Supplementary Information

Ethanol assisted synthesis of pure and stable amorphous calcium carbonate nanoparticles

Shao-Feng Chen,[a] Helmut Cölfen,[*b,c] Markus Antonietti,[b] *and* Shu-Hong Yu[*a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

a Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. Fax: +86 551 3603040; E-mail: shyu@ustc.edu.cn.
b Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, MPI Research Campus Golm, D-14424, Potsdam, Germany.
c present address: University of Konstanz, Physical Chemistry, Universitätsstr. 10, D-78457 Konstanz, Germany, Fax: +49 7531 883139; E-mail: Helmut.Coelfen@uni-konstanz.de

Experimental Section

Synthesis of ACC. 200 mg calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$ from Aldrich) were dissolved in 100 mL absolute ethanol (Merck), which the solution has initial pH value of about 7. This solution was placed in a glass bottle and covered by parafilm with several pores. Then the bottle and two glass bottles of ammonium bicarbonate (NH_4HCO_3) were left in a desiccator. After three days reaction, white ACC nanoparticles formed and suspended in ethanol solution with pH value of about 8. One bottle of the white dispersion was centrifugated and redispersed in 5 mL of absolute ethanol for formation of a concentrated ACC nanoparticle dispersion. The molar concentration of the final dispersion is about 0.27 $mol \cdot L^{-1}$.

Crystallization of ACC. The total volume of reaction solution is 10 mL, and the final concentration of $CaCO_3$ is 40 mM. For fabricating $CaCO_3$ fibres, 1.5 mL ACC dispersion, 6.5 mL absolute ethanol and 1.5 mL distilled water with pH 8-12 were mixed together and sonicated for 20 seconds. For fabricating calcite dendritic structures, 1.5 mL ACC dispersion, 6 mL absolute ethanol and 2.5 mL 1M NaOH solution were mixed together and sonicated for 20 seconds. All of the final crystals were filtered and washed with acetone, then dried in a vacuum oven at room temperature for characterization.

Characterization. X-ray diffraction (XRD) patterns were recorded by a PDS 120 diffractometer (Nonius GmbH, Solingen) with Cu Kα radiation (λ = 1.542 Å). The FT-IR spectra are collected by Varian 1000 FT-IR. SEM images were collected by a JEOL JEM-6330F microscope. TEM images were obtained by a Zeiss EM 912Ω microscope. A SW55 swing out rotor in a Beckman L70 preparative ultracentrifuge was used for preparative

separation of the CC nanoparticles at 15000 rpm at 25 °C for 10 min. (Beckman Coulter, Palo Alto, CA) An analytical ultracentrifuge Optima XL-I (Beckman Coulter Palo Alto CA) was used to analyze the particle distribution of the amorphous calcium carbonate, nanoparticles in 12 mm titannium centerpieces (Nanolytics, Potsdam) by Rayleigh interference optics at 5000 rpm and 25 °C. The sedimentation coefficient distribution was analyzed without diffusion correction using the program Sedfit by P. Schuck (https://sedfitsedphat.nibib.nih.gov/software/default.aspx). The sedimentation coefficient were converted to the hydrodynamic diameter d_H assuming hard spheres and using:

$$d_H = \frac{18\eta s}{\sqrt{\rho_P - \rho}}$$

with ρ_P = particle density, ρ = solvent density, η = solvent viscosity, s = sedimentation coefficient and d_H = hydrodynamic particle diameter.

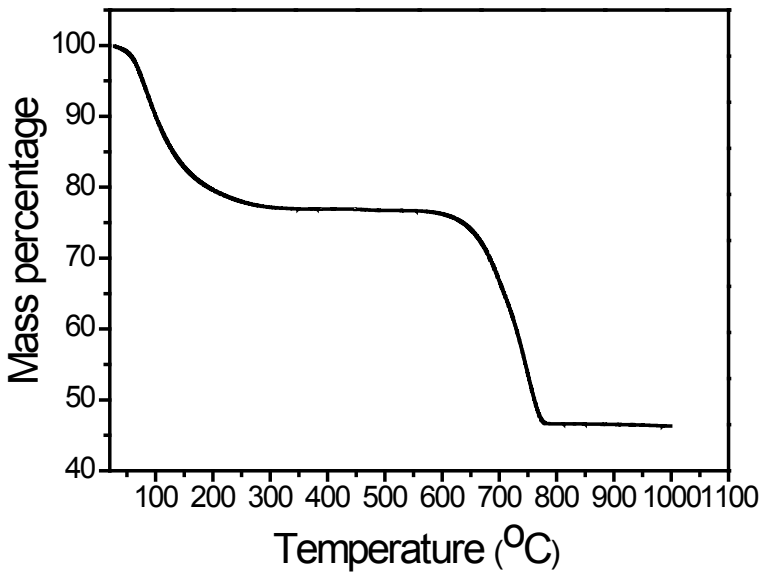

Fig. S1 TG curve of the hydrated ACC.

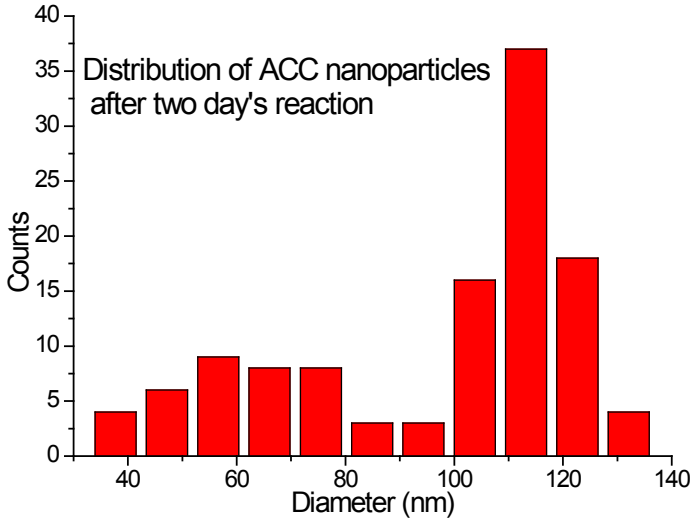

Fig. S2 The statistical analysis of the ACC nanoparticle size shown in Figure 3c. The ACC nanoparticles were synthesized after two days' reaction.

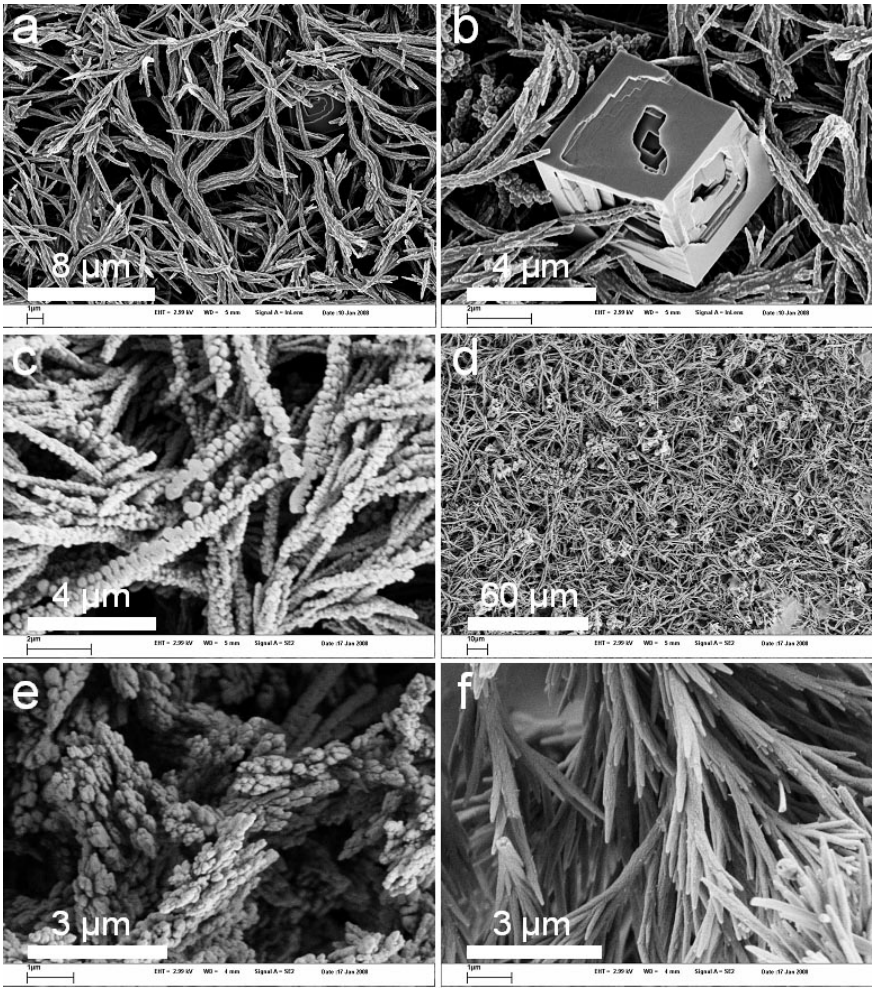

Fig. S3 Scanning electron microscopy (SEM) images of $CaCO_3$ crystals at different pH values: a-b) 1.5 mL water, pH 8; c-d) 1.5 mL water, pH 12; e) vateite phase, 1.5 mL water, pH 12.5; f) calcite dendritic crystal, 2.5 mL 1 M NaOH solution.