Article

Synthesis and Characterization of Micron-Sized Spherical Calcium Carbonate Regulated by Sodium Carboxymethyl Cellulose

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ABSTRACT: Spherical calcium carbonate particles were prepared with sodium carboxymethyl cellulose (CMC) as an addition agent by using a double decomposition reaction. We studied the effects of the additional amount of CMC on the morphology and crystal forms of calcium carbonate. The morphology and size of the product were characterized by using a scanning electron microscope (SEM). We found that with the continuous increase of the additional amount of CMC, the number of prepared spherical calcium carbonate particles gradually increases. When the additional amount of CMC is 50% of the mass of calcium carbonate generated by the reaction, all calcium carbonate becomes micron-scale spherical calcium carbonate particles. The method can be used for the preparation of spherical calcium carbonate. The X-ray diffraction (XRD) was used to test the crystal form of calcium carbonate prepared by adding different qualities of CMC. It has been found that both calcite type and vaterite type calcium carbonate exist, but with the increase of the additional amount of CMC, the number of fingerprint peaks and amplitude deviated from the baseline increased gradually. These results show that the proportion of amorphous calcium carbonate is significantly increased as the additional amount of CMC increases. The study provides a reference for exploring the preparation conditions of calcium carbonate microcapsules and the mechanism of crystal form transformation.

Keywords: Sodium carboxymethyl cellulose; Microcapsule; Spherical calcium carbonate; Morphology; Crystal form

1. Introduction

Calcium carbonate is an inorganic material with important economic value. It is widely used in the fields of daily chemicals, medicine, rubber, and papermaking due to its convenient availability, low price, low toxicity, low pollution, high whiteness, and large filling amount [1–7]. In the production of calcium carbonate, the morphology, particle size distribution, and particle size of its particles are the key factors determining its application performance [8–10]. At present, there are many reports on the preparation of calcium carbonate with different morphologies, among which there are also some spherical calcium carbonates. For example, Yu et al. [11] synthesized monodisperse spherical calcium carbonate with a particle size of about 1–2 nm by the precipitation reaction of calcium chloride and sodium carbonate. Fuchigami et al. [12] synthesized the spheroidal calcium carbonate of the spheroid aragonite type. Jin et al. [13] used polystyrene Sodium sulfonate (PSS) to synthesize biocompatible inorganic spherical calcium carbonate and further synthesized core-shell structure and hollow sphere materials. M Abebe et al. [14] and others utilized food-grade friendly polymer additives to synthesize spherical and porous structured calcium carbonate particles. Such additives can be used to control the morphology and pore structure of calcium carbonate particles during the synthesis process, thereby offering new possibilities for calcium carbonate in various applications. The aforementioned studies indicate that polymer additives can effectively regulate crystal forms and particle morphology by complexing calcium ions, adsorbing crystal faces, and controlling surface energy [15]. Calcium carbonate is a polytype crystal of perovskite structure (ABO_3), which exists in calcite, aragonite, spheraragonite, and amorphous forms due to different accumulation modes. There are many ways to control the crystal shape, morphology, and size of calcium carbonate crystal particles, among which is a simple and effective method to regulate the crystal morphology and size by using

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additives [16,17]. It is generally believed that the mechanism by which additives affect crystal growth is either direct interaction into the crystal, adsorption on the crystal surface, or a change in the surface energy of the crystal face in the medium [18–21]. Water-soluble macromolecules can be selectively adsorbed or self-assembled into aggregates of different structures on the surface of calcium carbonate in an aqueous solution by molecular design and optimization. At the same time, water-soluble macromolecules provide crystallization points by adsorption on the crystal surface and reduce the nuclear energy, thus regulating the nucleation, growth and morphology of calcium carbonate crystals [22–25].

Sodium carboxymethyl cellulose (CMC) is the most widely used and the largest amount of cellulose water-soluble macromolecular material in the world, which can dissolve or swell in water to form a solution or dispersion. It has the advantages of excellent performance, convenient use, and is conducive to environmental protection, and it is widely used in various fields of the national economy. CMC is not only a good emulsifying stabilizer and thickener in food applications, but also has excellent freezing and melting stability and can improve the flavor of products and extend the storage time. As a natural cellulose derivative, CMC also exhibits outstanding biocompatibility and biodegradability, making it a green, non-toxic, and environmentally sustainable additive [26]. Compared to synthetic polymer regulators such as polyacrylic acid and polystyrene sulfonate, CMC does not release harmful by-products during usage and can degrade into harmless small molecules in natural environments, thereby minimizing secondary pollution. Therefore, the use of CMC as a morphological regulator in calcium carbonate synthesis aligns well with the principles of green chemistry and sustainable material development. Therefore, CMC was chosen in this study as the crystal form regulator based on both its excellent ability to control crystal morphology and environmental-friendly characteristics, which laid the foundation for its application in related industrial fields.

In this work, CMC was used to regulate the synthesis of spherical calcium carbonate. The resulting particles exhibited uniform size distribution, regular morphology, and tunable crystal structure, showing broad application potential across various industrial sectors [27,28]. For instance, spherical calcium carbonate can enhance the opacity, smoothness, and printability of paper; serve as a pharmaceutical excipient or drug carrier due to its biocompatibility and controlled-release characteristics; provide excellent UV-blocking performance in sunscreen and skincare products; act as a filler to improve the mechanical strength and thermal stability of plastics and rubbers; and improve gloss, dispersibility, and coverage in coatings. Although many additives have been used to regulate $CaCO_3$, CMC, as a green, cost-effective, and widely applied cellulose derivative, its regulatory mechanism in the construction of micron-sized spherical calcium carbonate is still lacking systematic research. Especially, its role in controlling crystal form transformation and inducing amorphous structure formation is not yet clear. Most existing literature focuses on the morphology regulation of nano-sized calcium carbonate particles, while the formation laws of micron-scale, highly uniform spherical structures are insufficiently studied.

In the process of preparing calcium carbonate using calcium chloride, calcium chloride can undergo a double decomposition reaction with sodium carbonate to produce calcium carbonate. This reaction has the advantages of high reaction activity, readily available raw materials, mild reaction conditions, and by-products that are easy to handle. These characteristics make calcium chloride an ideal raw material for the preparation of calcium carbonate. In this paper, sodium carbonate and calcium chloride were used as raw materials and CMC was used as an additive to prepare spherical calcium carbonate by double decomposition reaction, and the effects of different CMC addition amounts on the morphology and crystal shape of calcium carbonate were studied.

2. Experiment

2.1. Experimental Reagents and Instruments

Calcium chloride (AR), Tianjin Damao Chemical Reagent Factory production (Tianjin, China). Sodium carbonate (AR), China Pharmaceutical Company, Beijing procurement and supply station (Beijing, China). Sodium carboxymethyl cellulose (CMC AR), Tianjin Yuanli Chemical Co., Ltd. (Tianjin, China). The CMC used in this experiment was of low viscosity, with a viscosity of 60 mPa·s (in a 2% aqueous solution at 25 °C). CMC of this viscosity has a relatively low thickening effect, and the formed solution has good fluidity. It forms a transparent or semi-transparent solution in an aqueous solution with good solubility and dispersibility.

Electronic balance (FA1004), Shanghai Gaozhi Precision Instrument Co., Ltd. (Shanghai, China). Increasing Power Electric Mixer (DJIC), Jiangsu Dadi Automation Instrument Factory. (Jiangsu, China). Constant temperature electric magnetic stirrer (Feb-85), Changzhou Guohua Electric Appliance Co., Ltd. (Changzhou, China). Ultrasonic cleaner (KQ3200), Kunshan Ultrasonic Instrument Co., Ltd. (Kunshan, China). Electric blast drying box (101-1), Beijing Kewei Yongxing Instrument Co., Ltd. (Beijing, China). Miniature high-speed omnipotent disintegrator

(FW80), Zhengzhou Xingyang Huasheng Instrument Factory (Zhengzhou, China). Cold Field Emission Scanning Electron Microscope (SM-6701F), Electronic Optics Corporation of Japan (Tokyo, Japan). X-ray diffractometer (XRD-7000LX), Shimadzu Enterprise Management Co., Ltd. (Kyoto, Japan).

2.2. Synthesis of Micron Spherical Calcium Carbonate

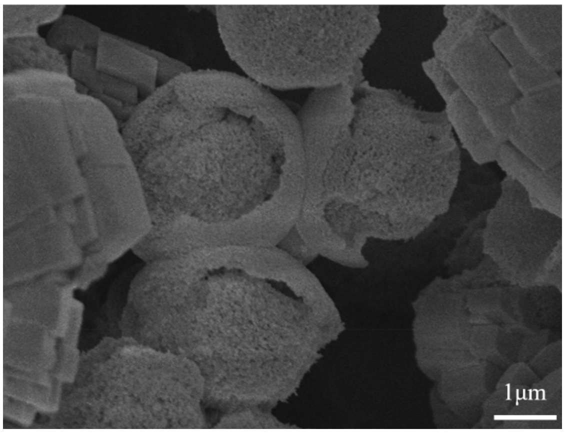
Weigh a certain amount of sodium carbonate and anhydrous calcium chloride, dissolve them with water, and prepare 0.1 mol/L sodium carbonate solution and 2 mol/L calcium chloride solution. A 0.1 mol/L, 200 mL sodium carbonate solution was added to 500 mL beakers, and the amount of calcium carbonate generated could be calculated according to the amount of sodium carbonate added. CMC with the mass of 5%, 30%, and 50% of calcium carbonate was added, respectively, and the stirring speed was set at 800 r/min. The solution was stirred to dissolve completely, and a stable, transparent sol system was formed in the solution. 2 mol/L 10 mL calcium chloride solution was slowly added to the above solution drop by drop, and after the drip was completed, the reaction was continued to stir for 30 min, and the aging was static for 12 h to obtain micron-sized spherical calcium carbonate particles. Filter, and then put the obtained precipitation into the electric blast drying oven, dry at 70 °C to constant weight, then pulverized and screened, then white calcium carbonate solid powder was obtained. The morphology and size of spherical calcium carbonate were observed using a scanning electron microscope, and the crystal shape of calcium carbonate was detected by X-ray diffractometer.

3. Experimental Results and Discussion

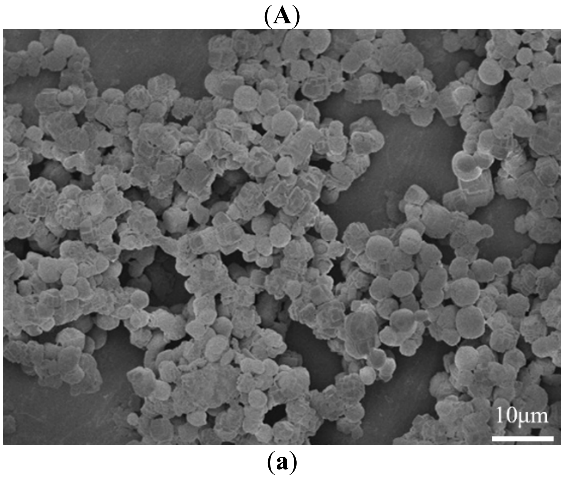
3.1. SEM Images of Calcium Carbonate When Different Amounts of CMC Were Added

The SEM photos of micron-scale spherical calcium carbonate particles prepared by changing the amount of CMC to 5%, 30%, and 50% of the mass of calcium carbonate are shown in Figure 1.

As can be seen from Figure 1, when the addition of CMC is 5%, the morphology of calcium carbonate particles is square or incompletely spherical, the particle size is about 3–4 μm, and the square surface is irregular, and the sphere is not full. When the amount of CMC is 30%, the morphology of calcium carbonate gradually changes from a square and irregular shape to a spherical shape. The spherical particles are full, but the particle size is not uniform. When the additional amount of CMC is 50%, the calcium carbonate formed is spherical, regular in shape, uniform in size, full particles, and with a particle size of about 2–3 μm.



(**A**)



(**a**)

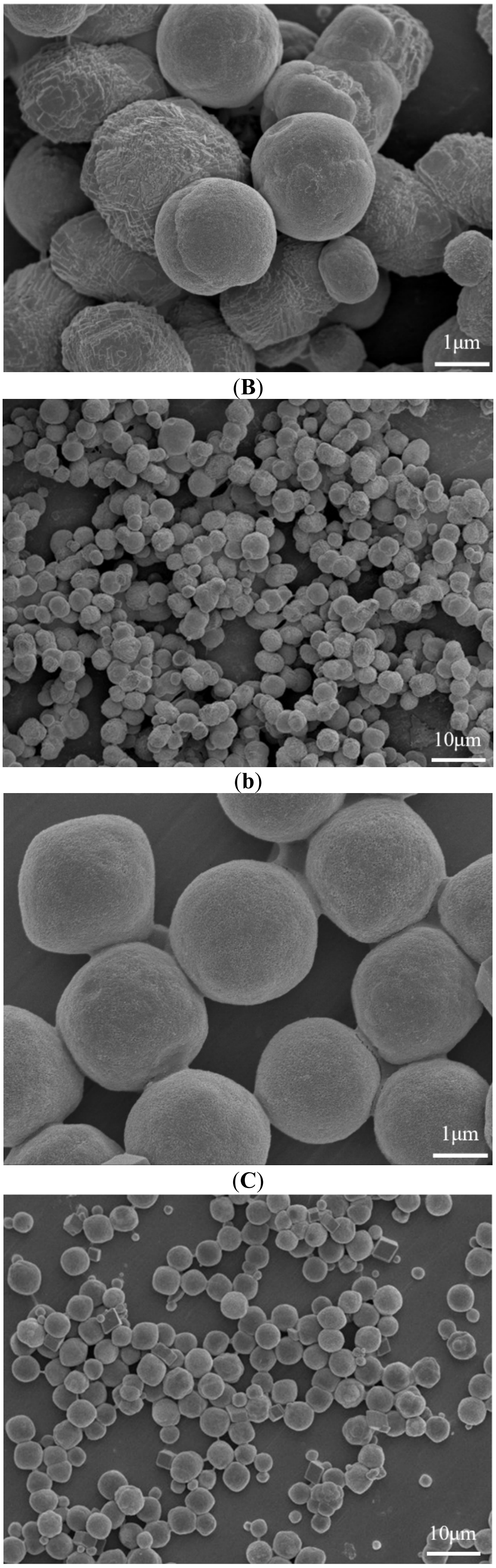
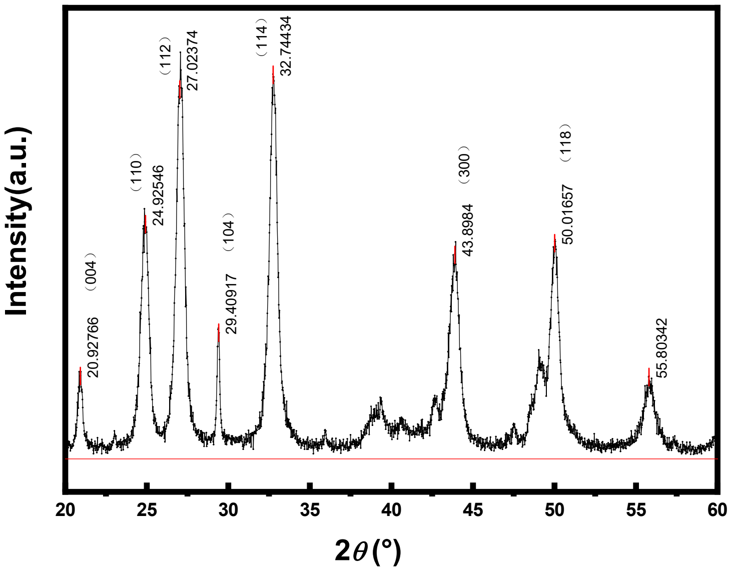


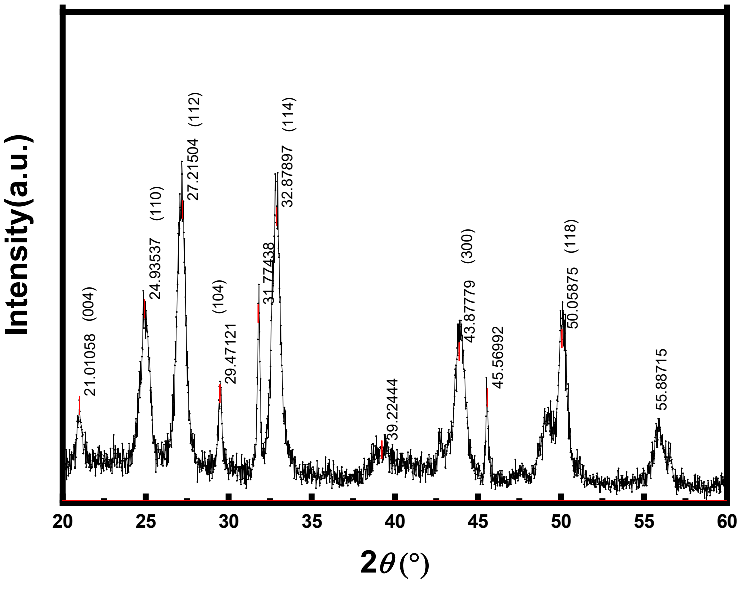
Figure 1. The SEM photos of spherical calcium carbonate particles prepared under different addition amounts of CMC at higher magnification ((**A**): 5%, (**B**): 30%, (**C**): 50%) and lower magnification (**a**): 5%, (**b**): 30%, (**c**): 50%).

3.2. X-ray Diffraction Pattern of Calcium Carbonate When Different Amounts of Sodium Carboxymethyl Cellulose (CMC) Were Added

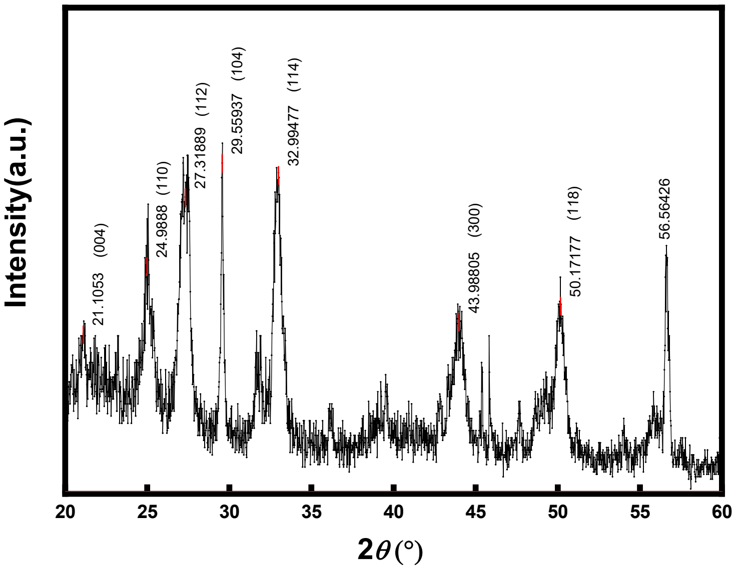
X-ray diffractometer was used to determine the diffraction pattern of micron-scale spherical calcium carbonate prepared by adding different amounts of CMC, as shown in Figure 2.



(a)



(b)



(**c**)

Figure 2. The XRD images of spherical calcium carbonate particles prepared under different addition amounts of CMC ((**a**): 5%, (**b**): 30%, (**c**): 50%).

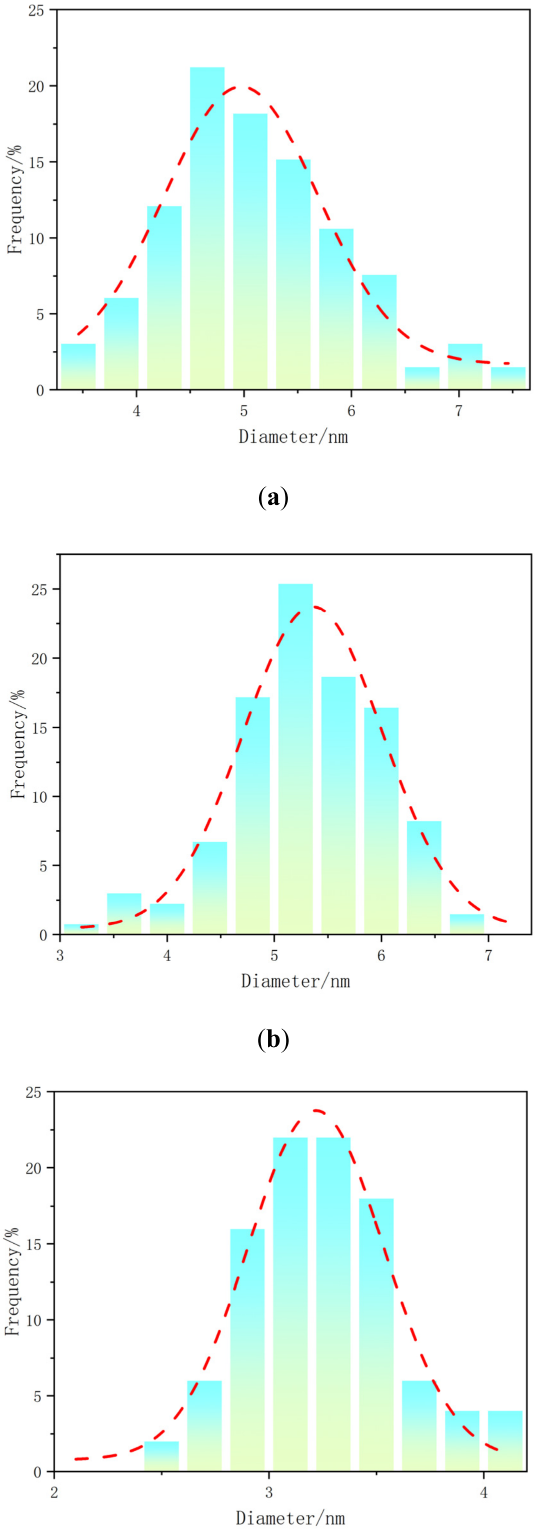
The physical and chemical structures of the particles were further analyzed by XRD. The standard peaks of vaterite and calcite crystals are consistent with PDF#33-0268 and PDF#47-1743, respectively. The diffraction peaks found at 2θ of 20.99, 24.90, 27.06, 32.78, 43.84, 50.08 are distributed to the (004), (110), (112), (114), (300), (118) plane diffractions of vaterite crystals, respectively; the peaks found at 2θ of 29.4, 35.8, 42.1, 48.6 are distributed to the (104), (110), (202), (116) plane diffractions of calcite crystals, respectively. Compared with the aragonite $CaCO_3$ PDF#41-1475 card, it is found that its standard spectrum mainly has diffraction peaks at 21.07°, 26.22°, 31.13°, 33.15°, 36.17, 37.90°, 38.61, 41.22°, 45.86°, and 50.25°.

It can be found that the diffraction peaks of spherical calcium carbonate (Figure 2a) mainly appear at 2θ of 20.93, 24.93, 27.02, 29.41, 32.74, 43.90 and 50.02. They are basically consistent with the standard X-ray diffraction pattern for calcite and vaterite, indicating that the prepared spherical calcium carbonate crystal form is mainly calcite and vaterite. The diffraction peaks of spherical calcium carbonate (Figure 2b) appear at 21.01, 24.94, 27.22, 29.47, 31.77, 32.88, 39.22, 43.88, 45.57, 50.06 and 55.89 are consistent with the standard X-ray diffraction patterns of calcite, vaterite and aragonite, indicating that the form of the spherical calcium carbonate crystals prepared is mainly calcite, vaterite and aragonite. The diffraction peaks of spherical calcium carbonate (Figure 2c) occur at 21.11, 24.99, 27.32, 29.56, 32.99, 43.99, 50.17 and 56.56, which are consistent with the standard X-ray diffraction patterns. This indicates that the form of the spherical calcium carbonate crystals prepared is mainly calcite, vaterite and aragonite.

3.3. Particle Size Distribution Diagrams

The particle size distribution diagrams of micron-sized spherical calcium carbonate prepared by adding different amounts of CMC are shown in Figure 3.

By observing the particle size distribution graph of spherical calcium carbonate particles prepared under different CMC addition amounts (as shown in Figure 3), we can find that the particle size distribution of spherical calcium carbonate particles prepared when the CMC addition amount is 5% is uneven (as shown in Figure 3a). When the CMC addition amount increases from 5% to 30% and then to 50%, the prepared calcium carbonate particles tend to be more complete, and the particle size of calcium carbonate particles tends to be more uniform (as shown in Figure 3b,c). The particle size tends to become smaller, with a size of about 3.2 μm.



(a)

(b)

(c)

Figure 3. The particle size distribution image of the prepared spherical calcium carbonate particles prepared under different addition amounts of CMC ((**a**): 5%, (**b**): 30%, (**c**): 50%). The dashed lines represents the fitting results of the particle size distribution bar graphs by using the Gauss equation.

3.4. Preliminary Discussion on the Mechanism of Preparing Calcium Carbonate

By adding CMC to prepare spherical calcium carbonate, CMC aqueous solution is used as the reaction medium so that CO_3^{2-} and Ca^{2+} in the CMC colloid diffusion reaction can produce calcium carbonate. Because the reactant forms a relatively stable state in the colloidal CMC, it is conducive to the uniform mixing of the reaction raw materials, and the micron and nanostructured materials can be prepared after drying and sintering curing. We believe that the additive CMC in the $CaCO_3$ crystallization system plays three roles: First, carboxylic acid groups in CMC participate in the nucleation and growth of calcium carbonate crystals by attracting calcium ions in the solution in the ionized state. Second, it is attached to the growth point of the crystal, which inhibits the aggregation and growth of $CaCO_3$ crystals. The conformation of a large number of CMC polymer chains in saturated calcium carbonate aqueous solution gradually curled. The calcium carbonate particles are wrapped up so that the calcium carbonate particles can not be combined into lower energy vaterite type or thermodynamically stable calcite type crystals, resulting in the increase of amorphous calcium carbonate form, and the third is the micron-level spherical calcium carbonate formed by stability. The adhesion of CMC can also adhere these amorphous calcium carbonate particles together to produce micron-scale spherical calcium carbonate eventually.

The regulatory mechanism of CMC on the crystallization process of calcium carbonate mainly reflects in the following three aspects: First, ion complexation and nucleation promotion: The carboxyl groups in CMC form complexes with Ca^{2+} ions in the solution, creating locally high saturation areas that act as nucleation sites, thereby promoting the nucleation of $CaCO_3$ crystals and generating smaller and uniformly distributed primary crystal grains. Second, crystal growth inhibition and polymorph stabilization: The CMC macromolecules can adsorb onto the high-energy crystal faces of $CaCO_3$ crystals, especially the surfaces of calcite or vaterite, thus inhibiting the preferential growth of crystals. This process prevents the transformation of metastable polymorphs into stable calcite, which is consistent with the phenomenon of increased amorphous peaks in the XRD (X-ray diffraction) patterns [29]. Third, spatial steric hindrance and morphological stabilization: The spatial steric hindrance effect of CMC chain segments inhibits further aggregation of particles. Its coating effect on primary $CaCO_3$ crystals tends to form regular spherical particles and reduces surface energy, thereby creating uniformly sized, morphologically complete micrometer-scale spherical structures.

4. Conclusions

(1) Different amounts of CMC will affect the morphology and crystal shape of calcium carbonate formed. When the amount of CMC is increased by 5%, 30% and 50%, the square calcium carbonate particles gradually decrease, while the spherical particles are relatively increased, the particles tend to be full and the particle size tends to be average, particle size tends to be smaller and the spherical calcium carbonate is formed more. When the amount of CMC is 50%, all the spherical calcium carbonate is formed.

(2) Calcium carbonate formed by adding different amounts of CMC, including calcite-type and vaterite-type calcium carbonate, but with the increase of CMC addition, the fingerprint peak gradually increased, and the deviation amplitude increased, indicating that the proportion of amorphous calcium carbonate increased significantly with the increase of CMC addition. This study provides a reference for exploring the formation and crystal transformation mechanism of calcium carbonate based on crystallization theory.

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Author Contributions

Conceptualization: N.W.; Formal analysis: J.Z., C.L.; Investigation: C.L., L.J.; Methodology: Y.W., J.Z.; Resources: Y.W.; Writing—original draft: N.W., Y.W.; Writing—review & editing: N.W., Y.W. All authors have read and approved the final version to be published.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

All relevant data are within the paper.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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