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Preparation Process, Surface Modification and Application Progress of Nano-calcium Carbonate

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Abstract: As an important inorganic functional material, nano-calcium carbonate (nano $CaCO_3$) was proposed in the 1980s and has been widely used in rubber, plastics, medicine, and paper industries because of its high specific surface area, good biocompatibility, and non-toxicity. In recent years, with the rapid development of the demand for nano-calcium carbonate, the research of nano-calcium carbonate at home and abroad has been deepening, and the related nano-calcium carbonate industry has developed quickly. Recently, many groups reported new preparation technologies, such as the physical, carbonization, compound decomposition, and emulsion methods. Among these proposed methods, the intermittent bubbling carbonization method is considered the most widely used classical process in the world. In the modification of nano $CaCO_3$, the activation mechanism of coupling agents, surfactants, inorganic substances, polymer modifiers, and the modification effects of different modifiers are introduced. In this paper, the new application progress of nano $CaCO_3$ in papermaking, daily chemical products, biomedicine, plastics, and construction materials is reviewed. In particular, nano $CaCO_3$ has excellent biocompatibility and low cytotoxicity, which greatly improves the mechanical properties of polymer composites. Finally, the problems to be further solved in the future development of nano $CaCO_3$ are analyzed and prospected, especially in preparing the high whiteness of nano-calcium carbonate from natural limestone with high iron content (>0.08%).

Keywords: Nano $CaCO_3$; Carbonization Process; Surface Modification; Reinforcing Applications

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1 Introduction

Nano $CaCO_3$ is defined as an inorganic nanomaterial with a particle size ranging from 1 to 100 nm. Due to the ultra-fine particles, it generates the small-size effect, surface effect, quantum size effect, and macroscopic quantum effect that ordinary $CaCO_3$ does not possess [1], which makes it exhibit unique activity in terms of photothermal resistance, magnetism, and catalytic performance. It turns it into a new type of inorganic functional material [2, 3]. It is widely applied in industries, including medicine, rubber, papermaking and plastics [4]. As people's

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demands for high-grade paper, automotive paints, and high-performance plastic products increase, nano $CaCO_3$ products are evolving towards refinement, specialization and functionalization, [5, 6] and its usage has permeated all aspects of our daily life and industrial production.

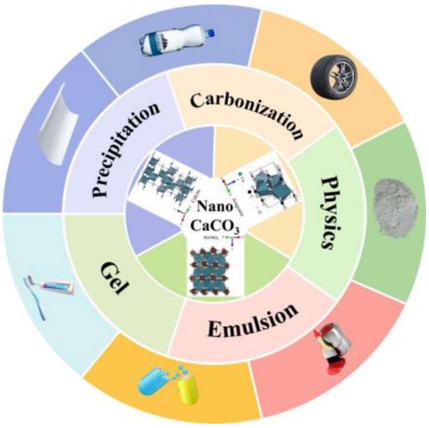

Figure 1 Structure, preparation and application of nano $CaCO_3$

With the rapid development of China's industry, nano $CaCO_3$ as a representative of lightweight $CaCO_3$ demand is growing domestically in Guangxi, Fujian, and Zhejiang provinces and cities, more than 30 nano $CaCO_3$ enterprises have emerged in 2023. China's nano $CaCO_3$ production and demand for 125,000 tons and 155,000 tons, respectively, appear in the market supply exceeds demand. Therefore, nano $CaCO_3$ production projects have been put into production, including the development of large-scale nano $CaCO_3$ producers with an annual output of 80,000 tons in Lijia Town, Jiande, and 50,000 tons in Zichuan. The commissioning of these projects will expand the production capacity of nano CaCO3 and promote the development of related industries. Therefore, in view of the booming development of China's nano $CaCO_3$ industry, this paper summarizes the preparation process of nano $CaCO_3$, surface modification and its application, focusing on the preparation process conditions of nano $CaCO_3$, the method of surface modification and the role of mechanism, and looks forward to the development prospects of nano $CaCO_3$.

2 Preparation Method of Nano $CaCO_3$

The particle size of $CaCO_3$ particles is on the nanometer scale, and it is difficult to produce highly active $CaCO_3$ nanoparticles with uniform particle size distribution and regular morphology by ordinary physical ball milling method [7]. In comparison with the physical method, the chemical method necessitates the utilization of sophisticated production equipment, a stringent process, and rigorous quality control measures for raw materials. It also entails the imposition of stringent controls on the reaction process in terms of mass transfer mode, reaction temperature, and crystallization nucleation to produce products that meet the stipulated criteria [8]. The principal chemical methods documented to date include carbonization, complex decomposition, gel, and emulsion processes.

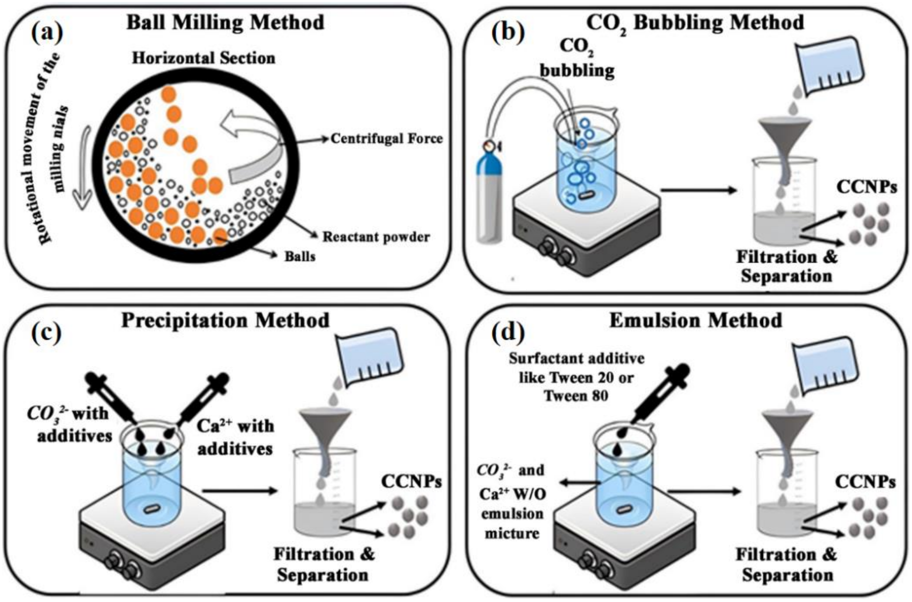

Figure 2 Schematic diagram of (a) physical method, (b) carbonization method, (c) complex decomposition, and (d) emulsion method for preparation of nano $CaCO_3$ [9]

2.1 Carbonization

The predominant method for the industrial production of calcium carbonate nanoparticles is the carbonation process, which involves the reaction of Ca^{2+} with H_2O and CO_3^{2-} to form $CaCO_3$. The schematic representation of this process is depicted in Figure 3. The initial step consists of calcinating high-quality limestone ore to yield CaO. Subsequently, CaO is subjected to a process of digestion with water, forming a $Ca(OH)_2$ suspension. The carbonation reaction process is classified into intermittent bubbling carbonation, intermittent stirring carbonation, continuous spray carbonation, supergravity carbonation, and the super liquid film carbonation enhanced process, which was recently invented by the team of Junqing Pan from the Beijing Institute of Chemical Technology. This improved process is classified according to the different ways of contacting CO_2 with the calcium hydroxide suspension. In accordance with production requirements, a specific crystal control agent is incorporated into the lime slurry, and CO_2 gas is introduced to facilitate the carbonation reaction, thereby yielding a nanoscale $CaCO_3$ slurry. Subsequently, the $CaCO_3$ slurry undergoes rapid dehydration, drying, and surface treatment to produce active nano $CaCO_3$ [10].

The lime carbonization process boasts several advantages, including convenient operation, controllable products, and high versatility. It can produce various crystalline forms, such as spherical, cubic, needle, flake, chain, and other nano $CaCO_3$ products, by adjusting reaction conditions and additives during the preparation process. This adaptability makes it well-suited to meet the diverse requirements of various industries.

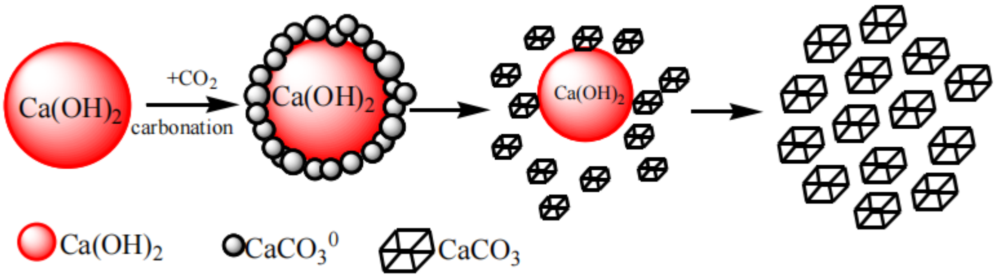

Figure 3 Synthesis of nano $CaCO_3$ by carbonization [11]

2.1.1 Intermittent Bubbling Carbonation

Intermittent bubbling carbonization is a widely used method, as illustrated in Figure 5(a) [1]. The process involves cooling the refined 5-8% due to the rapid nucleation process of calcium carbonate nanoparticles at temperatures above 25 ℃. This process is coupled with the release of significant amounts of heat from the $Ca(OH)_2$ carbonation process. The emulsion of $Ca(OH)_2$ is then cooled to below 25 ℃ before its introduction into the carbonation tower, where a specific concentration of lime kiln gas is passed through the tower base to facilitate the bubbling carbonation reaction. The process conditions, including carbonization temperature, calcium hydroxide concentration, and carbonization time, are readily controllable, enabling the preparation of nano $CaCO_3$ products with consistent particle size and regular morphology in batches. In the actual production process, the researchers installed a gas distributor at the bottom of the carbonization tower. This distributor combined the dispersing effect of the stirring paddle and baffle plate to strengthen the mass and heat transfer effect between the gas and the slurry. It, in turn, enhanced the carbonization reaction speed [12]. Despite the merits of batch production, such as its low investment and simple operation, the employment of a discontinuous carbonization process results in diminished production efficiency, protracted carbonization times, and concomitant disadvantages, including inter-batch variability of calcium carbonate, alkali return due to incomplete carbonization, and coarser particle size.

2.1.2 Intermittent Stirring Carbonation

The intermittent stirring carbonation method involves the incorporation of a multistage stirring paddle [13], a feature that is absent in the bubbling carbonation method. The latter involves the fragmentation of the CO_2 into minute bubbles through the process of stirring, thereby augmenting the gas-liquid contact area between CO_2 and $Ca(OH)_2$. This, in turn, leads to enhanced mass and heat transfer within the reaction system, culminating in more refined particle size of the nano $CaCO_3$ product. El-Sherbiny et al. [14] utilized pure lime, marble powder, and limestone to prepare three different lime emulsions with vigorous stirring, and CO_2 was passed to prepare calcium carbonate, to which cationic surfactant sodium oleate and anionic surfactant cetyltrimethylammonium bromide (CTAB) were These emulsions were subjected to vigorous stirring, followed by the introduction of CO_2 to yield nano-calcium carbonate particles of reduced size. Subsequent modification with sodium oleate resulted in particle sizes of 400 nm, 300 nm, and 340 nm. However, upon CTAB modification, the average size decreased to 20-40 nm, 40-90 nm, and 20-90 nm, respectively. The average particle size was reduced to 30-60nm, 50-80nm, and 50-120nm after CTAB modification. The intermittent stirring carbonization method requires a significant investment in equipment, leading to a more complex operation, a more uniform reaction, and a narrower particle size distribution. Further research and development in this area is currently underway [15].

2.1.3 Continuous Spray Carbonization Method

The continuous spray carbonization process entails atomizing $Ca(OH)_2$ emulsion under pressure into droplets with a diameter of approximately 0.1 mm. These droplets are then uniformly sprayed into the reactor from the top of the tower. During the droplet descent process, the droplets undergo a reaction with the CO_2 entering from the bottom of the tower counter currently [16]. The schematic diagram of the spraying device is shown in Figure 4(b). Due to the short carbonation time, this method generally employs two or three carbonation towers working in series to ensure the thorough carbonation of $Ca(OH)_2$ emulsion. During the spraying process, the $Ca(OH)_2$ emulsion is refined into ultrafine droplets, which significantly increases the gas-liquid contact area of $Ca(OH)_2$ and CO_2, promotes the nucleation process, and facilitates the obtaining of $CaCO_3$ products with fine and uniform particle size. It has been documented that the average particle size of calcium carbonate nanoparticles produced by this method can be regulated within the range of 30-40 nm. However, the practical implementation of this process has been hindered by several challenges, including the complexity of pressure nozzle and pipeline management during the carbonization process, as well as the substantial investment required in equipment [15, 17]. In recent years, novel carbonization reactors have been developed both domestically and internationally. These include the double-jet continuous process invented by Hebei University of Science and Technology, the tubular carbonization method, the inner-circulation carbonization method, the shear carbonization method, the beaker-type jet tower carbonization reactor of Central South University, and the ultrasonic cavitation method of Guangdong University of Technology. These processes have improved production efficiency. Given the exothermic nature of the carbonization process, coupled with the rapid nucleation rate of nano $CaCO_3$, the use of enhanced freezing devices to maintain a reaction temperature below 25 ℃ is imperative to ensure the production of nano-sized calcium carbonate products with a particle size distribution ranging from 20 to 80 nm. This approach has led to a substantial reduction in manufacturing costs and cooling energy consumption. Consequently, Hebei University of Science and Technology has conducted experiments on the preparation of nano calcium carbonate at elevated temperatures and concentrations, and has successfully completed industrial-scale testing of 10,000 tons at temperatures ranging from 30 to 75 ℃, without experiencing any freezing. This has yielded enhanced outcomes.

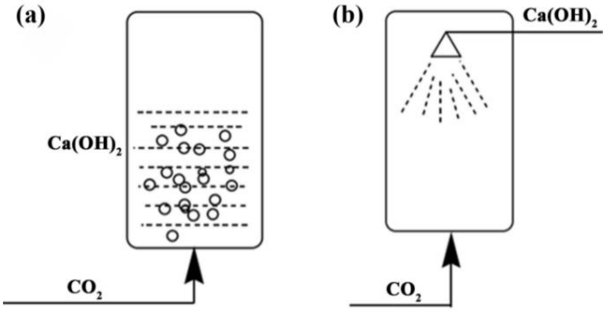

Figure 4 Comparison of bubbling carbonization and spray carbonization

2.1.4 Supergravity Carbonization Method

The production of calcium carbonate nanoparticles by supergravity carbonation [18] was proposed by Jianfeng Chen's team at Beijing University of Chemical Technology, and its production process is shown in Figure 5(d). The process employs reaction synthesis in a powerful centrifugal force field (supergravity field) generated by a high-speed rotating packing field. The process utilizes kiln gas and calcium hydroxide emulsion as raw materials, employing high-speed rotation to disperse $Ca(OH)_2$ emulsion into minute droplets and liquid film. This approach significantly enhances the contact area between gas, liquid, and solid phases, thereby accelerating the dissolution rate. calcium hydroxide and the carbonization rate, significantly reduces reaction time, yielding uniformly dispersed particles with an average size of 15-30 nm and a specific surface area as high as 62-77 m^{-2} g of the nano $CaCO_3$ products. This process has been implemented in Guangxi and other regions. However, due to the intricacy of the supergravity field technology, the substantial investment in equipment, and the high energy consumption of the high-speed rotation process, the process incurs high production costs, resulting in relatively lower production volumes compared to the intermittent carbonization method.

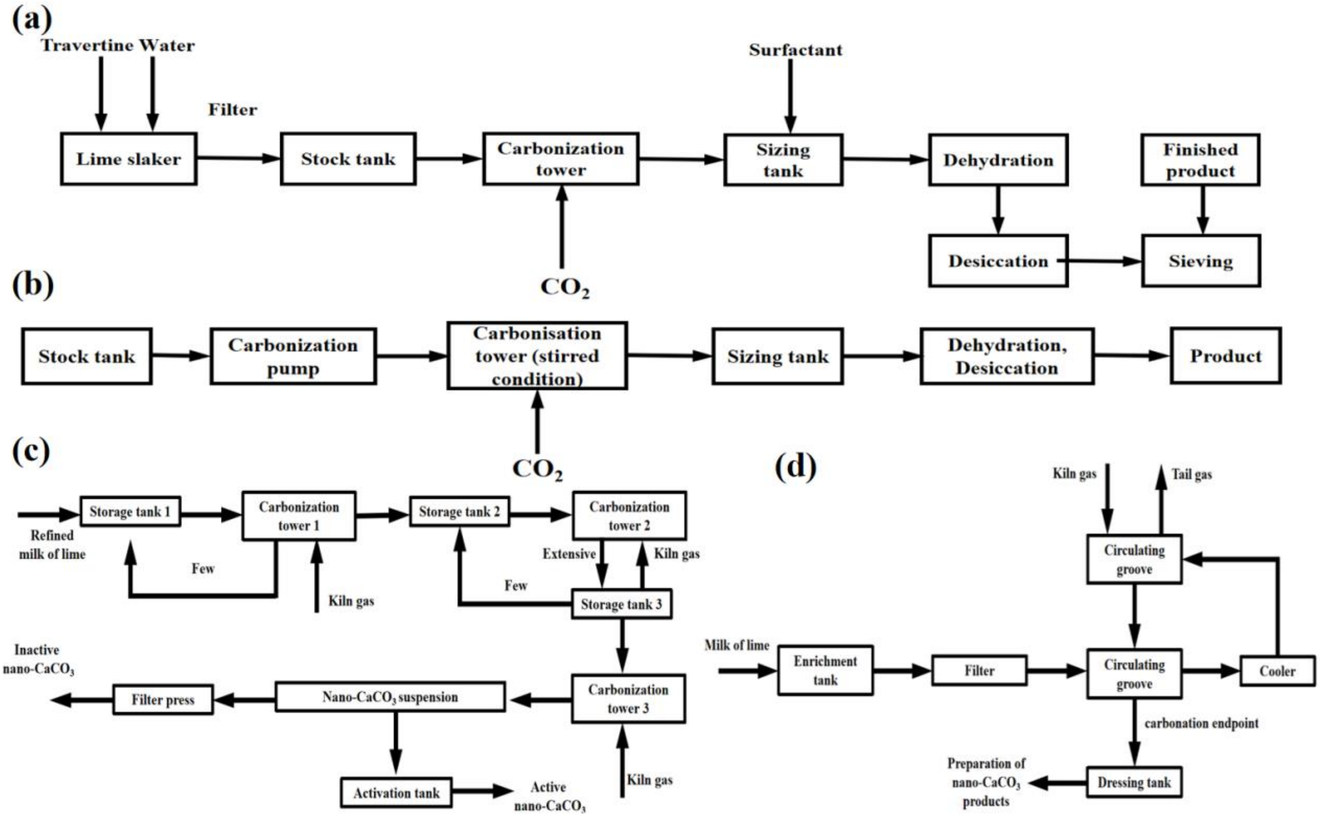

Figure 5 Schematic diagram of the process flow of (a), (b), (c) and (d) intermittent bubbling carbonization, intermittent stirring carbonization, continuous spray carbonization [19] and hypergravity carbonization [19]

2.2 Complex Decomposition

The carbonization method is generally applicable to the carbonization process of lime slurry. For calcium salt solutions, the complex decomposition method is generally used to prepare calcium carbonate nanoproducts [20]. This process establishes a reaction system involving Ca^{2+}, H_2O, CO_3^{2-}, and consists of the preparation of calcium carbonate nanoparticles through the mixing of calcium salt solutions (e.g., $CaCl_2$, $Ca(NO_3)_2$) containing calcium salts and carbonate solutions (e.g., Na_2CO_3, $(NH_4)_2CO_3$) under specific conditions. This method has been demonstrated to yield spherical calcium carbonate nanoproducts with high specific surface area by meticulously controlling the concentration of reactants, temperature, and supersaturation of calcium carbonate nuclei. The process is further enhanced by the guiding effect of crystallization inducers and surfactants. The purification and de-ironing of the calcium salt solution during the production process results in high-quality calcium carbonate nanoproducts with high purity and whiteness.

Rungpin et al. [21] reported the preparation of calcium carbonate nanoparticles with particle size distributions ranging from 30 nm to 100 nm by the complex decomposition method and investigated its reinforcing effect on polyvinyl chloride (PVC) composites. The tensile strength of nanocalcium carbonate-modified composites was found to be enhanced by a factor of 1.18, and the impact strength was increased by a factor of 1.1. Additionally, the composites exhibited superior flame retardancy and thermal stability. However, the complex decomposition method generally uses $CaCl_2$ as a raw material, resulting in a significant amount of Cl adsorbed on $CaCO_3$. This leads to increased product washing water consumption, difficulties in waste liquid reprocessing, and high production costs, and the method is seldom used in China at present [22].

2.3 Emulsion Method and Gel Method

The emulsion method and the gel method are both utilized to regulate the mass transfer rate between Ca^{2+} and CO_3^{2-} through the organic medium R, in order to construct a stable Ca^{2+}-R-CO_3^{2-} reaction system to form calcium carbonate nuclei and to control the growth process of the nuclei to prepare calcium carbonate nanoparticles. The distinction between these two methods lies in the nature of the organic medium R. The emulsion method typically employs liquid oils, such as paraffin oil and kerosene, as the organic medium, while the gel method utilizes organic gels, including organosilicon gels and agarose gels. It is noteworthy that the primary application of this reaction system is in experimental research and not in actual production settings. The emulsion method encompasses both microemulsion and emulsion film methods. The microemulsion method [23] involves the dissolution of soluble calcium salts and soluble carbonates in two microemulsions with identical compositions. The mixing reaction occurs under specific conditions, which regulate the nucleation and growth of the grains within a confined area. Subsequent to this process, the grains are separated from the solvent, forming calcium carbonate nanoparticles. The product size distribution falls within a few nanometers and tens of nanometers. This method has been shown to enhance the calcium carbonate content in the solution, facilitate separation and drying, and ensure the uniformity of the particles.

The emulsion membrane method [24] involves the preparation of nano $CaCO_3$ using kerosene as the membrane solvent, Span-80 as a surfactant and flow carrier, and two immiscible liquid mixtures of the oil and water phases. These mixtures are formulated under the high-speed stirring of an electric stirrer. Na_2CO_3 aqueous solution is dispersed as microdroplets in the oil phase to form an emulsion, then mixed with calcium hydroxide solution under stirring. Ca^{2+} in the Ca^{2+} enters into the interior of the microdroplets under stirring and reacts to form nano $CaCO_3$ particles. The gel method involves the diffusion of CO_3^{2-} and Ca^{2+} from the extremities or a single end, forming crystals within the gel. A distinctive feature of this method is the stability of the crystalline nuclei, which remain fixed as they create, enabling continuous observation and analysis of the crystallization process. The generation and growth rate of crystalline nuclei can be effectively regulated by controlling the gel's concentration, the concentrations of CO_3^{2-} and Ca^{2+}, the pH value, the type and concentration of additives, etc. It allows for the production of nano aragonite or calcite-type calcium carbonate products.

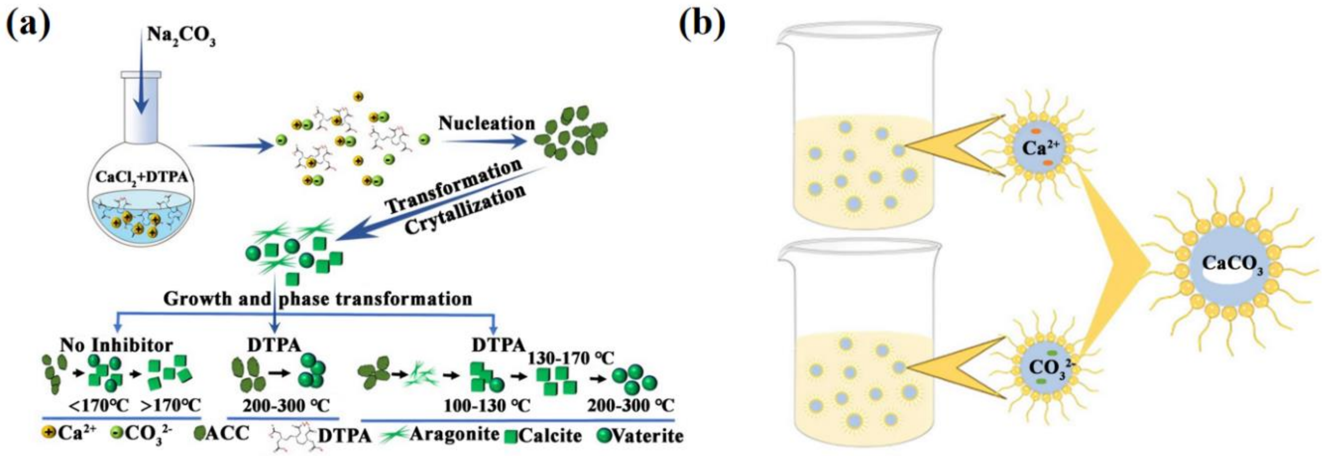

Figure 6 (a) Schematic diagram of precipitation, crystallization, and phase transformation process of nano-calcium carbonate prepared by metathesis [25]; (b) Schematic diagram of synthesis of nano-calcium carbonate by microemulsion method [39]

In summary, the carbonization process can utilize lime slurry and kiln gas as raw materials, aligning with the atomic economic reaction. These materials are widely available and inexpensive, can react in low temperatures and an aqueous environment, and require minimal equipment. The industrial mass production of this process has already been realized. However, the complex decomposition method can prepare high-quality nano $CaCO_3$ products. Nevertheless, there are problems with high water consumption for scrubbing, high cost for the mother liquor treatment, and complex process control. The inherent challenges of this process, namely the substantial water consumption during washing, the high cost of treating the mother liquor, and the complexity of process control, have hindered its widespread adoption. However, the practical implementation of this method has occurred in regions facing a shortage of high-quality limestone ore or where inexpensive calcium salts are available. The emulsion method has been demonstrated to offer enhanced controllability of the particle size during the preparation process. However, employing a substantial quantity of organic emulsifiers necessitates enhancing emulsion separation and purification efficiency in future endeavors to reduce costs.

3 Nano $CaCO_3$ Modification

Calcium carbonate nanoparticles possess hydrophilic hydroxyl groups on their surface and are generally alkaline, rendering them hydrophilic and oleophobic inorganic compounds. This physicochemical property of calcium carbonate nanoparticles is frequently linked to inadequate internal dispersion of organic polymers, impeding effective cross-linking and leading to defective material interfaces or the inability to function properly. Additionally, nano $CaCO_3$ exhibits a high propensity for secondary agglomeration and loss of nano-size effect due to its diminutive particle size and elevated surface energy. Surface modification is imperative to enhance the surface properties of nano $CaCO_3$ [26].

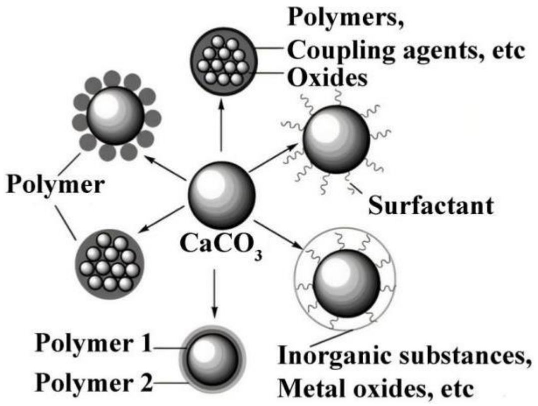

Figure 7 Structure diagram of nano $CaCO_3$ modified by different modifiers [27]

3.1 Coupling Agent Modification

-Si-OR (R usually stands for carbon chain) group undergoes an alcoholysis reaction in a silane coupling agent to form the -Si-OH group, which further reacts with -OH on the surface of nano $CaCO_3$ to form Ca-O-Si bonds. These chemical bonds are adsorbed on the surface of $CaCO_3$ to produce interfacial repulsion to reduce the surface free energy [28]. The underlying mechanism for this modification is illustrated in Figure 8(a). However, the challenges associated with preserving silane coupling agents and their high cost limit their practical applications [29]. Phthalate coupling agents are categorized into monooxygenated, chelated, and liganded. These agents form Ti-O bonds to improve the dispersion of calcium carbonate nanoparticles through hydrolysis of their alkyl portion to combine with -OH on the surface of $CaCO_3$ [30]. Phthalate coupling agents are used in small quantities and under mild operating conditions; however, they are expensive and toxic, harming the environment and operators. The aluminate coupling agent changes the properties of calcium carbonate nanoparticles by forming a molecular film on the surface of the nanoparticles, and its modification principle is shown in Figure 7. This modification principle is of particular interest, as it is both low in toxicity and green and easy to disperse, thus making it a more widely used agent. Lihua Liu et al. proposed [31] that adding an aluminate coupling agent to a nano $CaCO_3$ slurry enhanced specific surface area and degree of dispersion. This modification also led to a substantial improvement in the rheological properties of silicone sealant composites. Furthermore, recent studies have reported that surface modification of calcium carbonate nanoparticles by macromolecular coupling agents has significantly enhanced the elongation at break and processing properties of the materials [32].

3.2 Surface Active Agent

Surfactants encompass diverse substances, including fatty acids, resin acids, and their salts of organic matter, as well as cationic, anionic, nonionic, and polymer surfactants. The hierarchy of surfactant efficacy in enhancing dispersion is as follows: anionic, nonionic, cationic, and polymer surfactants. It is noteworthy that surfactant complexes exhibit superior performance compared to that of a single surfactant type. Fatty acids or fatty acid salts are anionic modifiers. They react with Ca^{2+} on the surface of calcium carbonate nanoparticles to form Ca^{2+}-COOR bonds, [33] as shown in Figure 8(b). Phosphate ester modifiers similarly react with Ca^{2+} on the surface of calcium carbonate nanoparticles to form a phosphate ester coating layer on the surface of calcium carbonate nanoparticles. The long-chain alkyl group at the other end of the modifier is compatible with the organic polymer, which substantially reduces the viscosity of the polymer and facilitates the dispersion of the material. Sarkar et al. [34] used lauric acid as a surface modifier, and the contact angle between calcium carbonate nanoparticles and water increased to 140°, which completes the transition from hydrophilic to hydrophobic-oleophilic nature of calcium carbonate nanoparticles. Wang et al. [35] carried out a modification study on calcium carbonate nanoparticles using chloroform as a solvent, and the modification was carried out using stearic acid, palmitic acid, and lauric acid as modifiers. The prepared calcium carbonate nanoparticles had activation degrees of 96%, 93%, and 91%, respectively, and, at the same time, their compatibility with liquid paraffin was improved. The utilization of surface modifiers by calcium carbonate nano manufacturers is predominantly attributable to their amphiphilic nature, variety, cost-effectiveness, ease of availability, superior modification efficacy, and the capacity for selective preparation of calcium carbonate nano with divergent surface properties.

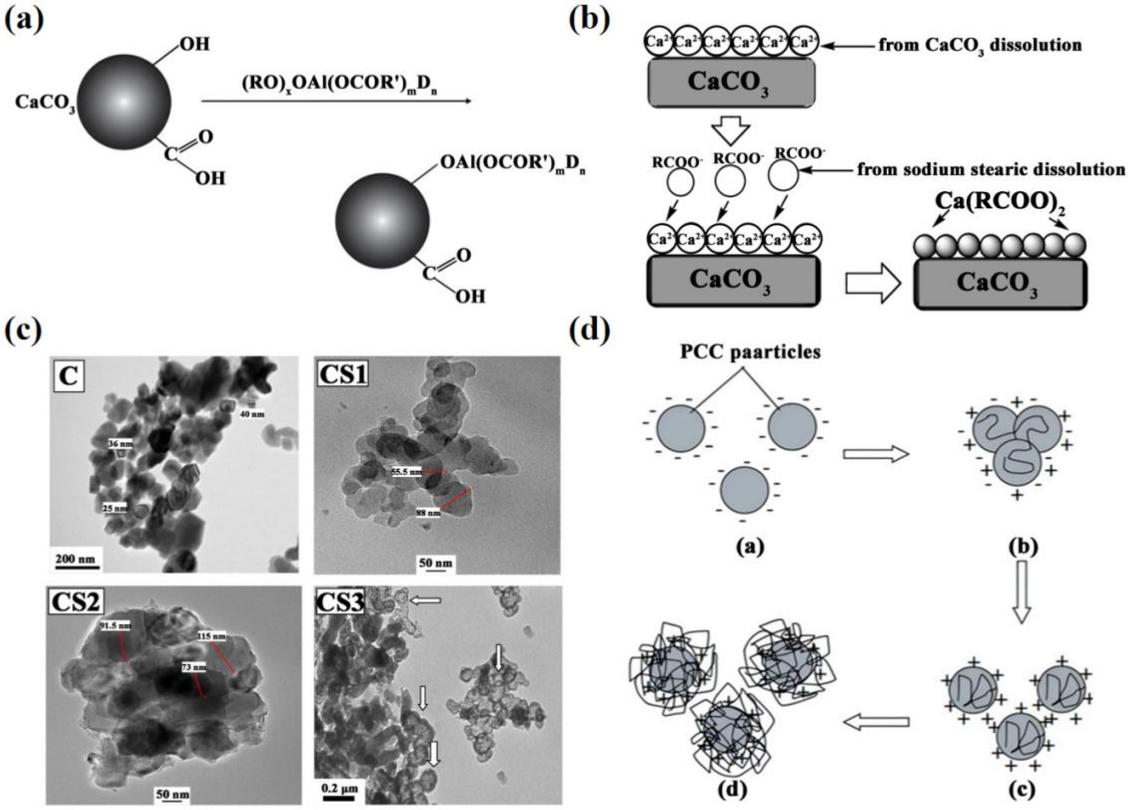

Figure 8 (a) Schematic diagram of modification of aluminate coupling agent [36]; (b) Schematic diagram of fatty acid salt modification [11]; (c) TEM diagram of SiO_2 modified nano-calcium carbonate [37]; (d) Schematic diagram of polymer modification [38]

3.3 Inorganic Modification

The presence of a significant number of hydroxyl groups on the surface of calcium carbonate nanoparticles results in weak alkalinity and acid resistance, thereby limiting its application in various materials. Modification of calcium carbonate nanoparticles using inorganic compounds, such as silicate, aluminate, and barium, can form a dense coating layer on the nanoparticle surface. This layer enhances the acid-resistance of the nanoparticles and prevents their interaction with internal -OH groups. It becomes impossible for H^+ to come into contact with the internal -OH, and the acid-resistance of calcium carbonate nanoparticles is improved. Roy et al. [39] modified the surface of calcium carbonate nanoparticles prepared using the sol-gel method using SiO_2 as filler for nitrile butadiene rubber (NBR), which was used as a filler in NBR. The results demonstrated that the modified calcium carbonate nanoparticles exhibited enhanced acid resistance, attributed to the incorporation of SiO_2 as a filler in NBR. A significant enhancement in the mechanical and thermal stability of NBR.

3.4 Polymer Modification

The directional adsorption of polymers on the surface of calcium carbonate nanoparticles has been demonstrated to modify the charge characteristics of the nanoparticle surface, leading to the formation of a physical or chemical adsorption layer. This modification is believed to prevent the agglomeration of calcium carbonate particles, thereby enhancing the dispersion effect. Two predominant theories have emerged concerning the polymer-modified calcium carbonate nanoparticle process. The first theory posits that a polymerization monomer initially adsorbs onto the surface of calcium carbonate nanoparticles, thereby triggering the polymerization reaction and ultimately forming a polymer film. The second theory asserts that calcium carbonate nanoparticles are added to the solution of the dissolved polymer, with the polymer gradually occupying the solvent adsorption sites adsorbed on the surface of calcium carbonate nanoparticles to form a coating film. For instance, the use of polymer PMMA to coat calcium carbonate nanoparticles can achieve nanoscale dispersion, thereby playing a crucial role in toughening and reinforcing polypropylene (PP) [40]. Polyolefin oligomers, such as calcium carbonate nanoparticles, demonstrate effective infiltration and adhesion to inorganic fillers. Maleic anhydride graft-modified polypropylene, polyacrylic acid and its salts, alkoxystyrene, polyethylene glycol, and reactive cellulose have been shown to enhance the wetting properties of calcium carbonate nanoparticles. These polar oligomers have the capacity to adsorb onto the surface of calcium carbonate nanoparticles, imparting them with charge characteristics and forming an adsorption layer. This layer prevents agglomeration, enhancing their dispersibility [41].

4 Application of Nano $CaCO_3$

Nano $CaCO_3$ boasts a range of distinctive properties attributable to its uniform nanoparticle size and diverse morphology. This versatile inorganic material applies to diverse fields, including industry, biology, and environmental protection. Its specific application areas are illustrated in Figure 9. The price of nano $CaCO_3$ ranges from RMB 2500 to 30,000 per ton, contingent on its specific application. Notably, the production of high-grade nano $CaCO_3$ is financially lucrative, offering significant economic returns.

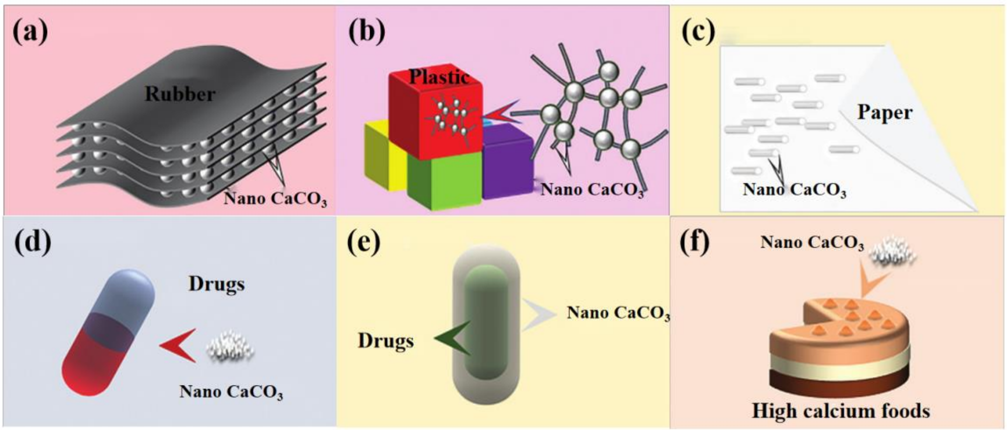

Figure 9 Application of nano $CaCO_3$ [42]

4.1 Reinforcing Applications in Plastics and Rubber Industries

Calcium carbonate nanoparticles are incorporated into rubber as inorganic fillers to enhance the tensile strength, constant elongation strength, and tear resistance of vulcanized rubber and the compression deformation of rubber products. Manufacturers sometimes use nano $CaCO_3$ instead of silica, which can reduce overall production costs. Recently, Roy et al. [39] employed calcium carbonate nanoparticles as a rubber filler and observed substantial enhancements in critical parameters, such as maximum rheological torque, curing rate indexes, and cross-linking degree, when comparing rubber with modified calcium carbonate nanoparticles. However, it was also observed that the incorporation of calcium carbonate nanoparticles led to an exacerbation of the vulcanization rate of the rubber and a significant increase in heat generation during mixing.

In a similar vein, calcium carbonate has been identified as a pivotal filler in the plastics industry. The superior particle dispersibility and lipophilic hydrophobicity of activated calcium carbonate have been demonstrated to significantly enhance the toughness, flexural strength, and thermal stability of plastic products, thereby enhancing their market competitiveness. At present, activated calcium carbonate nanoparticles have played a significant role as inorganic functional materials in polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and other plastics [43].

4.2 Application in Papermaking

The utilization of calcium carbonate nanoparticles (CCNP) within the paper industry has been demonstrated to enhance the tensile strength and whiteness of paper, augment its flatness and flexibility, and reduce the production cost of pulp. Kang et al. [44] pioneered the incorporation of PAM into GCC, resulting in the generation of PGCC. Subsequent injection of CO_2 into PGCC led to the formation of heterogeneous calcium carbonate (HCC) through the injection of CO_2 into PGCC. By manipulating the proportion of CaO during the preparation process, the rigidity of HCC can be tuned, enhancing its surface smoothness and improving the paper's tolerance to high shear forces during the papermaking process. The development of the high-grade paper industry and the expansion of functional calcium carbonate nanoparticles have led to the identification of significant application prospects for calcium carbonate nanoparticles in the field of coated paper.

4.3 Applications in Construction and Coatings

A substantial body of research [45-47] has demonstrated that the incorporation of calcium carbonate nanopowder can enhance the internal structure of cementitious materials, introduce a novel nanoscale architecture within the cementitious system, and address prevalent defects such as pores, porosity, and deterioration resulting from the alkali-silica reaction, which is commonly observed in the microstructure of concrete. This integration leads to an augmentation in the early mechanical properties and an enhancement in the long-term durability of cementitious materials. $CaCO_3$ nanopowder is a cost-effective and abundant nanomaterial, and its application in high-end cementitious materials shows great potential. Additionally, nano-calcium carbonate has a wide range of industrial applications, including in the coating sector [48]. Its incorporation into coatings enhances their volume, reduces cost, and improves stability, dispersion, gloss, and whiteness, thereby enhancing construction performance [49].

4.4 Applications in Daily Chemistry and Biomedicine

The utilization of calcium carbonate nanoparticles as fillers in cosmetic products, facial cleansers, toothpastes, and other daily chemical products has become pervasive, encompassing various facets of daily life. Concurrently, calcium carbonate nanoparticles have emerged as a promising drug carrier due to their unique characteristics. Their high specific surface area allows for the loading of numerous drugs for delivery, as evidenced by their capacity to carry drugs such as docetaxel, phosphates (BP), erythropoietin, and others [50, 51]. However, due to the nanosized and weakly alkaline nature of calcium carbonate nanoparticles, they are not suitable for use as carriers for large particle sizes and acidic drugs. Furthermore, excessive calcium intake increases the risk of thrombosis. Therefore, the development of calcium carbonate nanoparticles with larger particle size, more sites, and acid resistance is imperative. The use of nano $CaCO_3$ as a pharmaceutical raw material has also gained widespread attention in recent years. For example, in the field of traditional Chinese medicine, nano $CaCO_3$ is added to bone-cutting powder, which can be coated on the wound to play the role of rapid hemostasis, and the addition of nano $CaCO_3$ increases the specific surface area. area of the powder, which can help to promote the rapid coagulation of the blood [52]. Along with the development of bone repair technology in the field of medical science, nano $CaCO_3$ has shown great benefits in enhancing the biocompatibility and mechanical performance of the material. Compatibility and mechanical properties show potential for application [53].

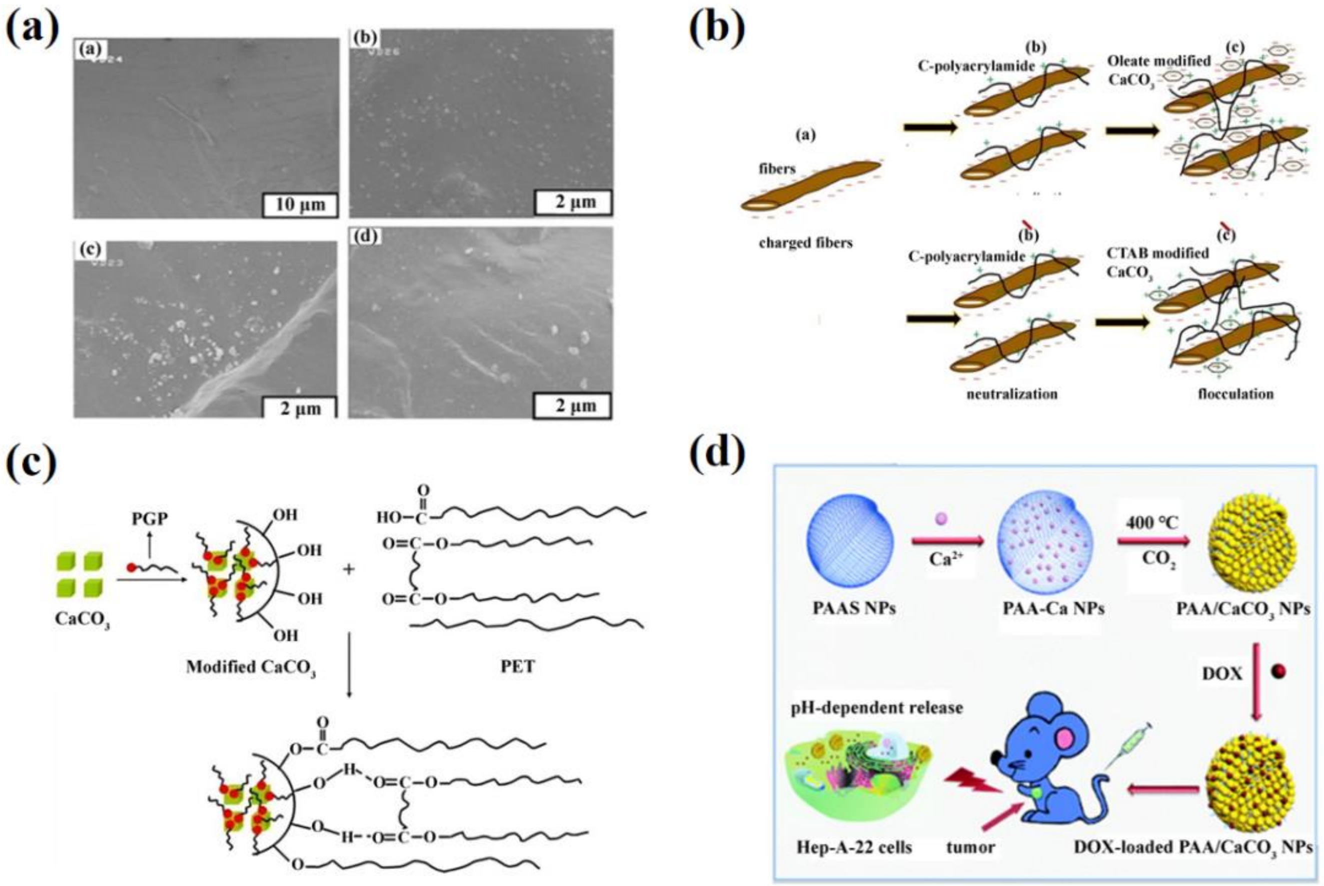

Figure 10 (a) The application of nano $CaCO_3$ in NR improves the dispersion performance; [54] (b) flocculation of nano $CaCO_3$ in paper pads; [14] (c) Application of nano $CaCO_3$ in PET; [55] (d) nano $CaCO_3$ as drug carrier [56]

In summary, nano $CaCO_3$ has been identified as a filler for plastics, with the capacity to enhance the mechanical properties of the materials and address the demands of daily life applications. Its utilization in papermaking has improved the physical characteristics of paper, including smoothness, whiteness, and transparency, along with enhanced mechanical resistance to tearing and rupture. Moreover, calcium carbonate nanoparticles exhibit favorable biocompatibility and low toxicity, which has led to their use as a delivery carrier for drugs, genes, and proteins. Additionally, they are employed in bone repair and replacement materials, enhancing the mechanical properties of compound polymer composites. These advantageous properties of calcium carbonate nanoparticles have led to their utilization in a variety of applications, performing diverse functions.

5 Conclusion

This paper reviews the latest advances in the preparation methods, surface modification, and application areas of calcium carbonate nanoparticles. The development and production of high-end modified calcium carbonate nanoproducts is an important way to meet the demand of high-end markets such as biomedicine and daily chemicals. It is anticipated that the large-scale implementation of nano $CaCO_3$ products with high whiteness and activity in plastics, rubber, coatings, papermaking, and biomedicine will drive advancements in the nano-calcium carbonate preparation process, leading to a reduction in production costs. This will result in a continuous improvement in the cost-effectiveness and utilization of nano $CaCO_3$. Conversely, the distinctive contribution of nano $CaCO_3$ in the domains of new inorganic fillers and high-end building materials and coatings is expected to stimulate technological advancement and product upgrading in the downstream industry, thereby reinforcing a positive effect.

6 Recommendation

In the study of the preparation process and industry market development of nano $CaCO_3$, it is also found that some problems in this field need to be solved, which restrict the large-scale application of nano $CaCO_3$, mainly as follows:

(1) The comprehension of the precipitation reaction of $CaCO_3$ remains in its nascent stages, and the nucleation and crystallization mechanisms of calcium carbonate nanoparticles require further comprehensive investigation. However, the CO_2 carbonation process, employing an economical and environmentally friendly method, yields a broad spectrum of $CaCO_3$ nanoparticle sizes, morphologies, and polycrystalline forms. Furthermore, the literature has documented the preparation of $CaCO_3$ particles with varying sizes, crystalline compositions, and morphologies through processes such as the Ca^{2+}-H_2O/organic solvent/additives/CO_3^{2-} precipitation system and the W/O emulsion method. However, the utilization of these processes to achieve large-scale nano $CaCO_3$ production remains a challenging endeavor that necessitates further research and development.

(2) Despite the extensive utilization of surface modification techniques and modified products of nano $CaCO_3$ to effectively regulate the surface polarity, hydrophilicity, and lipophilicity of nano $CaCO_3$, as well as the reactivity of the Ca However, significant research remains to be conducted to enhance the pH-responsiveness of nano $CaCO_3$ in biomedicine and environmental remediation applications, to achieve the controlled release of nano $CaCO_3$ within a specific pH range.

(3) The increasing exploitation of lime mines has led to a scarcity of high-quality limestone resources with low iron content. While there remains a relatively abundant supply of high-quality lime ores in the provinces of Guangxi, Zhejiang, and Fujian in China, the whiteness of nano-calcium carbonate products is directly influenced by the iron content of limestone, which can reach 0.05% or more in certain northern regions, such as Shaanxi and Hebei. For limestone with iron content of up to 0.08% or more, the whiteness value of the generally prepared calcium carbonate nanoparticles is between 91-92 at the highest, which necessitates surface whitening treatment to meet better the demands of high-end markets such as papermaking, high-grade coatings, and toothpaste. The most widely produced and utilized nanomaterials should be sustainably sourced from natural ores, ensuring effective utilization of waste resources.

Author Contributions

Author Contributions: Conceptualization and methodology, Junqing Pan, Man Zhao, and Luyao Yan; writing - original draft, writing, review & editing, formal analysis, and investigation, Luyao Yan; data curation, validation and supervision, writing - review & editing, Man Zhao; supervision, visualization, project administration and funding acquisition, Junqing Pan. Project administration, Hanyu Wang, Xin Jin, and Huasheng Zhan. All authors have read and agreed to the published version of the manuscript.

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.

Data Availability

The data are contained within the article.

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