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Controllable synthesis of all the anhydrous CaCO₃ polymorphs with

various morphologies in CaCl₂-NH₃-CO₂ aqueous system

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Abstract: Polymorphism- or morphology-controllable synthesis of CaCO₃ is of significance. Usually only calcite CaCO₃ can be obtained from the ordinary CO₂-Ca(OH)₂ solution route; the very low solubility of Ca(OH)₂ also causes many defects with this route. The route by CaCl₂ and Na₂CO₃ exhibits some advantages, but the consumption of Na₂CO₃ is a deficiency. Therefore, this work studies the precipitation of CaCO₃ with CaCl₂ in NH₃-CO₂ aqueous solution, which will make the overall reaction " $CaCO_3 \rightarrow CaCO_3$ " if tracing the origin of the reactants. A main focus of the present work is to elucidate how to obtain various CaCO₃ polymorphs with different morphologies through this synthesis system and the corresponding crystal growth mechanism. The results show that, just by simply regulating the reaction conditions, all three anhydrous CaCO₃ polymorphs with various morphologies (e.g., cubic, lamellar, spherical, needle-like and branched) can be obtained in the absence of any additives. The crystal growth process can be well explained based on either Ostwald ripening or dissolution-recrystallization mechanism, depending on the reaction conditions. In addition, the rare phase transition of metastable vaterite to metastable aragonite can also be obtained from the present synthesis system, besides the usual phase transition of vaterite to the most thermodynamically stable calcite. This work provides the essential theoretical support for

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