

Support information

Room temperature vortex fluidic synthesis of monodispersed amorphous proto-vaterite

Wenhong Peng, Xianjue Chen, Shenmin Zhu*, Cuiping Guo and Colin L. Raston*

Experiment detail

Preparation of amorphous calcium carbonate

VFD process

All chemicals used were purchased from Sigma–Aldrich and used without further purification. 0.1 M Na₂CO₃ and 0.1 M CaCl₂ were dissolved each in 2 mL Milli-Q-water and 10 mL of ethylene glycol (EG). ACC bulk materials were obtained by adding the above Na₂CO₃-EG and CaCl₂-EG solution separately prior to immediate processing in the VFD for 30 min using the confined mode of processing, with the mixture volume fixed at 4 mL at room temperature. The tilt angle of VFD was set at 45°. The rotation speed changes from 2000 rpm, 3000rpm to 4000 rpm. The mixed solution gradually turned milky. The precipitates were separated rapidly by centrifugation and washed sequentially using ethanol, methanol and acetone. The obtained ACC powders were dried for 1 h at 60°C. Dry ACC could be stored at room temperature for at least 2 weeks without any sign of degradation. Storage in ethanol gave equally good results.

Batch process

The same Na₂CO₃-EG and CaCl₂-EG solutions were mixed in a beaker by shaking with the precipitate immediately separated by centrifugation and washed sequentially using ethanol, methanol and acetone. The obtained ACC powders were dried for 1 h at 60°C.

Magnetic stirring process

The above Na₂CO₃-EG and CaCl₂-EG solution were chosen to mix in a 20 mL glass bottle using a 10 mm oval magnetic stirrer bar on a hot plate. The rotation speed was 500 rpm, and the reaction time 30 min, at room temperature. The precipitates were separated rapidly by centrifugation and washed sequentially using ethanol, methanol and acetone. The resulting ACC powders were dried for 1 h at 60°C.

Characterization:

FTIR spectroscopy measurements were recorded using a Perkin Elmer Spectrum 400 FTIR. The morphology of the sample was measured using a field emission environmental scanning electron microscope (FEI Quanta 450). TEM measurements were made using a Philips CM200 TEM with SAED patterns examined. TGA analysis was carried out using a TA instrument, with the ACC (~10 mg) analyzed from 30°C to 800°C at a heating rate of 10°C/min. Samples were contained in platinum cups during TGA and analysed in a flow of dry air. X-ray diffraction studies used a Bruker D4 Endeavor equipped with an X-ray source emitting Co K1 radiation.

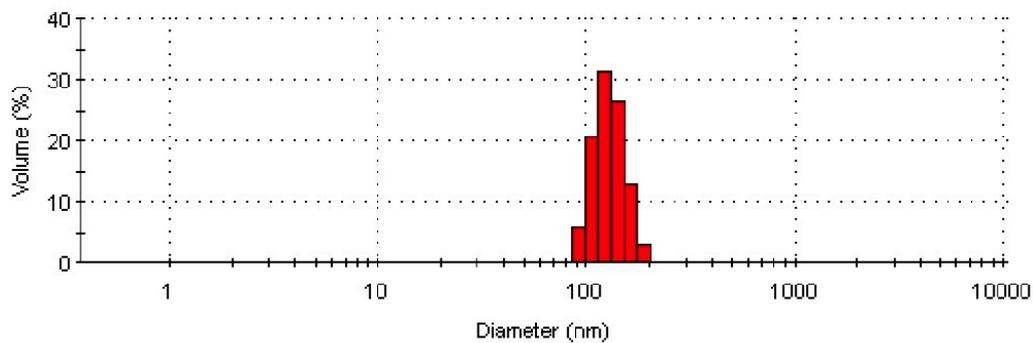


Fig. S1 Analysis of particle size distribution of amorphous calcium carbonate (ACC) particles produced using VFD, using dynamic light scattering (DLS) of particles dispersed in ethanol. Average hydrodynamic diameter is 154.3 nm.

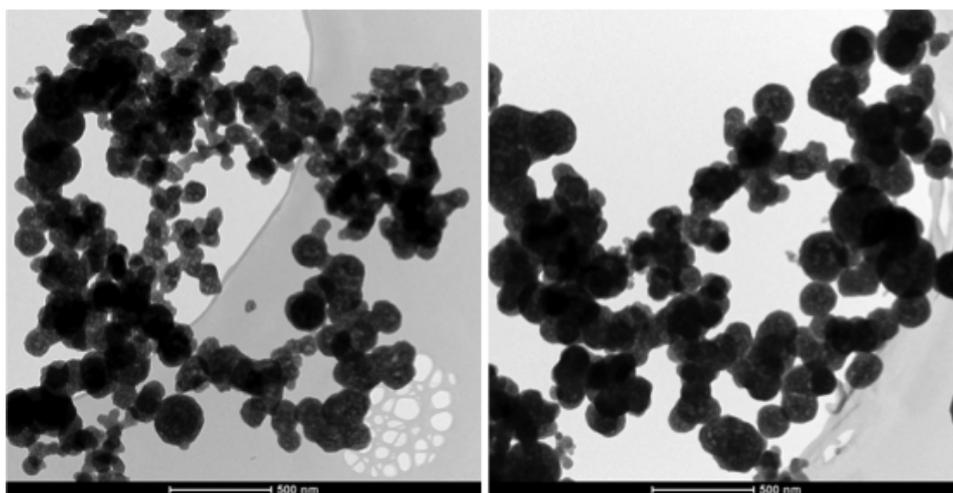


Fig. S2 TEM images of ACC particles taken directly after their formation, showing similar size and morphology compared with ACC particles similarly prepared, but stored for two weeks in ethanol.

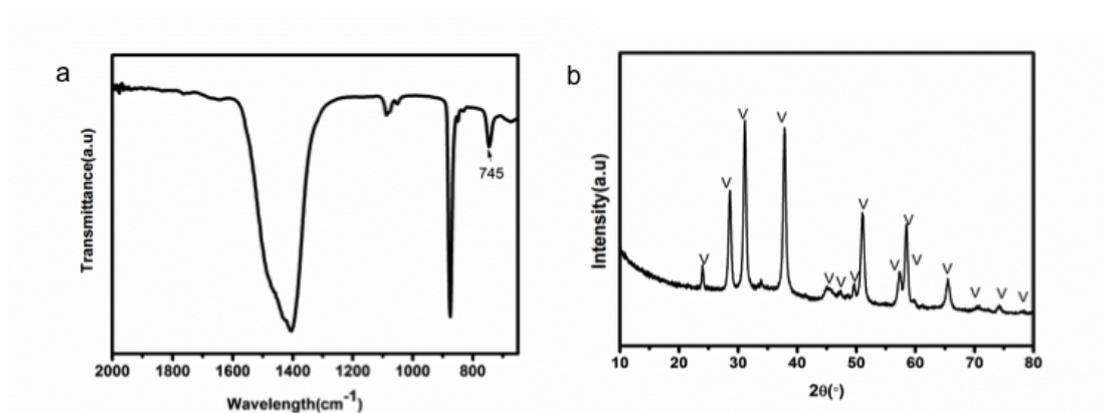


Fig. S3 FTIR (a) and XRD (b) of the calcium carbonate produced using magnetic stirring. For the latter, peaks associated with the presence of vaterite polymorph are marked with a (v).

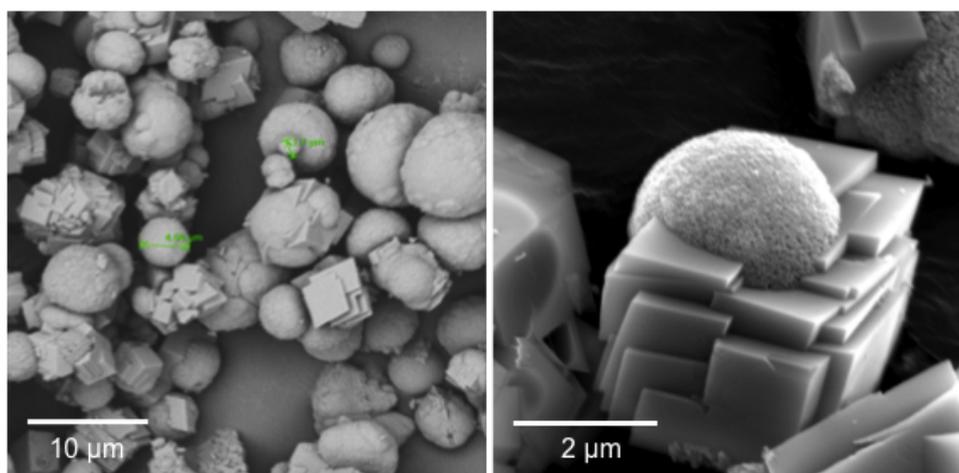


Fig. S4 SEM images showing ACC and crystalline calcium carbonate particles, and inter-grown composites thereof, formed using purely aqueous solutions of CaCl_2 and Na_2CO_3 in the VFD under the same conditions as for the formation of ACC particles alone, confirming that the presence of ethylene glycol is a prerequisite for the formation of stable ACC nanoparticles.