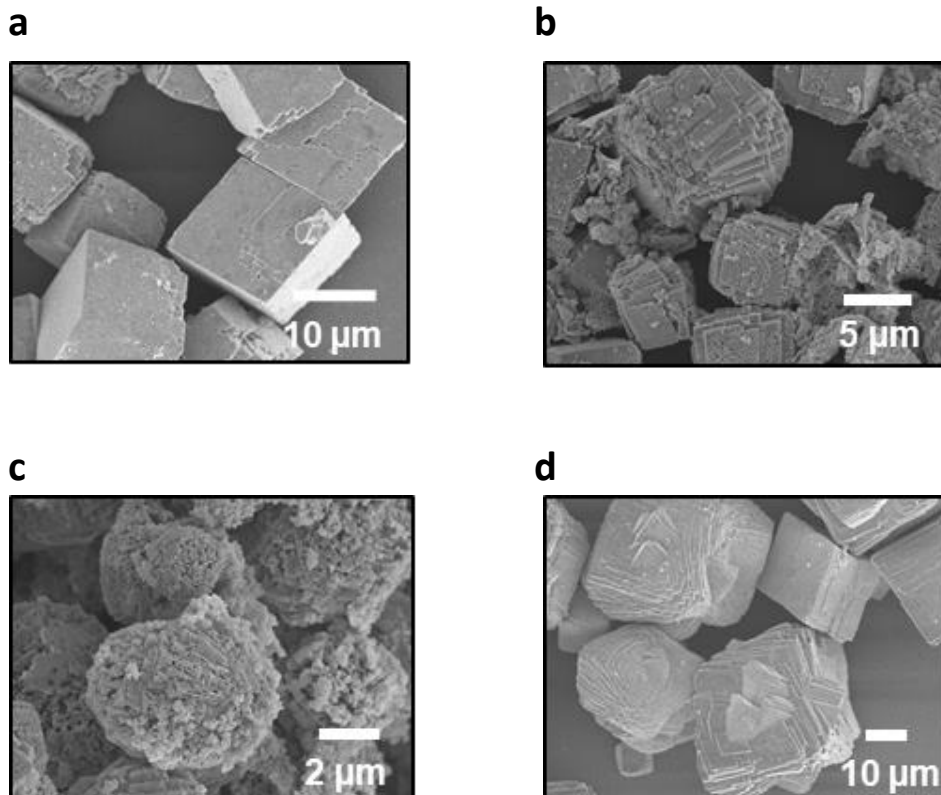
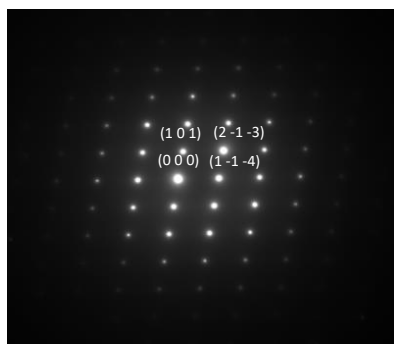
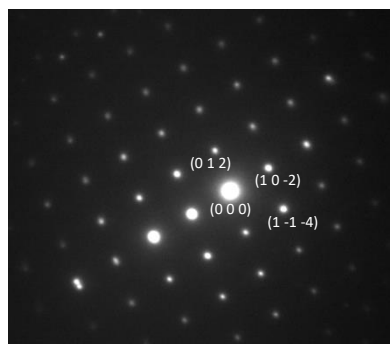
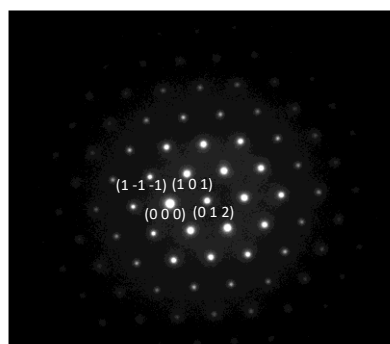




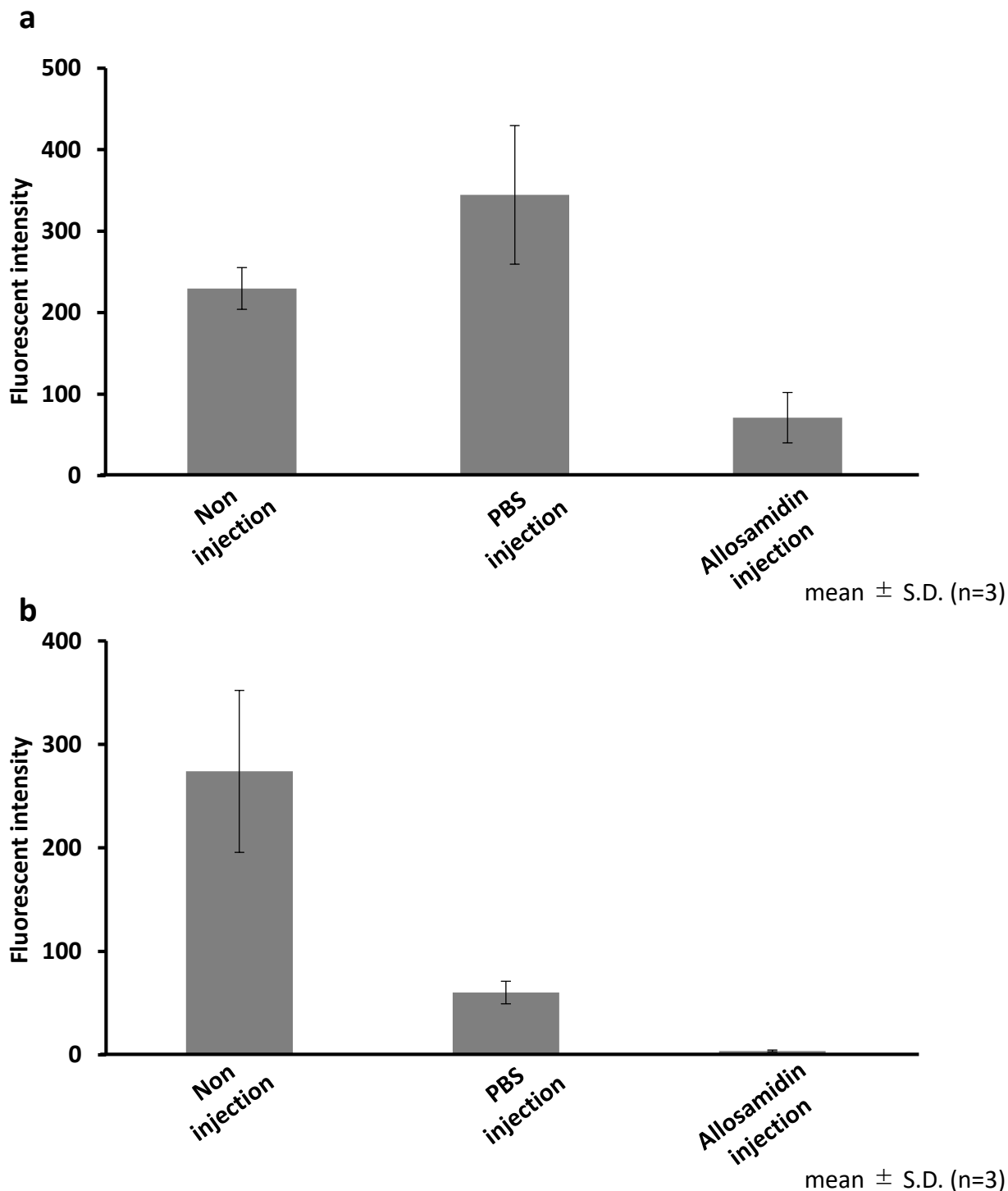
Supplementary Figure 1. SEM images of the synthesized calcite crystals.

a-c, the calcite crystal synthesized in chitin gel treated with chitinolytic enzymes at different concentration. a, 0 mg/mL; b, 0.12 mg/mL; and c, 1.2 mg/mL chitinolytic enzymes. d, calcite crystal synthesized in chitin nanofiber solution.

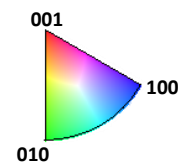
a**b****c****d**

Supplementary Figure 2. SAED pattern of a cross-section of synthesized calcite crystals.

All SAED patterns were obtained from the whole area of left images of Fig 1a-d. a-c, the calcite crystal synthesized in chitin gel treated with chitinolytic enzymes at different concentration. a, 0 mg/mL; b, 0.12 mg/mL; and c, 1.2 mg/mL chitinolytic enzymes. d, calcite crystal synthesized in chitin nanofiber solution.



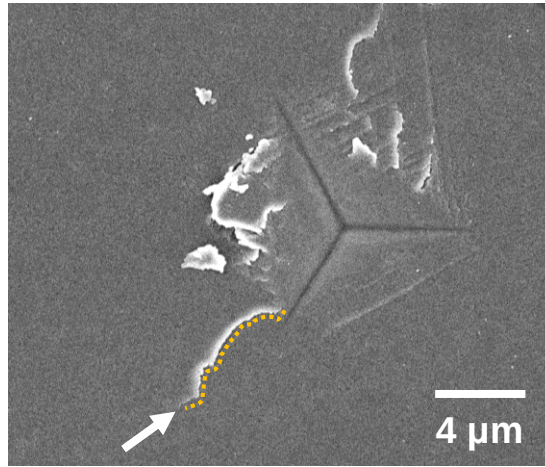
Supplementary Figure 3. Activity of chitinolytic enzymes from the mantle tissue. Activities of chitinolytic enzymes were measured; a, 4 days and b, 32 days after the first injection of allosamidin. A concentration of total proteins of each solution extracted from the mantle tissue was aligned at 125 $\mu\text{g}/\text{mL}$ using an absorption spectrophotometer. Fluorescence intensity of substances liberated from the substrate by chitinolytic enzymes was measured as the chitinolytic activity.

a**b**

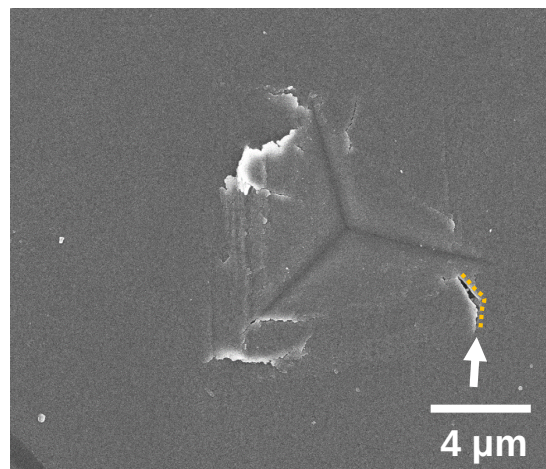
Supplementary Figure 4. Crystallographic orientation maps on the surface of prismatic layer.

The surface of prismatic layer was observed by SEM for EBSD measurements. a, prisms of non-injection; b, prisms of allosamidin injection. Colors denote the crystallographic direction according to the right insert. Visualized information on the direction of prisms was described as a diagram of hexagonal system within each prism.

a



b



Supplementary Figure 5. Scanning electron microscopy images of the impression on the calcite prism after nanoindentation.

The surface of prismatic layer was observed by SEM after measurements of nanoindentation.

a, non-injection. b, allosamidin injection. Arrows denote a crack caused by nanoindentation. The length of crack penetration on (b) became shorter compared to (a) as indicated by white arrows and yellow dotted lines.