Synthesis of pure nanocalcite with targeted sizes and surface areas

JUAN DIEGO RODRIGUEZ-BLANCO[1,2], DINA BELOVA[2], DENIS OKHRIMENKO[2], MARCEL CECCATO[2], IMANE MOUNIB[2], DOMINIQUE J. TOBLER[2]

[1]Department of Geology, Museum Building, School of Natural Sciences, Trinity College Dublin, Ireland. rodrigjd@tcd.ie

[2]NanoScience Center, Department of Chemistry, University of Copenhagen, Copenhagen, Denmark.

Calcite forms abiotically and biogenically in a wide range of natural environments (e.g., soils, caves, calcifying marine organisms, hot springs). The crystallisation of calcite is highly affected by variables like temperature, solution pH, and especially foreign ions, organics in solution and impurities. As a consequence natural calcite usually consists of μm-sized crystals with low surface areas and its chemistry includes common ions like Mg^{2+}, Sr^{2+}, PO_4^{3-}, SO_4^{2-} as well as organics. In some exceptional cases high surface area calcite can be found in nature, like the vast deposits of biogenic calcite nanoparticles in chalk formed by coccolithophorids, with μm-sized (0.1-3 μm) calcite plates and surface areas around 2-8 m^2g^{-1}. However, this calcite contains impurities (i.e., polysaccharides originally produced by the algae to control coccolith size and morphology), which also act as inhibitors for the recrystallization of chalk.

The synthesis of nm-sized calcite with high surface areas is also achievable in the laboratory. Two types of methods are frequently used: (i) carbonation of $Ca(OH)_2$ seeds in solution and (ii) use of crystal growth inhibitors, such as organics and micro-emulsions. Although these methods produce nanocalcite with high surface areas (e.g., 10 to 40 m^2/g), the final product is not pure calcite and also contains different (in)organics (e.g., vaterite, $Ca(OH)_2$ seeds encapsulated in calcite, organics used during the synthesis process). Besides, these methods often require a long synthesis time (hours to days).

In this work we show a facile protocol consisting of a combination of precipitation from solution and solid-state crystallisation methods to rapidly synthesise nm-sized calcite with targeted particle sizes (between 70 to 320 nm) and BET surface areas (between 5 to 25 m^2g^{-1}). This protocol allows a quick (< 30 min) synthesis of dry pure nanocalcite not containing any other solid phases or (in)organic ions. This nanomaterial has high potential for environmental applications like enhanced remediation technologies (e.g. removal of pollutants from soils and groundwater).