Synthesis of $CaCO_3$ Nanoparticles Using Amino Acids

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Statement of Purpose: $CaCO_3$ has been widely investigated for diverse biomedical applications including diagnosis, treatment and theranostics due to its excellent biocompatibility/biodegradability and pH-sensitive properties.[1, 2] $CaCO_3$ has been well used in orthopaedics. Here we report a cost-effective and environmentally-friendly method to synthesize $CaCO_3$ nanoparticles.

Methods: A chemical solvent made of amino acids and bases was prepared by dissolving certain amounts of a base (e.g., NaOH) and an amino acid (e.g., glycine) at a certain molar ratio and mixing. CO_2 gas was bubbled into the solvent and a mass flow controller was used to control the CO_2 flow rate. After a defined duration of CO_2 bubbling, $CaCl_2$ was added and the solvent was vortexed briefly. Then precipitates were observed and collected by centrifugation and washed with deionized water to obtain high purity nanoparticles.

Results: X-ray diffraction (XRD**)** studies found that the solid precipitates were pure calcite, the most stable phase of $CaCO_3$. Scanning and transmission electron microscopy showed that the $CaCO_3$ were nanoparticles which had an average diameter of approximately 70 nm (**Fig. 1)**. In addition, the morphology of $CaCO_3$ varied with the amino acid species and the amino acid doses. Compared with solvent without amino acid, it was found that amino acid played a critical role in producing nanoparticles; in the absence of amino acids, microparticles instead of nanoparticles were formed. Moreover, the size of the particles could be controlled and a variety of unique $CaCO_3$ products including cubic-shape nano-particles, ellipsoidal nano-particles, bone-like porous particles, spherical microparticles and corn-like nano-rods were achieved. Nuclear magnetic resonance studies found that the amino acid reacted with CO_2 to form carbamate first, and then carbamate was hydrolyzed into bicarbonate which then reacted with Ca^{2+} to form $CaCO_3$ nanoparticles.

Discussions: An innovative method was developed based on amino acid salt solvents to synthesize $CaCO_3$ nanoparticles. The production of $CaCO_3$ nanoparticles from CO_2 is significant, because it not only converted CO_2 to minerals that are stable but the products also have broad applications across various industries. According to reports by Grand View Research[3] and Market Research Community,[4] the global market for $CaCO_3$ nanoparticles was valued at US$ 8.4 billion in 2022, and will further increase due to the increasing demand for sustainable materials in various industries.

Conclusions: In this study, an innovative strategy based on amino acids was developed to produce $CaCO_3$ nanoparticles of approximately 70 nm. Fundamentally important, we clearly demonstrated that it was the amino acids (e.g., glycine) that dictated the formation of $CaCO_3$ nanoparticles.

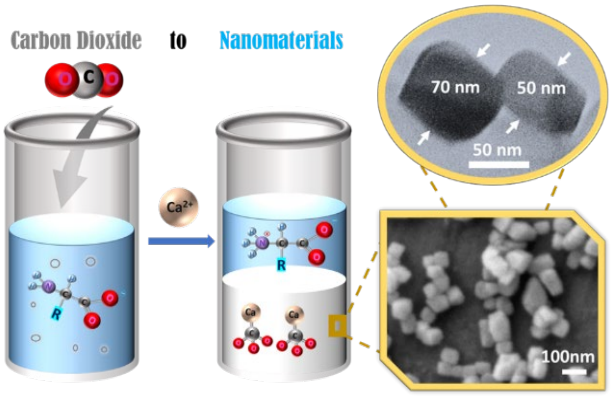

Fig. 1. $CaCO_3$ nanoparticles were synthesized using amino acids reacting with CO_2 and $CaCl_2$.

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