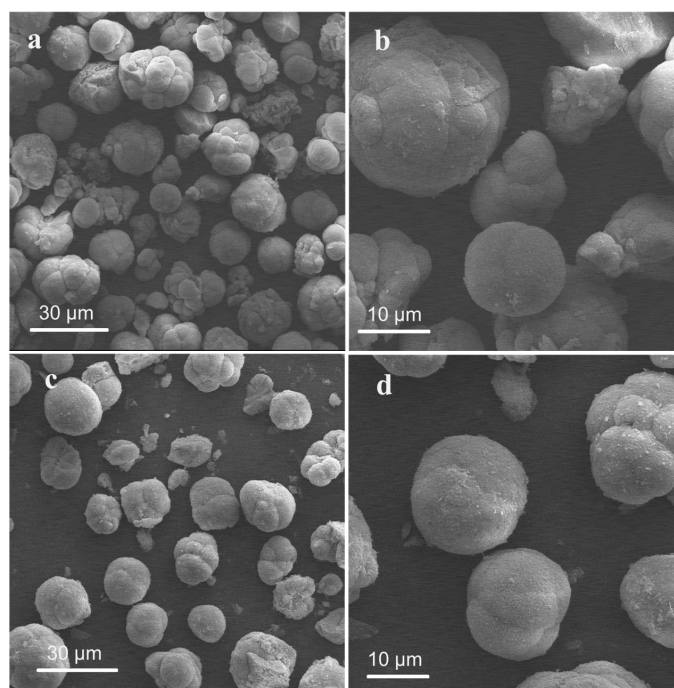


Figure 11. SEM images of CaCO_3 -20 SDBS-12 (a,b); CaCO_3 -20 SDBS-6 (c,d).

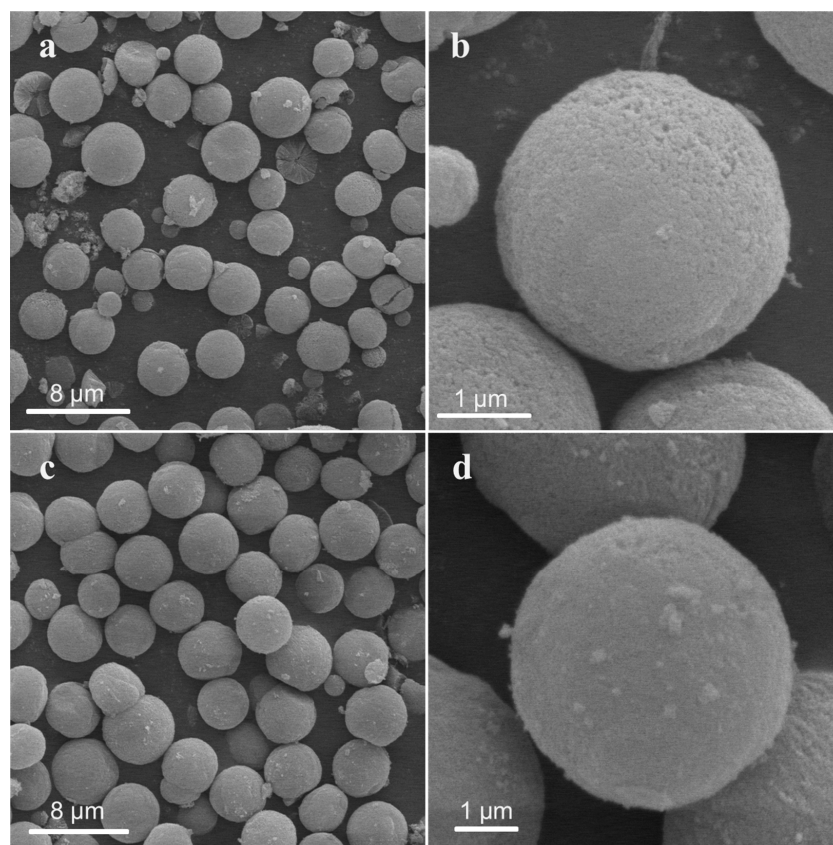


Figure 12. SEM images of CaCO_3 -10 SDBS-12 (a,b); CaCO_3 -10 SDBS-6 (c,d).

Although the particle size after the addition of PEG is relatively small, the calcium carbonate particles obtained are less uniformly dispersed than CaCO₃-10 SDBS-6. It can be seen that SDBS can effectively regulate the morphology of calcium carbonate, and the particle size of about 2~3 μm can be obtained when the additive amount is 0.05 mmol. Information on samples by adding different surfactants as additives is shown in Table 3.

Table 3. Information on different samples.

Name	Morphology	Particle Size (μm)
CaCO ₃ -0.5 PEG-24	cube	1~2
CaCO ₃ -10 CTAB-24	cube	5~7
CaCO ₃ -HD-24	sphere	6-14
CaCO ₃ -20 SDBS-12	sphere	10~12
CaCO ₃ -20 SDBS-6	sphere	10~12
CaCO ₃ -10 SDBS-12	sphere	2~3
CaCO ₃ -10 SDBS-6	sphere	2~3

Compared with other approaches, the preparation route in this study is simple, and the morphology and particle size of CaCO₃ particles are controlled by adding different additives. After the addition of SDBS, the CaCO₃ particles transform into a spherical shape with a particle size of 2~3 μm . The effects of different types of additives on the morphology and size of CaCO₃ particles are summarized in Table 4.

Table 4. Effects of additives on morphology, polymorphism, and size of CaCO₃ particles.

Additive	Additive(s) Concentration(s)	Morphology	Particle Size (μm)	Reference
SDBS	0.47 mM	Spheres	2–3	This work
PEG	1 g L ^{−1}	Cubes	8	[42]
SDBS	5 mM	Spheres + Cubes	3–8	[30]
SDS	5 mM	Spheres	3–4	[30]
CTAB	0.01 M	Cubes	5	[31]
DTAB ¹	12.5~20 mM	Multi-petal flowers	0.6–0.8	[43]
PEG, SDS	1 g L ^{−1} PEG + 3.5 mM SDS	Hollow spheres	3–6	[44]
DDAB, [C ₁₂ mim]Br	5 Mm DDAB+ 7.5~20 mM [C ₁₂ mim]Br	Flower shaped	0.3 (petal length)	[45]

¹ DTAB: dodecyltrimethylammonium bromide; DDAB: didodecyltrimethylammonium bromide; [C₁₂mim]Br: 1-dodecyl-3-methylimidazolium bromide.

3.1.4. Structural Analysis of CaCO₃

The four prepared nano-micro CaCO₃ samples correspond to different types of additives: inorganic acids, organic acids, and surfactants were tested by using XRD and FT-IR. When the SDBS is used as attritive, calcium carbonate particles are obtained with a spherical shape, so the sample was tested by using XRD and FT-IR.

The XRD results are shown in Figure 13. CaCO₃-10 H₂SO₄-24 exhibits a calcite structure. Peaks correspond to (hkl) values of (104), (113), and (202). CaCO₃-5 AA-24 and CaCO₃-0.5 PEG-24 show similar diffraction peaks and the same calcite structure but different peak intensity. The (hkl) values corresponding to the peaks are (104), (113), (110), (112), etc., are in good agreement with the reference calcite monomer cell (JCPDS 05-0586). The high number of mixed peaks in the three samples indicates that the sample contains incomplete reactants. CaCO₃-10 SDBS-12 is a mixture of ettringite and calcite (JCPDS 05-0586). The peaks correspond to the (hkl) values of (104), (113) and (114), which are in good agreement with the structural crystal cell values of JCPDS 33-0268.

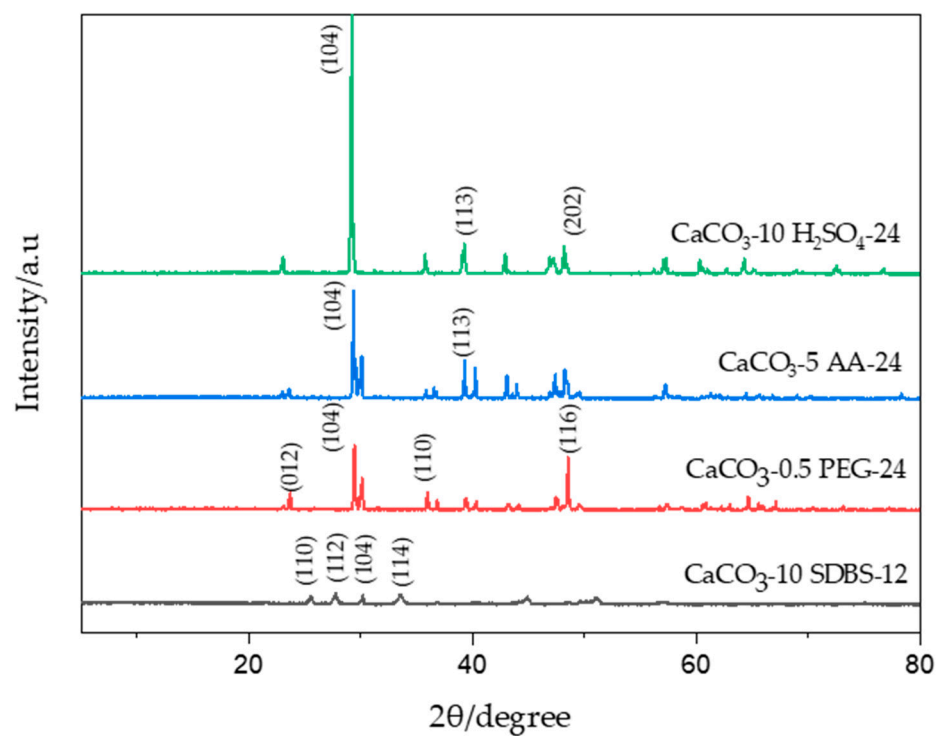


Figure 13. XRD spectra of CaCO_3 with different additive types.

The FT-IR spectroscopy technique was used for the characterization of the functional groups in the particle. The infrared spectra of the synthesized CaCO_3 particles are shown in Figure 14.

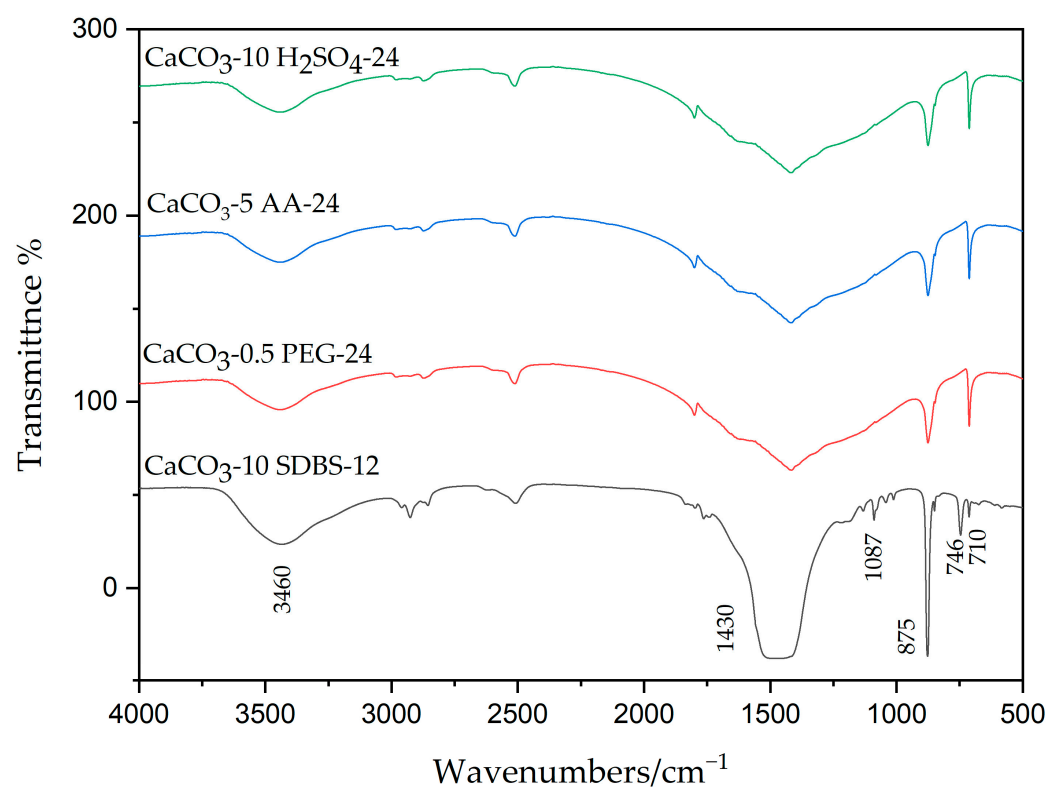


Figure 14. FT-IR spectra of CaCO_3 with different additive types.

Four samples have absorption peaks at 3460 cm^{-1} , 1430 cm^{-1} , 876 cm^{-1} , and 711 cm^{-1} . The peaks at 876 cm^{-1} and 711 cm^{-1} are the characteristic peaks of out-of-plane bending vibration (ν_2) and shear bending vibration (ν_4) of calcite, respectively. And the ν_2 peaks are strong and sharp, indicating that the CaCO_3 particles prepared are mainly the calcite crystal type. The peak at 1430 cm^{-1} corresponds to the C-O antisymmetric tensile vibration in CaCO_3 . Apart from the characteristic absorption peaks of calcite, 3460 cm^{-1} corresponds to the hydroxyl (-OH) groups that can be attributed to the physically adsorbed water molecules [46]. CaCO_3 -10 SDBS-12 has new absorption peaks at 1087 cm^{-1} and 746 cm^{-1} corresponding to symmetrical stretching vibration and shear bending vibration respectively in vaterite form, indicating the presence of the vaterite phase [47]. This is consistent with the observation from the XRD results.

3.2. Mechanism Exploration

The results show that the types of additives have significantly different influences on the crystal shape, particle size, and dispersity of CaCO_3 particles. The particles prepared by using acid additives were cubic in shape and $3\sim 7\text{ }\mu\text{m}$ in size. The particles prepared by using alcohol additives were cubic in shape and $5\sim 7\text{ }\mu\text{m}$ in size. After adding the anionic surfactant SDBS, CaCO_3 particles become spherical, the particle size becomes smaller, and the dispersion is more uniform. After the addition of the non-ionic surfactant PEG and the cationic surfactant CTAB, the CaCO_3 particles have a cubic structure with a particle size of about $1\sim 7\text{ }\mu\text{m}$.

Inorganic acids can affect the formation of nano-micro calcium carbonate through surface etching via chemical reactions. Organic acid additives contain carboxyl groups. In the process of crystal growth, the effect of carboxylic acids on the particle size and shape of the prepared CaCO_3 is not achieved by changing the interfacial tension, but rather by blocking its growth on the surface of the crystal nucleus [39,40]. The adsorption effect of CaCO_3 on salt is stronger than that of carboxylic acid on free calcium ions, so that crystallization can be inferred due to acid being adsorbed on CaCO_3 particles during the crystal growth process. Thus, it influences crystal growth but does not alter crystal nucleation. As the amount of carboxylic acid adsorbed on CaCO_3 particles increases, the inhibition effect on crystal growth is more significant, the particle size gradually decreases, and the morphology is more uniform. Because acetic acid, salicylic acid, and EDTA have different structures and amounts of carboxyl groups, they have different inhibitory effects on crystal growth, so the morphology of calcium carbonate particles obtained are slightly different.

Due to the electrostatic matching effect between the hydroxyl group contained in pentaerythritol and Ca^{2+} in solution, the tiny grains of CaCO_3 will consume more energy when they are precipitated from solution. This energy value is the interface energy of the new phase. The larger the interface energy during crystal precipitation, the nucleation rate will be greatly slowed down, and the particle size of CaCO_3 crystal will increase, resulting in the particle size of nanoparticle CaCO_3 crystals not decreasing and the formation of cuboidal CaCO_3 crystals [41].

PEG is a kind of non-ionic surfactant, which can be adsorbed on a neutral (1 0 4) face. Thus, the reaction between hydrated CO_3^{2-} and Ca^{2+} ions on the (1 0 4) face is inhibited to a certain extent, and the growth rate of the (1 0 4) crystal plane is slowed down, resulting in the final formation of the plate-like morphology [40]. The benzene ring of SDBS regulates the polarity of the micellar surface, and the strong polarity makes the crystal nucleus of CaCO_3 more easily adsorbed on the micellar/bulk phase interface of SDBS so as to grow into vaterite. In the SDBS system, vaterite is formed during the entire crystallization process in the presence of SDBS. SDBS can preferentially induce the transition of amorphous CaCO_3 to the favorable crystalline phase and inhibit the production of another crystalline phase by the molecule match and electrostatic interaction in the CaCO_3 /surfactant systems, and eventually, the addition of SDBS resulted in the formation of vaterite [30].

4. Conclusions

In summary, nano-micro CaCO_3 crystals of different shapes and sizes were obtained by using different types of additives. When the additive was acid or alcohol, the particle size of CaCO_3 was 3~7 μm , and the particles had a cubic structure. When the non-ionic surfactant PEG and cationic surfactant CTAB were added, the particles had a cubic structure, and the particle size was about 1~7 μm . When household detergent was added, the CaCO_3 particles were spherical, and the particle size was 6~14 μm . When 0.05 mmol anionic surfactant SDBS was applied, the CaCO_3 particles were in spherical shape. Particles were dispersed uniformly, and the particle size was about 2~3 μm . This study provides a useful reference for the morphology and particle size control of nano-micro CaCO_3 . This approach could be applied to produce high value-added products by using calcium carbide slag. It could play a key role for the sustainable development of the chlor-alkali chemical industry.

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