



Chemical Communications

COMMUNICATION

Electronic Supplementary Information (ESI) for

A solvothermal method for synthesizing monolayer protected amorphous calcium carbonate clusters

Shengtong Sun, Denis Gebauer and Helmut Cölfen*

Experimental

Synthesis of PCDA monolayer protected ACC cluster

In a typical procedure, as shown in Fig. 1, 10 mM anhydrous CaCl_2 and 4 mM 10,12-pentacosadiynoic acid (PCDA, Aldrich) were dissolved in 200 mL of ethanol. Note that commercially obtained PCDA always contains oligomeric impurities, and thus the PCDA ethanolic solution was filtered with a 0.45 μm PTFE filter before use giving a transparent solution. After that 336 mg of NaHCO_3 powder (4 mmol) and 0.63 mL of NH_4OH (25% in water) were added into the solution and the solution was capped tightly in a blue-cap glass bottle (Duran[®], Schott pressure plus). The initial pH of the solution was ~ 8 . The bottle was then put in an oil bath at 100 °C for 3 days. White precipitates together with the resultant Na_2CO_3 powder were gradually found at the bottom of the bottle. Centrifugation (9000 rpm, 5 min) was used to collect all the solids, which were then dissolved in small amounts of toluene with the assistance of ultrasonication. To remove Na_2CO_3 , the turbid solution was filtrated with the filtrate being dropped into a large volume of ethanol to give white precipitates. Centrifugation (9000 rpm, 5 min) was again used to collect these precipitates followed by dissolution in toluene and precipitation in ethanol. This dissolution-precipitation cycle was repeated for at least 6 times to remove any possible impurities. Finally, for storage, the precipitate was dissolved in toluene or dried in vacuum at room temperature for 1 h.

To confirm that the product from NaHCO_3 decomposition is really Na_2CO_3 , large amount of toluene was added to the precipitate after the first centrifugation to dissolve all the ACC clusters. Centrifugation was performed again to collect the solid residues. The solid was then washed with toluene and ethanol followed by drying in air for XRD and TGA measurements.

Characterization

TEM images and selected area electron diffraction were acquired on a Zeiss Libra 120 microscope operating at 120 kV. High-resolution TEM and energy dispersive X-ray (EDX) data were acquired on a JEOL JEM-2200FS microscope (high-

resolution TEM) operating at 200 kV. TEM samples were prepared from the cluster toluene solution (~0.5 mg/mL) on conventional TEM grids (carbon-coated copper grids, 400 mesh, supplied by Quantifoil GmbH). Dynamic light scattering (DLS) measurement on diluted ACC cluster solution in toluene (0.1 mg/mL) was performed on a Malvern Nano-ZS ZEN 3600 particle sizer (173° back-scattering) at room temperature. UV-vis spectra of the cluster and PCDA in hexane were collected on a Varian Cary 50 Bio UV/vis Spectrophotometer. Attenuated-total-reflection-infrared spectroscopy (ATR-FTIR) was carried out on a Perkin Elmer device (Spectrum100 FTIR, equipped with a diamond ATR crystal). X-ray powder diffraction (XRD) data were acquired on a D8 ADVANCE and DAVINCI.DESIGN (Bruker) X'pert diffractometer with Cu K α radiation. Thermal gravimetric analysis (TGA) was performed on a Netzsch STA 449 F3 with a heating rate of 10 K/min under air flow. The matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF MS) spectrum was recorded on a Bruker Microflex MALDI-TOF with α -cyano-4-hydroxycinnamic acid (HCCA) as matrix and toluene as solvent.

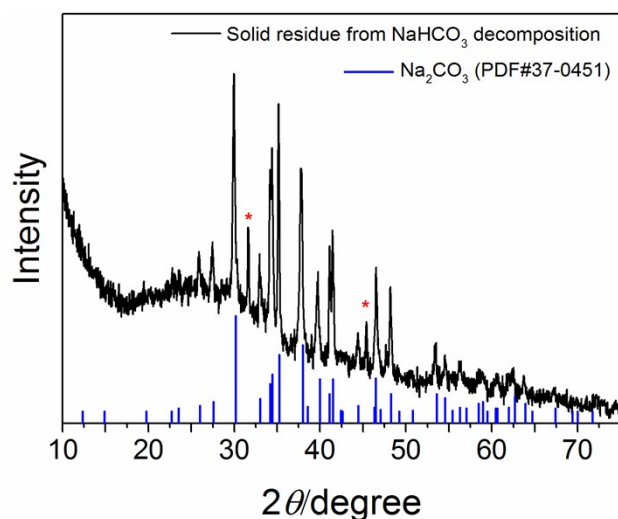


Fig. S1 XRD profile of the solid residues from NaHCO₃ decomposition comparing with the standard data of Na₂CO₃ (PDF#37-0451). The similarity reveals that the product from NaHCO₃ decomposition is really Na₂CO₃. The peaks labeled by asterisks (*) might come from minor amount of NaCl formed in the solution.

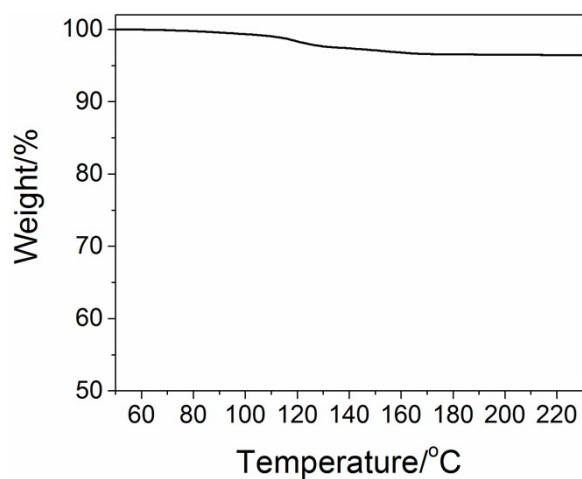


Fig. S2 TGA curve of the solid residues from NaHCO_3 decomposition showing only 3.5% weight loss from 50 to 200 °C that may come from the adsorbed water. This further proves that NaHCO_3 decomposes into Na_2CO_3 in the solvothermal condition.

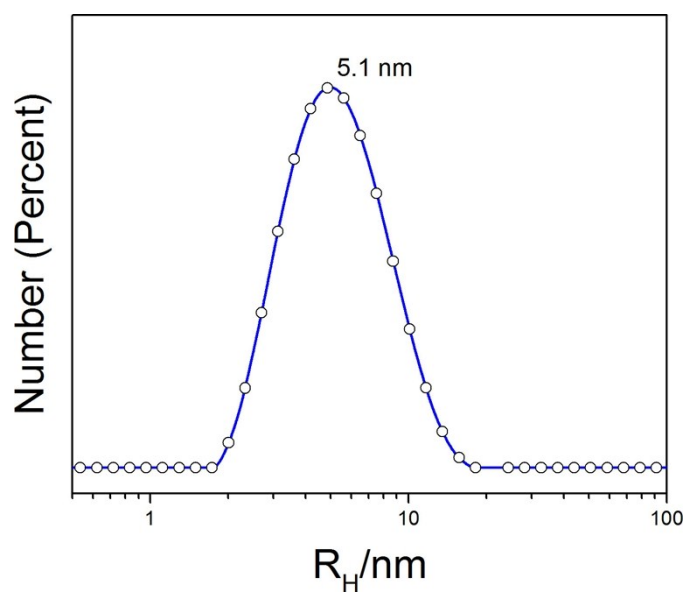


Fig. S3 DLS size distribution (number weighted) of PCDA protected ACC cluster in toluene.

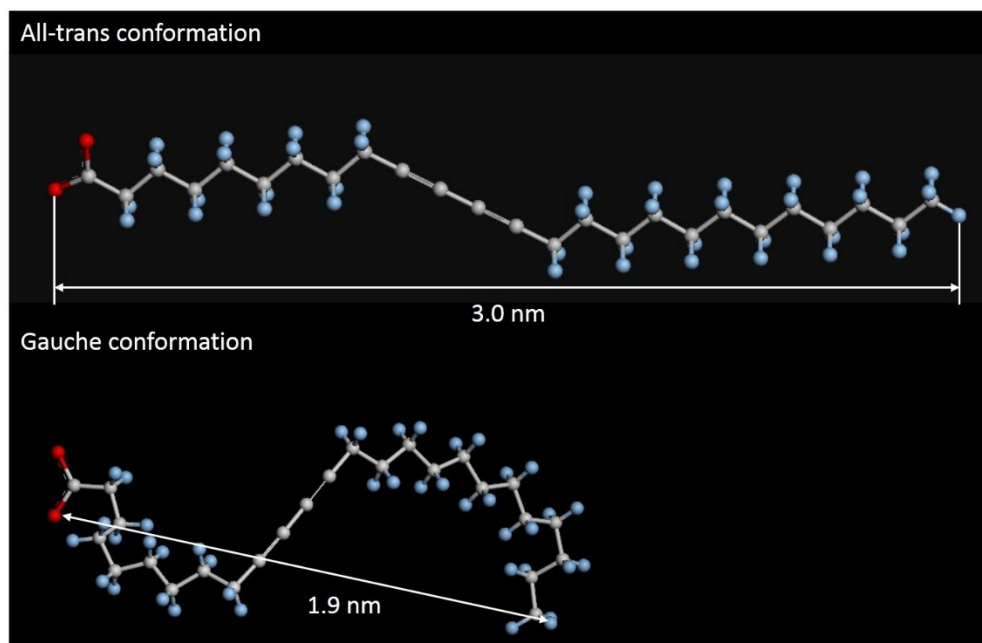


Fig. S4 Structural models of the all-trans and gauche conformations of deprotonated PCDA molecules. The chain lengths of these two models are also labelled. Red atoms represent O, while blue for H and grey for C.