

## Supporting Information

### Morphological study of fibrous aragonite in the skeletal framework of a stony coral

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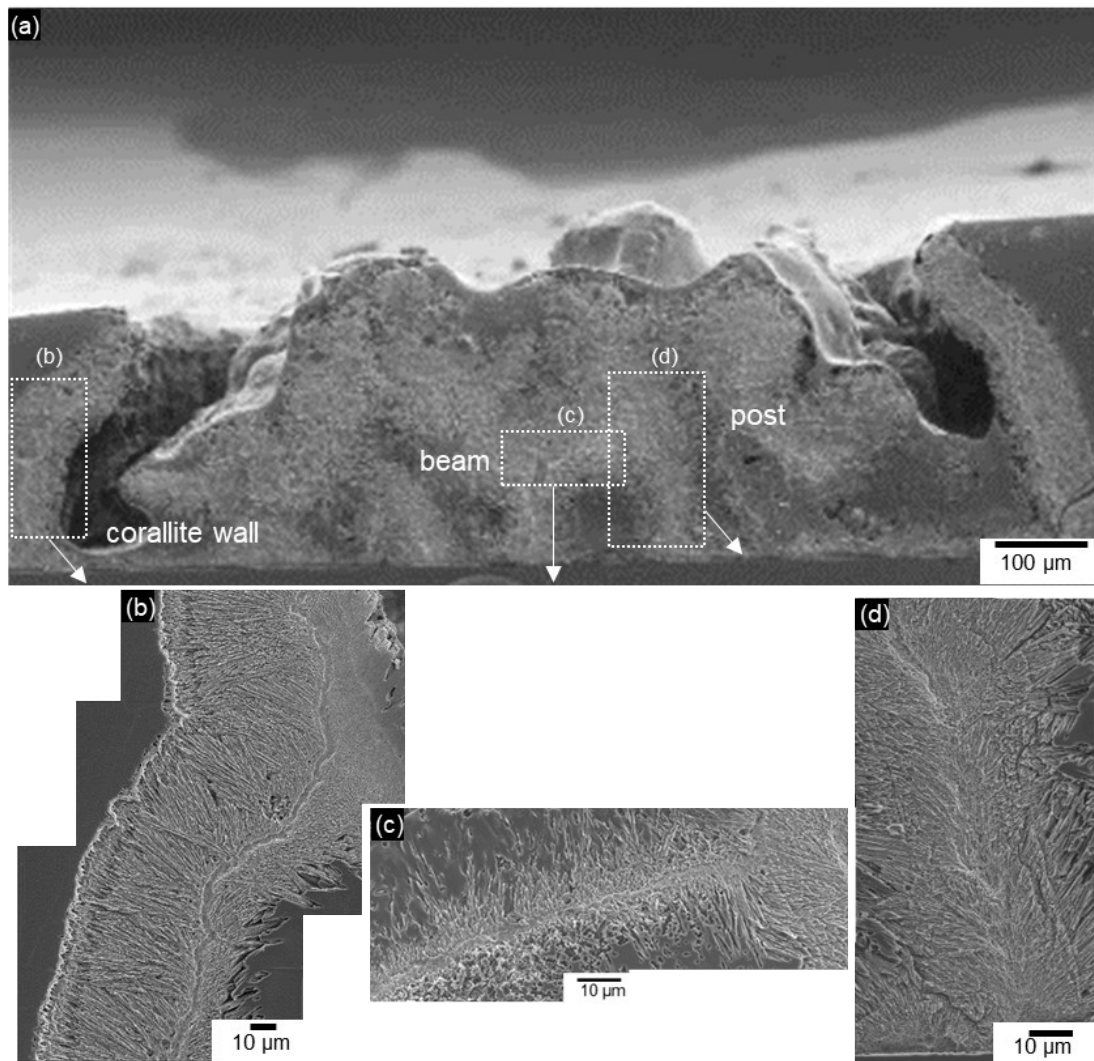
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Enlarged Cross-sectional SEM images of a juvenile coral skeleton (Fig. S1)

Details of preparation procedures for curved aragonite nanorods (Fig. S2)

Details of preparation procedures for parallel arrays of fluorapatite nanorods (Fig. S3)

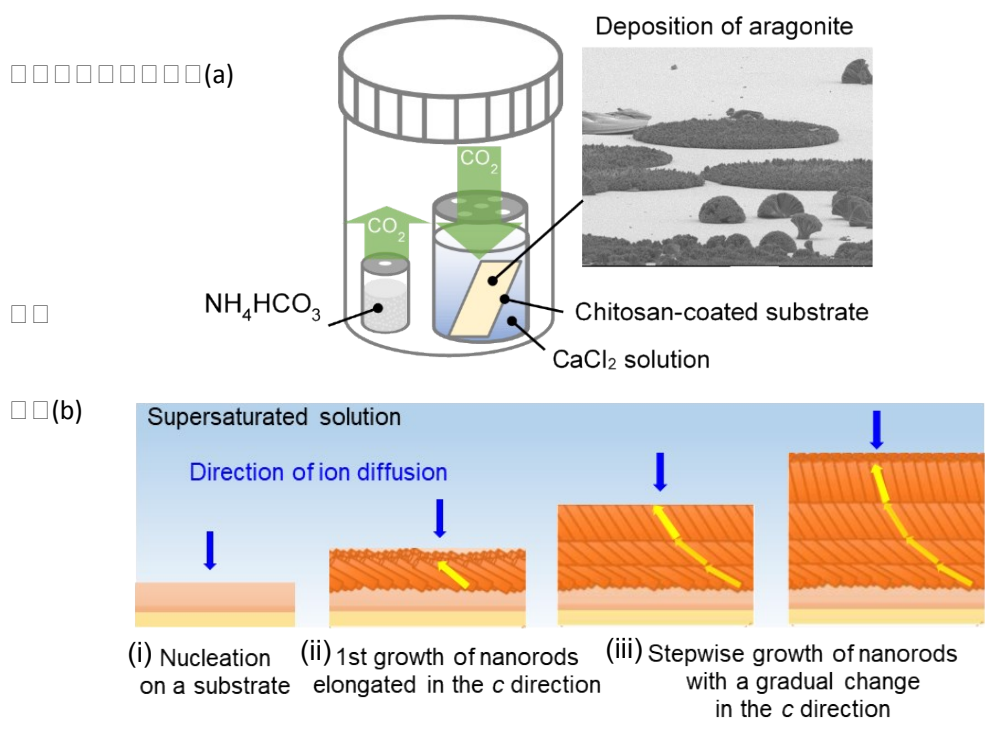
Details of preparation procedures for radial structures of aragonite nanorods (Fig. S4).



**Fig. S1.** Cross-sectional SEM images of a juvenile coral skeleton. (a) A whole body, (b) the corallite wall, (c) a beam of the septum, and (d) a post of the septum.

**Details of preparation procedures for curved aragonite nanorods.<sup>1</sup>**

As shown in Fig. S2a, crystal growth of aragonite nanorods was performed on a chitosan-coated glass substrate in a calcium chloride ( $\text{CaCl}_2$ ) solution supersaturated by the introduction of carbon dioxide ( $\text{CO}_2$ ) generated by the decomposition of ammonium hydrogen carbonate ( $\text{NH}_4\text{HCO}_3$ ). The vessel was then covered with aluminum foil having several pinholes and placed in a closed 600  $\text{cm}^3$  polystyrene container with 3.0 g of  $\text{NH}_4\text{HCO}_3$ . An anhydrous chitosan layer was prepared on a glass slide by spin-coating of an acetic acid solution of chitosan (Wako Pure Chemical), neutralizing with diluted ammonia water, and baking at 260  $^\circ\text{C}$  on a hot plate for 1 min in air. We produced basal planar films of aragonite on the anhydrous chitosan layer in a  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  solution containing  $2.4 \times 10^{-3}$  wt % poly(acrylic acid) (PAA, Mw: 250000, Sigma-Aldrich) at 35  $^\circ\text{C}$  and  $[\text{Ca}^{2+}] = 10 \text{ mmol/dm}^3$  for 24 h in the  $\text{CO}_2$  diffusion system (Fig. S2b-i). We then developed the basal planar films into microarrays by the subsequent overgrowth of crystalline rods. Aragonite crystals grew on the basal film at 25  $^\circ\text{C}$  and  $[\text{Ca}^{2+}] = 20 \text{ mmol/dm}^3$  for 24 h (Fig. S2b-ii). We performed further growth of aragonite several times by immersion in a fresh solution. Stepwise curving growth of aragonite nanorods were observed on the substrate (Fig. S2b-iii). The samples were washed after the reaction with purified water and then dried at room temperature.

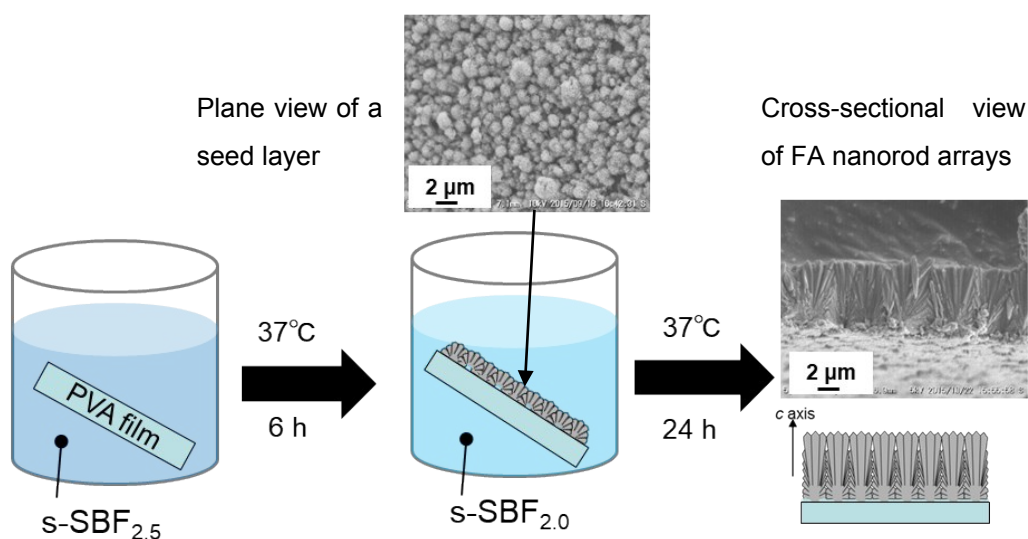


**Fig. S2.** Schematic illustration of the reaction system for crystal growth of aragonite on a chitosan-coated substrate (a) and stepwise growth of aragonite nanorods on a substrate.

### Details of preparation procedures for parallel arrays of fluorapatite nanorods.<sup>2</sup>

Simulated body fluid (SBF) that is a buffered mineralization solution containing various ions of human blood plasma is commonly used for preparation of hydroxyapatite. Fluorapatite (FA) nanorods were produced in an SBF-based solution simplified by the removal of minor ions, such as  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ . The basic precursor solution (s-SBF) was prepared by mixing HCl (Junsei Chemical),  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4$  (Junsei Chemical), and NaCl (Kanto Chemical) with purified water. The concentrations of  $\text{Ca}^{2+}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$  were 2.5, 1.0, 142.0, and 141.0  $\text{mmol dm}^{-3}$ , respectively. The pH was adjusted to 7.2 by adding tris(hydroxymethyl)aminomethane (Junsei Chemical) to control the growth conditions of apatite crystals. The ion concentrations in the supersaturated solutions were increased to promote the nucleation and regulate the growth rate (s-SBF<sub>x</sub>, X = 2.0 or 2.5). The ion concentrations in s-SBF<sub>x</sub> were X times higher than those in s-SBF. The concentration of the fluoride ion was set to 1.50  $\text{mmol dm}^{-3}$ .

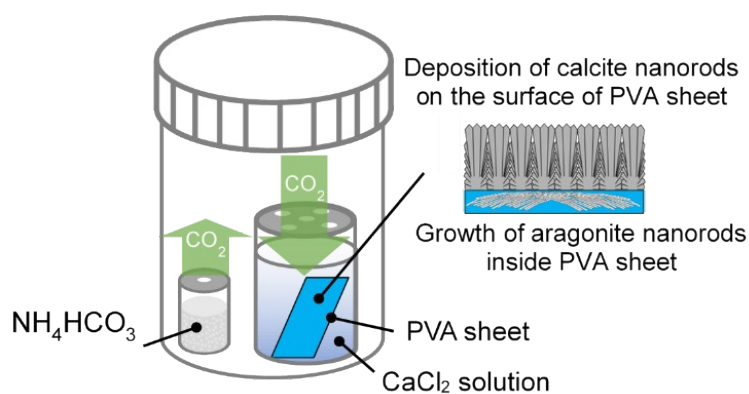
A polyvinyl alcohol (PVA) film (Aisero Solublon® MA, saponification rate >99.5%, Mw: 1700, 25  $\mu\text{m}$  thick) supported on a polypropylene plate using masking tape was used as a substrate for the nucleation of apatite crystals. As shown in Fig. S3, we used s-SBF<sub>2.5</sub> to promote the heterogeneous nucleation as a seed layer on the PVA surface. The solution was kept at 37 °C for 6 h. The resulting products were washed with pure water at room temperature and air-dried at 60 °C for 24 h. Crystal growth for oriented FA nanorod arrays was promoted by changing the growth medium to s-SBF<sub>2.0</sub> after washing with purified water to enhance the crystal growth on the seed layer. The solution was kept at 37 °C for 24 h. Repetition of the exchange of the growth medium by a freshly prepared s-SBF<sub>2.0</sub> was performed after 24 h to continue the crystal growth. The resulting products were washed with pure water and air-dried at 60 °C for 24 h.



**Fig. S3.** Schematic illustration of the reaction system and growth behavior of FA nanorods on a PVA film.

### Details of preparation procedures for radial structures of aragonite nanorods.<sup>3</sup>

As shown in Fig. S4, radial growth of aragonite nanorods inside a PVA sheet was performed in a  $\text{CaCl}_2$  solution ( $10 \text{ mmol/dm}^3$ ) containing PAA (Mw: 1800, Sigma-Aldrich) by the introduction of  $\text{CO}_2$  generated by the decomposition of  $\text{NH}_4\text{HCO}_3$  at  $25^\circ\text{C}$ . The solution of  $10 \text{ mmol dm}^{-3} \text{ CaCl}_2 \cdot 2\text{H}_2\text{O}$  containing a  $14 \text{ mmol dm}^{-3}$  carboxy group of PAA. The pH value was adjusted to 9.0 with the addition of ammonia water. The vessel was then covered with aluminum foil having several pinholes and placed in a closed  $600 \text{ cm}^3$  polystyrene container with  $3.0 \text{ g}$  of  $\text{NH}_4\text{HCO}_3$ . A PVA sheet (Aisero Solublon<sup>®</sup> MA) supported on a polypropylene plate using masking tape was used as a substrate. The solution was kept at  $25^\circ\text{C}$  for 96 h. The formation of aragonite nanorods were observed in the PVA sheet, although calcite grains were produced on the polymer surface.



**Fig. S4.** Schematic illustration of the reaction system for crystal growth of aragonite inside a PVA sheet.

### References

1. M. Suzuki, Y. Oaki and H. Imai, *Cryst. Growth Des.* 2016, **16**, 3741–3747.
2. K. Nakamura, Y. Oaki and H. Imai, *CrystEngComm* 2017, **19**, 669–674.
3. Y. Nagai, Y. Oaki and Y. Imai, *CrystEngComm* 2018, **20**, 1656–1661.