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A Review Study On Nano- And Microstructural Calcium Carbonate (Caco₃): Polymorphism, Synthesis Pathways, Structure–Property Relationships, And Advanced Applications

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Abstract

Calcium carbonate ($CaCO_3$) is one of the most abundant inorganic materials on Earth and plays a pivotal role in geological, biological, and industrial systems. In recent years, nano- and microstructured forms of $CaCO_3$ have attracted considerable scientific interest due to their polymorphic versatility, tunable physicochemical properties, biocompatibility, and environmental sustainability. This review provides a comprehensive and critical synthesis of current knowledge on $CaCO_3$, focusing on its crystal polymorphism, nano- and microstructural properties, synthesis strategies, and characterization techniques. The influence of reaction parameters, additives, and environmental conditions on phase stability and morphology is systematically discussed. Furthermore, the review highlights the environmental significance of $CaCO_3$ in the global carbon cycle, along with its expanding applications in construction, biomedicine, drug delivery, environmental remediation, and advanced functional materials. Key challenges related to scalability, reproducibility, and polymorph control are addressed, and future research directions are proposed. This review aims to serve as a consolidated reference for researchers working in materials science, nanotechnology, environmental engineering, and biomedical fields.

Keywords: Calcium carbonate, polymorphism, nanomaterials, microstructures, synthesis, biomineralization, sustainability

1. Introduction

Calcium carbonate ($CaCO_3$) is a naturally occurring inorganic compound widely distributed in sedimentary rocks, marine environments, and biological systems. It constitutes the principal mineral phase of limestone, chalk, marble, and travertine and forms the structural basis of shells, corals, and skeletal frameworks of numerous marine organisms. Due to its abundance, low cost, chemical stability, and non-toxic nature, $CaCO_3$ has long been exploited in diverse industrial sectors, including construction, paper manufacturing, plastics, paints, pharmaceuticals, and agriculture (Wang et al., 2019). With the rapid advancement of nanoscience and materials engineering, research interest has shifted toward nano- and microstructured $CaCO_3$, which exhibits properties markedly different from those of bulk material. At reduced length scales, $CaCO_3$ demonstrates enhanced surface reactivity, modified mechanical behavior, improved dispersibility, and tunable optical and biological responses. These attributes have enabled its integration into high-value applications such as drug delivery systems, tissue engineering scaffolds, smart coatings, catalysts, and environmental remediation technologies. Advances in nanotechnology have enabled the fabrication of nano- and microstructured $CaCO_3$ materials with enhanced surface area, tunable polymorphism, and improved functional performance. These attributes have expanded the applicability of $CaCO_3$ into high-value domains such as drug delivery, tissue engineering, catalysis, and environmental remediation (Chen et al., 2019; Li et al., 2021).

2. Crystal Chemistry and Polymorphism of Calcium Carbonate

2.1 Fundamental Crystal Structure of Calcium Carbonate ($CaCO_3$)

Calcium carbonate ($CaCO_3$) is an ionic inorganic compound composed of divalent calcium cations (Ca^{2+}) and planar carbonate anions (CO_3^{2-}). The fundamental crystal structure of $CaCO_3$ is governed by the spatial arrangement and electrostatic interactions between these ions, which ultimately determine its polymorphism, stability, and physicochemical properties. The carbonate ion adopts a trigonal planar geometry, with a central carbon atom covalently bonded to three oxygen atoms via resonance-stabilized C–O bonds, resulting in equivalent bond lengths and a delocalized electronic structure (Dove & Rimstidt, 1994; Han & Bai, 2020). In $CaCO_3$ crystals, calcium ions are coordinated by oxygen atoms from neighboring carbonate groups. The coordination environment of Ca^{2+} varies depending on the specific polymorph, typically ranging from six- to nine-fold coordination. These coordination differences give rise to distinct lattice symmetries and packing densities observed among calcite, aragonite, and vaterite. The balance between electrostatic attraction, lattice energy, and steric constraints governs the overall stability of each crystal structure (Gómez-Morales et al., 2019).

At the atomic scale, $CaCO_3$ crystal structures consist of alternating layers of calcium ions and carbonate groups arranged in periodic lattices. In the most stable polymorph, calcite, Ca^{2+} ions are octahedrally coordinated by six oxygen atoms, forming a trigonal (rhombohedral) lattice with space group $R–3c$. The carbonate groups are oriented perpendicular to the crystallographic *c*-axis, resulting in strong anisotropy and characteristic rhombohedral cleavage planes (Han & Bai, 2020). This highly ordered arrangement minimizes lattice strain and accounts for the thermodynamic stability of calcite under ambient conditions. In contrast, aragonite exhibits an orthorhombic crystal system with space group *Pmcn*, where Ca^{2+} ions are nine-fold coordinated by oxygen atoms. This higher coordination number leads to a denser atomic packing and increased lattice energy, rendering aragonite metastable at room temperature and pressure but favored under high-pressure conditions and in many biological environments (Rodriguez-Blanco et al., 2008). Vaterite, the least stable polymorph, possesses a more disordered hexagonal structure with variable calcium coordination and partially rotationally disordered carbonate groups, contributing to its high surface energy and rapid phase transformation (Fantazzini et al., 2008).

The fundamental crystal structure of $CaCO_3$ is also sensitive to external factors such as temperature, pressure, solution chemistry, and the presence of impurities or foreign ions. Substitutional incorporation of ions such as Mg^{2+}, Sr^{2+}, or Ba^{2+} into the $CaCO_3$ lattice can distort the crystal framework, alter lattice parameters, and stabilize or destabilize specific polymorphs (Goldstein et al., 2012). These substitutions play a critical role in natural biomineralization processes and engineered synthesis strategies aimed at controlling crystal phase and morphology. At the nanoscale, deviations from ideal crystal structures become increasingly significant. Surface atoms experience reduced coordination and higher surface energy, leading to structural disorder, lattice strain, and enhanced reactivity. Nano-sized $CaCO_3$ particles often exhibit defects, grain boundaries, and amorphous regions, which influence nucleation pathways, polymorphic transformations, and dissolution behavior (Sanders et al., 2015). Understanding these fundamental structural characteristics is essential for designing $CaCO_3$-based nano- and microstructural materials with tailored properties for advanced technological and biomedical applications.

2.2 Aragonite

Aragonite is a metastable polymorph of calcium carbonate ($CaCO_3$) that crystallizes in the orthorhombic crystal system and exhibits physical and structural characteristics distinct from those of calcite. Although thermodynamically less stable than calcite under ambient temperature and pressure, aragonite plays a crucial role in geological processes, biomineralization, and advanced material applications due to its higher density, greater mechanical strength, and unique crystal architecture (Han & Bai, 2020). Crystallographically, aragonite belongs to the orthorhombic space group *Pmcn*. In this structure, calcium ions (Ca^{2+}) are coordinated by nine oxygen atoms derived from surrounding carbonate (CO_3^{2-}) groups, forming a more densely packed lattice compared to calcite. This higher coordination number results in increased lattice energy and structural rigidity, which contributes to the enhanced mechanical properties of aragonite, such as higher hardness and elastic modulus (Rodriguez-Blanco et al., 2008; Gómez-Morales et al., 2019). The carbonate groups in aragonite are arranged in alternating orientations within the lattice, leading to anisotropic crystal growth and characteristic needle-like or fibrous morphologies. These elongated crystal habits are commonly observed in both natural and synthetic aragonite and are particularly advantageous in biological systems where mechanical reinforcement is required (Dove & Rimstidt, 1994). The anisotropy also influences optical and dissolution properties, making aragonite more reactive than calcite under certain environmental conditions. Aragonite is commonly stabilized in high-pressure environments and aqueous systems enriched with magnesium ions (Mg^{2+}). Magnesium acts as a crystal growth inhibitor for calcite by distorting its lattice, thereby favoring the nucleation and growth of aragonite. This phenomenon is frequently observed in marine environments, where elevated Mg^{2+}/Ca^{2+} ratios promote aragonite precipitation over calcite (Goldstein et al., 2012). Consequently, aragonite is the dominant polymorph in many marine biominerals, including coral skeletons and mollusk shells. From a thermodynamic perspective, aragonite is metastable and tends to transform into calcite over geological timescales. This phase transformation can occur via solid-state rearrangement or dissolution–reprecipitation mechanisms, depending on environmental conditions such as temperature, pH, and fluid chemistry (Rodriguez-Blanco et al., 2008). At the nanoscale, the metastability of aragonite is further influenced by surface energy effects, which can temporarily stabilize aragonite nanoparticles and nanofibers.

In biomineralization, aragonite formation is often biologically controlled through organic matrices and macromolecules that regulate nucleation, crystal orientation, and growth kinetics. Proteins, polysaccharides, and acidic biomolecules interact with Ca^{2+} and CO_3^{2-} ions to stabilize aragonite and prevent its transformation into calcite. This biologically mediated stabilization has inspired bioinspired synthesis strategies for producing aragonite-based nanomaterials with enhanced mechanical performance and hierarchical architectures (Sanders et al., 2015). Due to its higher solubility relative to calcite, aragonite is more sensitive to environmental changes such as ocean acidification. The dissolution of aragonitic marine skeletons under decreasing pH conditions poses significant ecological risks to coral reefs and marine biodiversity. Understanding the crystal structure and stability of aragonite is therefore essential for predicting the impacts of climate change on carbonate-based marine ecosystems (Han & Bai, 2020). In engineered materials, synthetic aragonite has gained attention for applications requiring high strength, bioactivity, and anisotropic reinforcement, including bone tissue scaffolds, biodegradable composites, and functional fillers. Its unique crystal structure and morphology make aragonite an attractive alternative to calcite in specialized nano- and microstructural applications.

3. Physicochemical Properties of Nano- and Microstructured $CaCO_3$

3.1 Mechanical Properties of Nano- and Microstructured Calcium Carbonate ($CaCO_3$)

The mechanical properties of calcium carbonate ($CaCO_3$) are strongly influenced by its crystal polymorphism, particle size, morphology, and hierarchical structure. While bulk $CaCO_3$ is generally characterized as a brittle and relatively soft mineral, its nano- and microstructured forms exhibit significantly enhanced mechanical performance, particularly when incorporated into composite systems (Li et al., 2021; Wang et al., 2019).

3.1.1 Effect of Polymorphism on Mechanical Behavior

The three principal polymorphs of $CaCO_3$—calcite, aragonite, and vaterite—exhibit distinct mechanical characteristics due to differences in crystal symmetry and atomic packing density. Calcite, with its trigonal crystal structure and six-fold coordination of Ca^{2+} ions, displays moderate hardness and cleavage along rhombohedral planes, which limits its fracture resistance. In contrast, aragonite possesses an orthorhombic structure with nine-fold calcium coordination, resulting in higher density, elastic modulus, and fracture toughness (Han & Bai, 2020). Aragonite's needle-like or fibrous crystal morphology contributes to its superior mechanical performance in natural biominerals, such as mollusk shells and coral skeletons, where it acts as a reinforcing phase capable of dissipating stress and preventing catastrophic failure (Rodriguez-Blanco et al., 2008). Vaterite, although mechanically weaker and thermodynamically unstable, can still provide transient mechanical reinforcement at the nanoscale due to its high surface energy and rapid transformation behavior (Ma et al., 2020).

3.1.2 Size and Morphology Effects

At the nanoscale, $CaCO_3$ particles exhibit size-dependent mechanical strengthening, primarily due to grain refinement and the increased contribution of surface and interfacial effects. Nano-$CaCO_3$ particles typically display higher hardness and compressive strength compared to their bulk counterparts, as the reduction in grain size suppresses crack initiation and propagation (Bao & Bohrmann, 2019). Morphology also plays a critical role. Spherical nanoparticles enhance isotropic reinforcement, while rod-like, fibrous, or whisker-shaped $CaCO_3$ structures provide anisotropic mechanical reinforcement by facilitating stress transfer along preferred directions. Hierarchical microstructures combining nano- and micro-scale features further improve toughness by promoting crack deflection, bridging, and energy dissipation mechanisms (Chen et al., 2019).

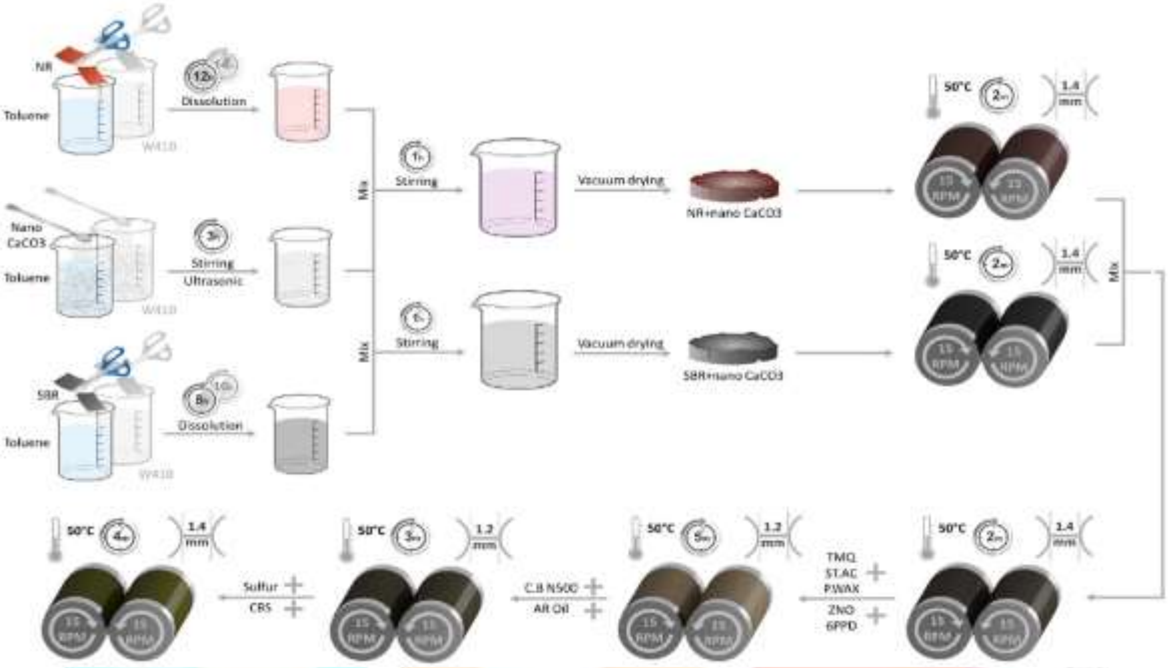
3.1.3 Reinforcement Mechanism in Composite Materials

Nano- and microstructured $CaCO_3$ is widely used as a reinforcing filler in polymer, ceramic, and bio-composite materials. The primary strengthening mechanisms include load transfer from the matrix to the rigid $CaCO_3$ particles, restriction of polymer chain mobility, and enhancement of interfacial adhesion through surface functionalization (Li et al., 2021).

As illustrated schematically, applied stress is transferred from the softer matrix to the stiffer $CaCO_3$ particles, resulting in increased tensile strength, Young's modulus, and impact resistance. Surface-modified $CaCO_3$ nanoparticles exhibit improved dispersion and stronger interfacial bonding, which significantly enhances composite mechanical performance while minimizing particle agglomeration (Wang et al., 2019).

3.1.5 Implications for Engineering Applications

The enhanced mechanical properties of nano- and microstructured $CaCO_3$ make it suitable for applications requiring lightweight reinforcement, improved durability, and cost-effectiveness. These include construction materials, biodegradable polymers, biomedical implants, and protective coatings. Understanding the structure–mechanical property relationship is therefore essential for tailoring $CaCO_3$-based materials for high-performance engineering and biomedical applications.



3.2 Thermal and Chemical Stability of Nano- and Microstructured Calcium Carbonate ($CaCO_3$)

The thermal and chemical stability of calcium carbonate ($CaCO_3$) is a critical factor governing its performance in geological, industrial, environmental, and biomedical applications. These stability characteristics are strongly influenced by polymorphic form, particle size, crystallinity, surface area, and surrounding chemical environment, particularly when $CaCO_3$ is engineered at the nano- and micro-scale (Bao & Bohrmann, 2019; Li et al., 2021).

3.2.1 Thermal Stability and Decomposition Behavior

Thermally, $CaCO_3$ is stable under ambient and moderately elevated temperatures; however, it undergoes endothermic thermal decomposition at high temperatures, typically above ~825 °C, yielding calcium oxide (CaO) and carbon dioxide (CO_2) according to the reaction:

$$\mathrm{CaCO_3}(s) \rightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

This decomposition process, commonly referred to as calcination, is widely exploited in lime and cement production. The exact decomposition temperature depends on factors such as particle size, crystal structure, heating rate, and atmospheric conditions (Wang et al., 2019).

At the nanoscale, $CaCO_3$ exhibits reduced thermal stability compared to bulk material. Nano-$CaCO_3$ particles possess higher surface-to-volume ratios and increased surface energy, which lower the activation energy required for decomposition. Consequently, nano-sized $CaCO_3$ may begin decomposing at temperatures several tens of degrees lower than bulk $CaCO_3$, as observed in thermogravimetric analysis (TGA) studies (Bao & Bohrmann, 2019). Polymorphism also plays a decisive role in thermal behavior. Calcite, being the most thermodynamically stable polymorph, generally exhibits the highest decomposition temperature, whereas aragonite and vaterite decompose at slightly lower temperatures due to their metastable crystal structures and higher lattice strain (Han & Bai, 2020). The presence of structural defects, amorphous regions, or dopant ions can further influence thermal stability.

3.2.2 Chemical Stability and Reactivity

Chemically, $CaCO_3$ is stable in neutral and alkaline environments but reacts readily with acidic solutions. In the presence of acids, $CaCO_3$ undergoes rapid dissolution accompanied by the release of carbon dioxide gas:

$$\mathrm{CaCO_3}(s) + 2H^+(aq) \rightarrow \mathrm{Ca}^{2+}(aq) + \mathrm{CO_2}(g) + H_2O(l)$$

This acid–base reactivity forms the basis for numerous applications, including antacid formulations, acid neutralization in wastewater treatment, soil pH regulation, and carbon sequestration processes (Goldstein et al., 2012). Nano- and microstructured $CaCO_3$ materials exhibit enhanced chemical reactivity relative to bulk $CaCO_3$ due to their increased surface area and abundance of reactive surface sites. As particle size decreases, dissolution rates increase significantly, particularly under acidic conditions. This property is especially advantageous in biomedical drug delivery systems, where controlled dissolution enables pH-responsive release of therapeutic agents (Ma et al., 2020).

3.2.3 Influence of Polymorphism on Chemical Stability

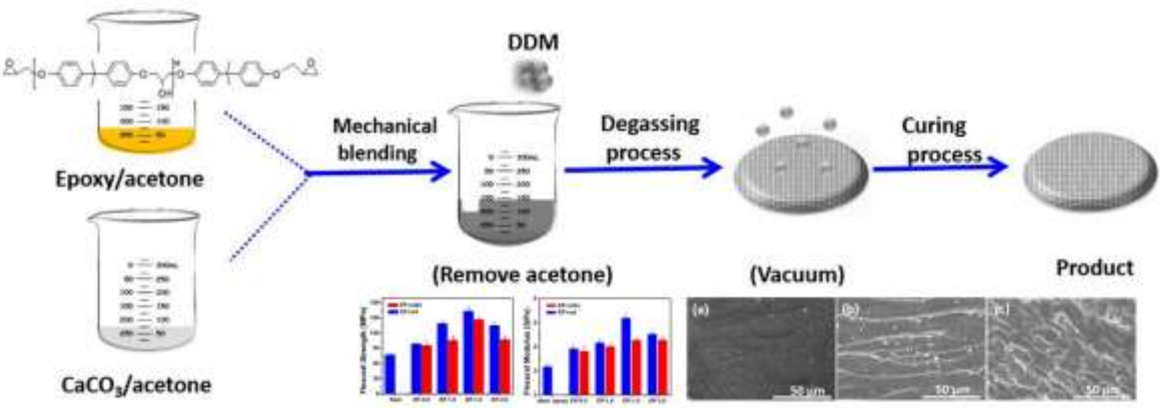
Among the $CaCO_3$ polymorphs, calcite is the least soluble and most chemically stable, while aragonite exhibits intermediate solubility and vaterite is the most soluble and chemically reactive. The higher solubility of aragonite and vaterite arises from their higher lattice energy and structural disorder, which facilitate ion detachment at the solid–liquid interface (Rodriguez-Blanco et al., 2008). In aqueous environments, metastable polymorphs tend to transform into calcite over time through dissolution–reprecipitation mechanisms. These transformations are accelerated at elevated temperatures, low pH, and high ionic strength, conditions frequently encountered in natural aquatic systems and industrial processes (Gómez-Morales et al., 2019).

3.2.4 Environmental and Biomedical Implications

The thermal and chemical stability of $CaCO_3$ has significant implications for environmental sustainability and biomedical performance. In marine environments, aragonitic $CaCO_3$ structures are particularly vulnerable to ocean acidification, where decreasing pH enhances dissolution rates, threatening coral reefs and calcareous organisms (Han & Bai, 2020). In biomedical applications, the controlled chemical instability of nano-$CaCO_3$ is advantageous. Its rapid dissolution under mildly acidic physiological conditions (e.g., tumor microenvironments or intracellular lysosomes) enables targeted drug release and biodegradability, minimizing long-term accumulation in the body (Chen et al., 2019).

3.4 Surface Chemistry and Reactivity

The surface chemistry of $CaCO_3$ nanoparticles governs their interaction with solvents, biomolecules, and polymers. Surface functionalization through polymers, surfactants, or bio-molecules improves dispersion, stability, and biocompatibility, enabling tailored performance in biomedical and environmental systems.



4. Synthesis Strategies for CaCO$_3$ Nano- and Microstructures

4.1 Precipitation Methods for the Synthesis of Calcium Carbonate (CaCO$_3$) Nano- and Microstructures

Precipitation methods represent the most widely employed and versatile approach for synthesizing calcium carbonate (CaCO$_3$) nano- and microstructured materials. These wet chemical techniques are favored due to their simplicity, low cost, scalability, and precise control over reaction parameters, making them suitable for both laboratory-scale research and industrial production (Xu & Ma, 2019; Wang et al., 2019).

4.1.1 Fundamental Principle of Precipitation

The precipitation of CaCO$_3$ is based on the controlled reaction between soluble calcium salts (e.g., calcium chloride, calcium nitrate, or calcium hydroxide) and carbonate sources (e.g., sodium carbonate, ammonium carbonate, or dissolved carbon dioxide) in an aqueous medium. The fundamental reaction can be represented as:

$$\mathrm{Ca}^{2+}(aq) + \mathrm{CO}_3^{2-}(aq) \rightarrow \mathrm{CaCO}_3(s)$$

Supersaturation of the solution triggers nucleation, followed by crystal growth and aggregation. The rate of nucleation relative to crystal growth determines particle size, morphology, and polymorphic outcome. Rapid nucleation typically favors the formation of smaller particles and metastable phases, whereas slower nucleation promotes larger, thermodynamically stable crystals (Gómez-Morales et al., 2019).

4.1.2 Influence of Reaction Parameters

pH

Solution pH is one of the most critical parameters influencing $CaCO_3$ precipitation. Alkaline conditions (pH 8–10) generally favor calcite formation, while near-neutral or slightly acidic conditions promote the formation of aragonite and vaterite. Changes in pH directly affect carbonate ion availability and supersaturation levels, thereby controlling polymorphic selection (Han & Bai, 2020).

Temperature

Temperature influences both nucleation kinetics and crystal growth rates. Lower temperatures tend to stabilize metastable polymorphs such as vaterite, whereas higher temperatures favor the formation of calcite due to enhanced atomic mobility and lattice reorganization (Rodriguez-Blanco et al., 2008).

Reactant Concentration and Mixing Rate

High reactant concentrations and rapid mixing increase supersaturation, leading to burst nucleation and the formation of nano-sized $CaCO_3$ particles. Conversely, dilute solutions and slow mixing favor controlled crystal growth and micro-scale structures. Homogeneous mixing is essential to avoid local supersaturation gradients that can cause broad particle size distributions (Xu & Ma, 2019).

4.1.3 Role of Additives and Modifiers

Organic additives, polymers, and surfactants are frequently introduced during precipitation to regulate crystal growth and prevent particle agglomeration. Molecules such as citrate, polyvinylpyrrolidone (PVP), chitosan, and polyethylene glycol selectively adsorb onto specific crystal faces, inhibiting anisotropic growth and stabilizing metastable polymorphs (Liu et al., 2019). Inorganic ions such as Mg^{2+}, Sr^{2+}, and PO_4^{3-} can incorporate into the $CaCO_3$ lattice or adsorb on crystal surfaces, altering lattice parameters and favoring aragonite or vaterite formation. These effects closely mimic natural biomineralization processes observed in marine organisms (Goldstein et al., 2012).

4.1.4 Aging, Ripening, and Phase Transformation

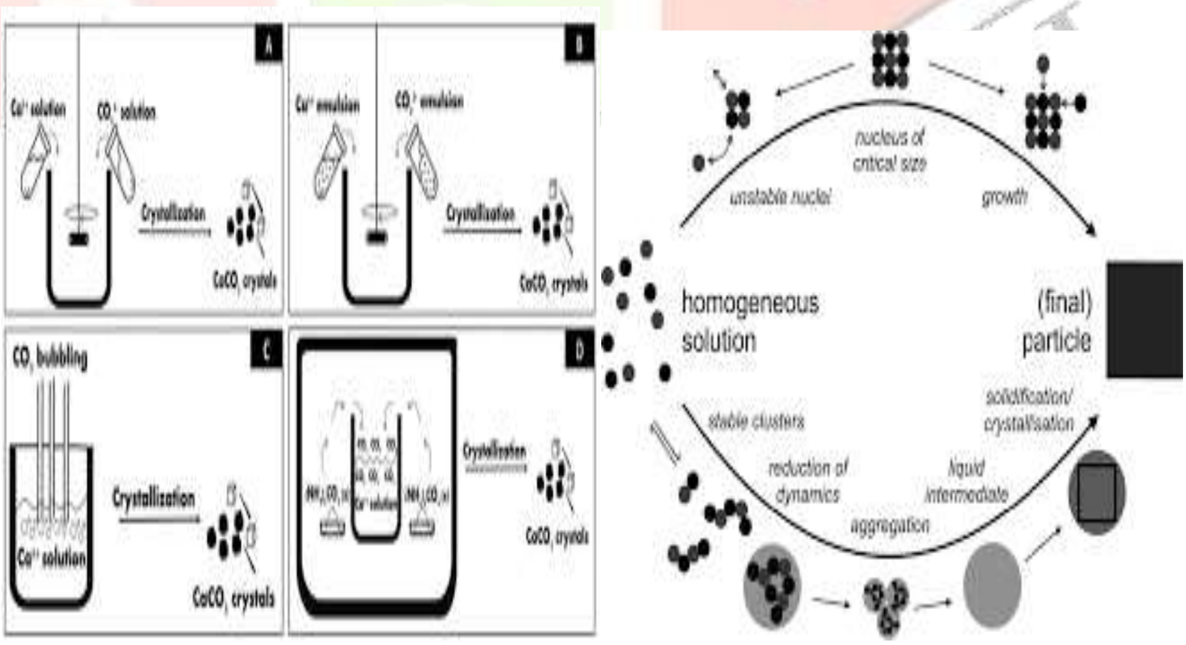
Following precipitation, $CaCO_3$ particles often undergo **aging or ripening**, during which metastable phases may transform into more stable polymorphs through dissolution–reprecipitation mechanisms. Ostwald ripening leads to particle coarsening, reduced surface energy, and increased crystallinity. Controlling aging time is therefore essential for preserving desired nano- or microstructural features (Rodriguez-Blanco et al., 2008).

4.1.5 Advantages and Limitations

Precipitation methods offer several advantages, including low energy consumption, ease of scale-up, and compatibility with green synthesis principles. However, challenges remain in achieving **precise polymorph control, narrow particle size distributions, and reproducibility**, particularly at large scales. Advanced strategies such as continuous-flow precipitation and microfluidic reactors have been developed to overcome these limitations (Xu & Ma, 2019).

4.1.6 Applications of Precipitated $CaCO_3$

Precipitated calcium carbonate (PCC) synthesized via precipitation methods is extensively used as a filler in paper, plastics, paints, and coatings. At the nanoscale, precipitated $CaCO_3$ finds applications in drug delivery, biodegradable composites, catalysis, and environmental remediation, owing to its tunable size, morphology, and surface chemistry (Chen et al., 2019).



5. Characterization Techniques

5.1. Spectroscopic Techniques

Spectroscopic techniques play a crucial role in elucidating the chemical bonding, crystal structure, polymorphic composition, and surface chemistry of calcium carbonate ($CaCO_3$) nano- and microstructured materials. Unlike diffraction and microscopy methods, spectroscopy provides molecular- and atomic-level information regarding functional groups, lattice vibrations, and local coordination environments. Among the most widely employed spectroscopic techniques for $CaCO_3$ characterization are Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, and solid-state nuclear magnetic resonance (NMR). FTIR spectroscopy is one of the most extensively used techniques for identifying $CaCO_3$ polymorphs and probing carbonate bonding environments. The vibrational modes of the carbonate (CO_3^{2-}) ion give rise to characteristic absorption bands, enabling differentiation between calcite, aragonite, and vaterite (Han & Bai, 2020). Typical FTIR spectra of $CaCO_3$ exhibit four fundamental vibrational modes: the asymmetric stretching mode (ν_3), symmetric stretching mode (ν_1), out-of-plane bending mode (ν_2), and in-plane bending mode (ν_4). The position, intensity, and splitting of these bands vary among polymorphs due to differences in crystal symmetry and carbonate ion orientation. For instance, calcite shows strong absorption near 713 cm^{-1} (ν_4), whereas aragonite exhibits distinct bands around 700–715 cm^{-1} and 855 cm^{-1}, while vaterite displays multiple split bands due to its lower structural order (Rodriguez-Blanco et al., 2008). FTIR spectroscopy is particularly valuable for nano-$CaCO_3$, where peak broadening and shifts can indicate reduced crystallinity, lattice strain, and surface functionalization. Additionally, FTIR is widely used to confirm surface modification of $CaCO_3$ particles with polymers, surfactants, or biomolecules, which is essential for biomedical and composite applications (Chen et al., 2019).

5.2 Raman Spectroscopy

Raman spectroscopy complements FTIR by providing vibrational information based on changes in molecular polarizability. It is especially effective for distinguishing $CaCO_3$ polymorphs due to its high sensitivity to lattice vibrations and crystal symmetry. Raman spectra of $CaCO_3$ typically display a strong symmetric stretching (ν_1) band near 1085 cm^{-1}, whose exact position and bandwidth differ among calcite, aragonite, and vaterite (Han & Bai, 2020). Calcite exhibits a sharp ν_1 Raman peak around 1086 cm^{-1}, reflecting its high crystallinity and structural order. In contrast, aragonite and vaterite show broader and slightly shifted peaks due to lattice distortion and disorder. Raman spectroscopy is therefore particularly useful for detecting polymorphic mixtures and monitoring phase transformations during synthesis or aging processes (Gómez-Morales et al., 2019). An important advantage of Raman spectroscopy is its non-destructive nature and minimal sample preparation, enabling in situ and real-time analysis of $CaCO_3$ crystallization from solution. This capability has been widely exploited to study nucleation pathways, amorphous calcium carbonate (ACC) intermediates, and polymorphic transformations under controlled conditions (Sanders et al., 2015).

5.3 Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy

Solid-state NMR spectroscopy provides detailed insights into the local atomic environment and coordination geometry of $CaCO_3$ at the molecular level. Nuclei such as ^13C and ^43Ca are commonly investigated to probe carbonate carbon environments and calcium coordination, respectively (Fantazzini et al., 2008). ^13C magic-angle spinning (MAS) NMR is particularly effective for distinguishing $CaCO_3$ polymorphs, as each polymorph exhibits characteristic chemical shifts and line shapes corresponding to the local symmetry of carbonate groups. Calcite shows a narrow resonance peak indicative of high structural order, whereas aragonite and vaterite exhibit broader peaks reflecting increased disorder and multiple carbonate environments (Fantazzini et al., 2008). MR spectroscopy is also uniquely suited for studying amorphous calcium carbonate (ACC) and nano-sized $CaCO_3$, where long-range order is absent or limited. Through NMR, researchers can investigate early-stage nucleation, hydration states, ion pairing, and phase evolution mechanisms that are not accessible by X-ray diffraction alone (Sanders et al., 2015).

5.4 Significance and Limitations

Collectively, spectroscopic techniques provide complementary and indispensable information for understanding $CaCO_3$ nano- and microstructures. FTIR and Raman spectroscopy are rapid, accessible, and effective for polymorph identification and surface chemistry analysis, while solid-state NMR offers unparalleled insight into local structural environments and phase transformations. However, each technique has limitations. FTIR spectra may suffer from band overlap, Raman spectroscopy can be affected by fluorescence, and NMR requires specialized instrumentation and long acquisition times. Therefore, a combined spectroscopic approach, integrated with diffraction and microscopy techniques, is recommended for comprehensive characterization of $CaCO_3$-based materials (Wang et al., 2019).

6. Environmental and Biological Significance

$CaCO_3$ plays a fundamental role in the global carbon cycle by regulating ocean alkalinity and acting as a long-term carbon sink. In biological systems, $CaCO_3$ is essential for skeletal formation and mineral homeostasis. Its biodegradability, abundance, and low toxicity make it environmentally benign and suitable for green material design.

7. Industrial and Biomedical Applications

Industrially, $CaCO_3$ is indispensable in cement, paper, plastics, paints, and pharmaceuticals. Nano- and microstructured $CaCO_3$ has enabled advanced biomedical applications, including drug delivery carriers, bone tissue scaffolds, bio-imaging agents, and antimicrobial composites. Environmental applications include wastewater treatment, heavy metal adsorption, and soil remediation.

8. Challenges and Future Perspectives

Despite its versatility, challenges remain in achieving reproducible large-scale synthesis, precise polymorph control, and long-term stability of nano-$CaCO_3$. Future research should emphasize green synthesis routes, bio-inspired mineralization, hybrid composite systems, and life-cycle assessment to ensure sustainable development.

9. Conclusion

Nano- and microstructured calcium carbonate represents a multifunctional, sustainable material with immense potential across scientific and technological domains. Understanding its polymorphism, synthesis–property relationships, and environmental interactions is essential for unlocking next-generation applications. Continued interdisciplinary research will further expand its role in materials science, biomedicine, and environmental engineering.

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