Supporting Information

Thermally Induced Fragmentation of Nanoscale Calcite

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Experimental procedures

The aqueous dispersion of calcite nanorods was prepared by the carbonation of $Ca(OH)_2$, as shown in our previous article. Calcite nanoblocks were synthesized in a 200-cm^3 aqueous dispersion of 42.5 g dm^{-3} $Ca(OH)_2$ through carbonation by the introduction of CO_2 at a rate of 3 dm^3 min^{-1}. The pH of the dispersion (~13) started to decrease when the carbonation reaction finished. We monitored the pH value of the dispersion continuously with a pH meter (DKK-TOA GST-2739C, Japan) during the carbonation. The basic dispersion of the calcite nanoblocks was maintained at a constant temperature in the range of 4−25°C. The calcite nanorods elongated in the c-axis direction were formed in the dispersion by stirring for 336 h. The nanorods were separated by centrifugation and were then redispersed in ethanol.

Homogeneous films having millimeter-scale wide and micrometer-scale thick were prepared on a silicon substrate by evaporation-driven self-assembly using ethanol dispersion containing calcite nanorods. Substrates that were treated by acetone with ultrasonication were placed in the ethanol dispersion in a glass vial. Nanorods were accumulated on the surface of the substrate as the dispersion medium was evaporated at room temperature. The film thickness can be controlled by changing the nanorod concentration of the ethanol dispersion. The concentration was adjusted to 18 g/dm^3 to obtained relatively thick films (~5 μm) through evaporation of ethanol within 20 h. The dispersibility of the nanorods in ethanol was improved by the modifying agent. Monolayers of the calcite nanorods fabricated by the evaporation-driven self-assembly were obtained by addition of poly(acrylic acid) (PAA, MW: 5000 $gmol^{-1}$, 0.14 g/dm^3) into the ethanol dispersion and decreasing the concentration of calcite nanorods (0.19 g/dm^3). The organic components of the PAA–modified nanorods were removed through oxidation in air around 300°C.

We analyzed nanograins obtained by drying the filtered dispersion with thermogravimetry (TG, SII TG/DTA7200, Japan, performed with a flow of air), X-ray diffraction (XRD, Bruker D8 Advance, Germany, operated at 40 kV and 25 mA), scanning electron microscopy (SEM, Hitachi S-4700, Japan and JEOL JSM-7100F, Japan, operated at 5.0 kV), and transmission electron microscopy (TEM, FEI Tecnai F20, USA, operated at 200 kV) with selective area electron diffraction (SAED). For TEM observation, the nanorods was scraped off a substrate and dropped on a copper grid covered with a collodion film. We observed the morphological changing of the nanograins on the substrate.

Additional data

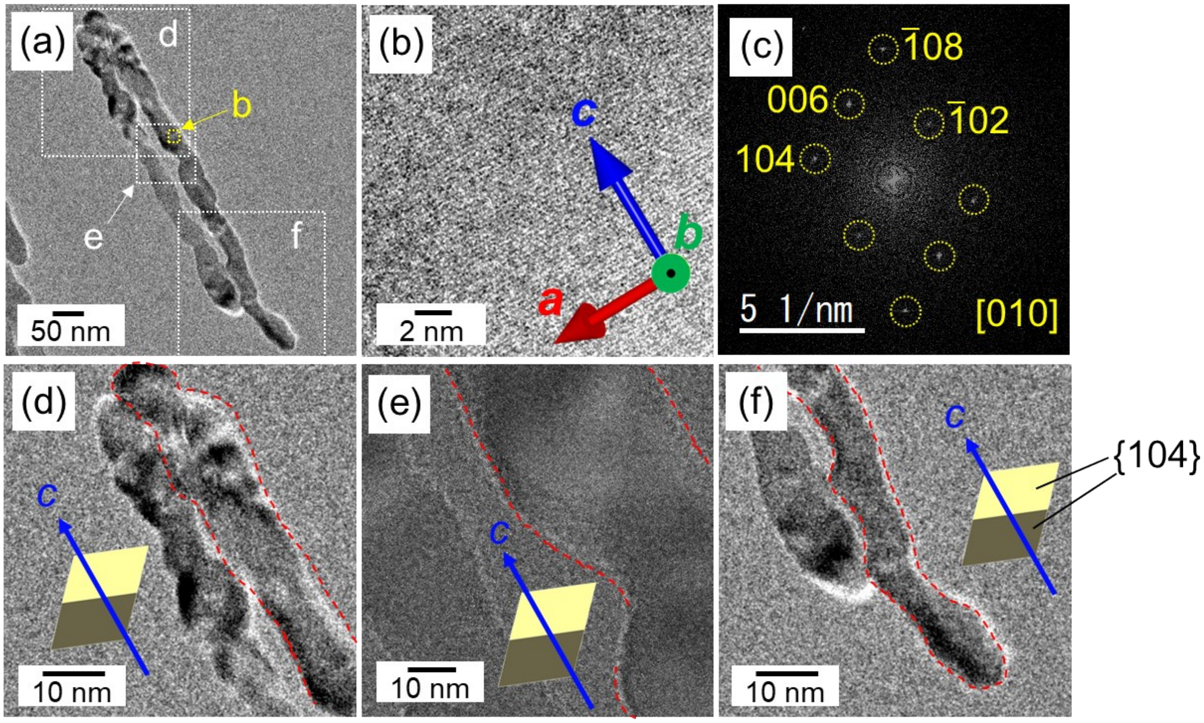

Fig. S1 TEM (a,d-f) and HRTEM (b) images and FFT pattern (c) of calcite nanorods. Red dotted lines show the metastable surface other than the {104} plane.

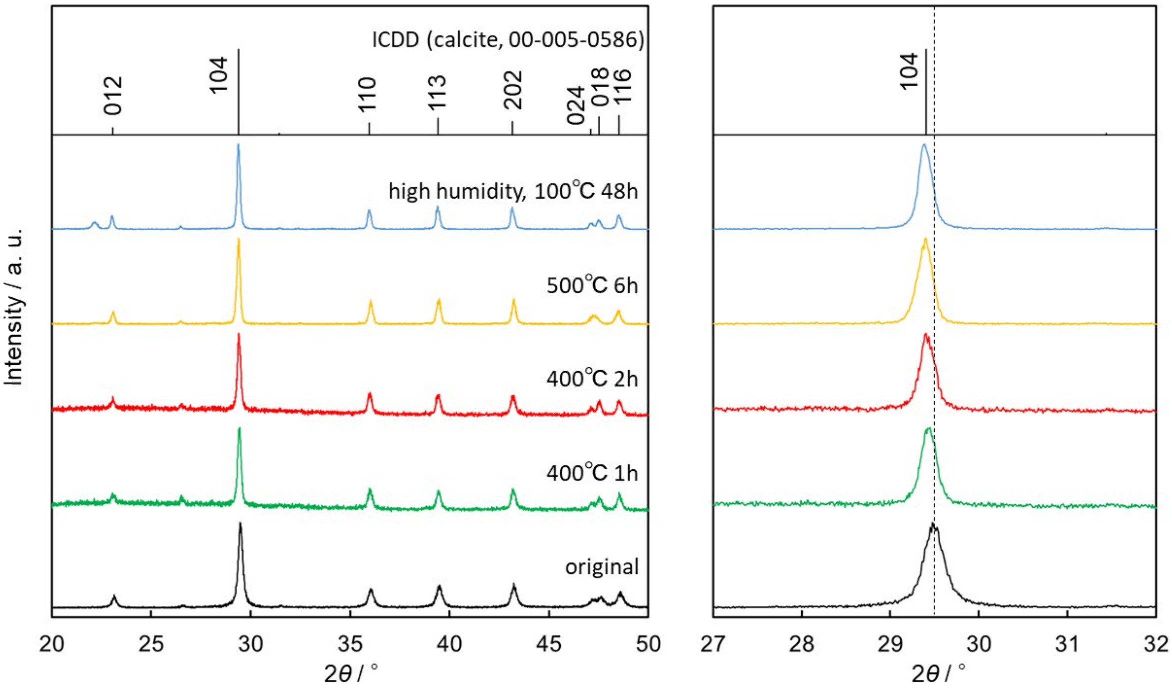

Fig. S2 XRD patterns of calcite nanorods before (original) and after treatments. The right figure is an enlarged pattern in the range of 27-32° of the left figure. The dotted line indicates the peak angle of the 104 signal for the original nanorods.

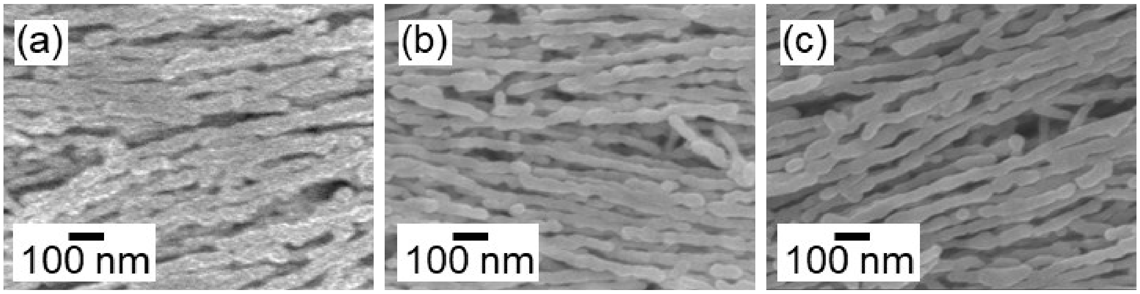

Fig. S3 SEM images of calcite nanorods deposited on a silicon substrate before treatment (a) and heated at 350°C for 3 (b) and 24 h (c).

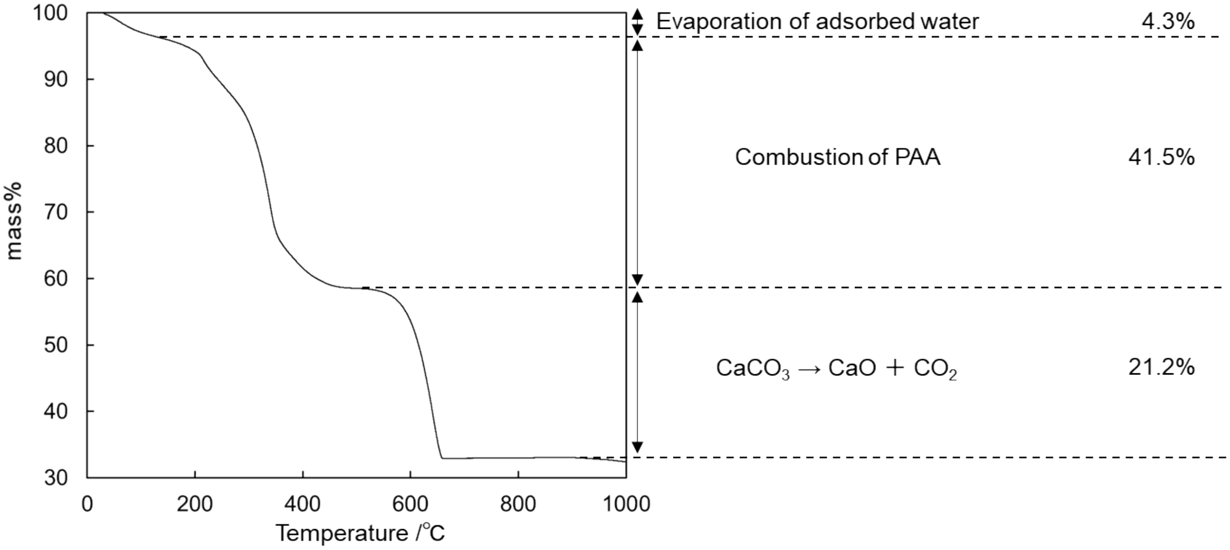

Fig. S4 A typical TG curve of calcite nanorods covered with PAA in air.