

Electronic Supplementary Information (ESI)

A Hierarchical Self-Similar Structure of Oriented Calcite with Association of an Agar Gel Matrix: Inheritance of Crystal Habit from Nanoscale

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Detailed Experimental Method

Procedure: Stock solutions containing 0.3 mol dm^{-3} (M) calcium chloride anhydrous (CaCl_2 , Junsei Chemical, 95.0 %) were prepared using purified water at room temperature. A certain amount of agar powder (Junsei Chemical) was added into 20 cm^3 of the stock solution and then boiled to prepare a homogeneous solution around $80\text{--}100^\circ\text{C}$. After these materials completely dissolved, agar gels containing calcium ions were obtained with cooling of the solutions at 4°C in several hours. The agar concentration (C_{ag}) varied in a range between 0.1 and 8.0 wt.-%. The gels were placed in a desiccator filled with CO_2 formed by the decomposition of fresh $(\text{NH}_4)_2\text{CO}_3$ at 25°C . After 3 days, the agar matrix put in hot purified water around $80\text{--}100^\circ\text{C}$ to remove agar molecules and then washed with purified water. Finally, the resultant calcite precipitates were dried at room temperature.

Characterization: The crystal morphologies were observed by a field-emission scanning electron microscope (FESEM, FEI Sirion operated at 2.0 kV) and a field-emission transmission electron microscope (FETEM, FEI Tecnai F20 operated at 200 kV) with selected area electron diffraction (SAED). For FETEM observation, the powdered sample was dispersed in purified water and then the dispersion liquid was dropped on copper grid supported with collodion membrane. The crystal structure was determined by using X-ray diffraction (XRD, Rigaku Rad-C with $2\theta/\theta$ scanning). The remaining agar molecules were

estimated from the thermogravimetry-differential thermal analysis (TG-DTA, Seiko Instruments, TG-DTA 6200).

Supplementary Figure

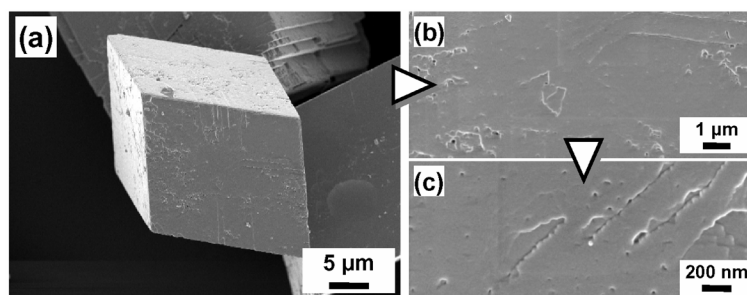


Figure S1. Typical FESEM images of the resultant calcite at C_{ag} 0.2 wt.-%. The smooth surfaces were observed on these images and the submicrometric units and the nanocrystals were not formed in this condition. In contrast, the hierarchical self-similar structure was obtained with an increase in the initial agar concentration (Figure 1 in the main text).