

## Supporting information

### **Coral-mimetic production of aragonite films from CO<sub>2</sub> captured by biogenic polyamine**

Kohei Takashina,<sup>1</sup> Hiroto Watanabe,<sup>1</sup> Yuya Oaki,<sup>1</sup> Yoshikazu Ohno,<sup>2</sup> Ko Yasumoto<sup>2</sup> and Hiroaki Imai<sup>1\*</sup>

*1. Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan.*

*2. School of Marine Biosciences, Kitazato University, 1-15-1, Kitazato, Minami-ku, Sagamihara 252-0373, Japan.*

*\*Email: hiroaki@applc.keio.ac.jp*

p. S2. (Fig. S1) Spatial variation of pH at the skeletal formation in a polyp of a stony coral

(Fig. S2) SEM images and schematic illustration of the skeleton of a stony coral

p. S3. (Fig. S3) Schematic illustrations for experimental procedures

p. S4. (Fig. S4) A typical SEM image and XRD pattern of precipitates prepared in the solution

(Fig. S5) The relationship between the *c* axis and the (012) plane in an aragonite rod

p. S5. (Fig. S6) Cross-sectional SEM images of aragonite films grown without putrescine

(Fig. S7) Molecular formula of alginate and SEM images of aragonite rods with and without alginate

p. S6. (Fig. S8) Cross-sectional SEM images of aragonite films with addition of alginate

(Eqs. S1–S3) Chemical equations for the reactions of putrescine with CO<sub>2</sub> in water

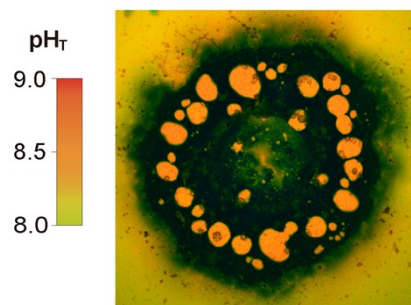


Fig. S1 Spatial variation of pH at the skeletal formation in a polyp of a stony coral.<sup>1</sup>

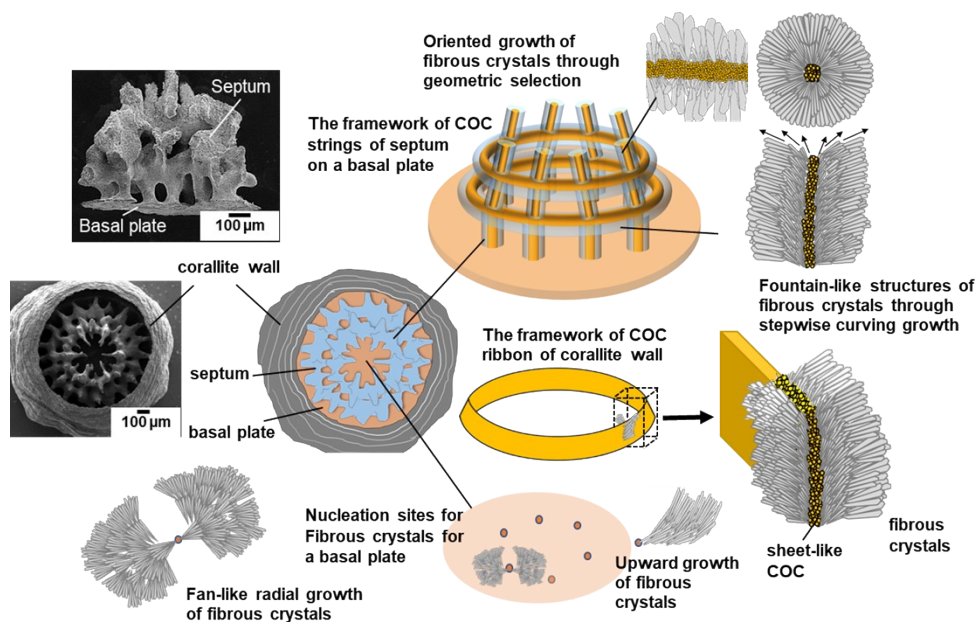


Fig. S2 SEM images and schematic illustration of the skeleton of a stony coral.<sup>2</sup> Reproduced from ref. 2 with permission from the Royal Society of Chemistry.

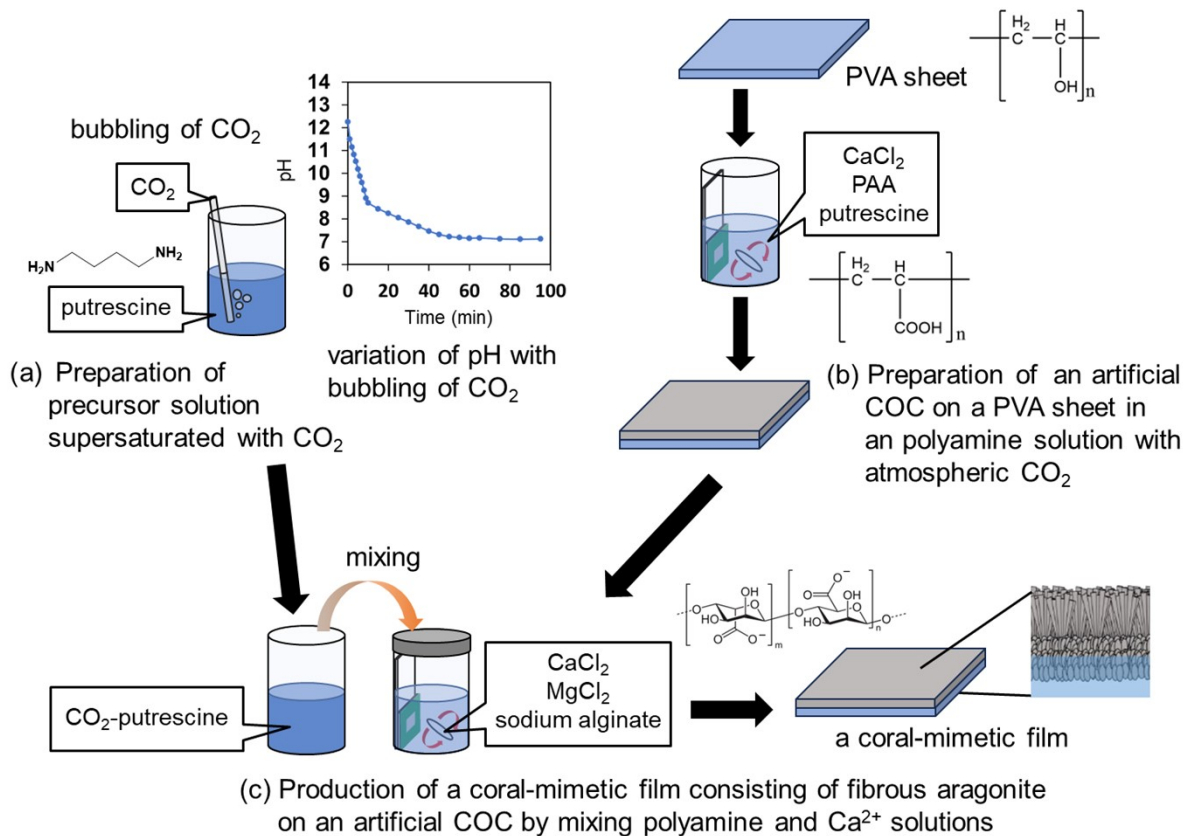


Fig. S3 Schematic illustrations for experimental procedures. (a) Preparation of precursor solution supersaturated with CO<sub>2</sub>. (b) Preparation of an artificial COC on a PVA sheet in a polyamine solution with atmospheric CO<sub>2</sub>. (c) Production of a coral-mimetic film consisting of fibrous aragonite on an artificial COC by mixing polyamine and Ca<sup>2+</sup> solutions.

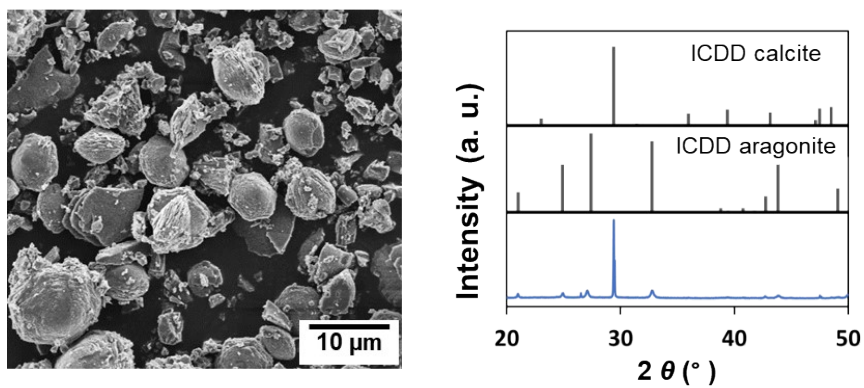


Fig. S4 A typical SEM image and XRD pattern of precipitates prepared in the solution. Calcite powder was formed through homogeneous nucleation without PAA.

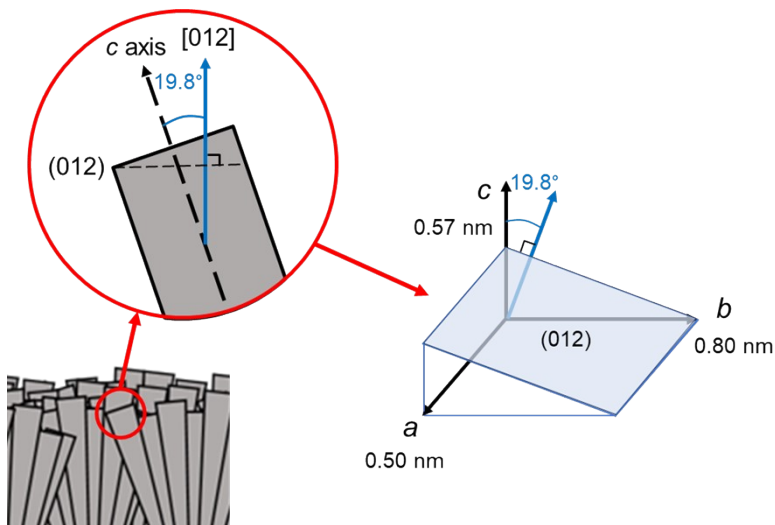


Fig. S5 Schematic illustrations that indicate the relationship between the  $c$  axis and the (012) plane in an aragonite rod.

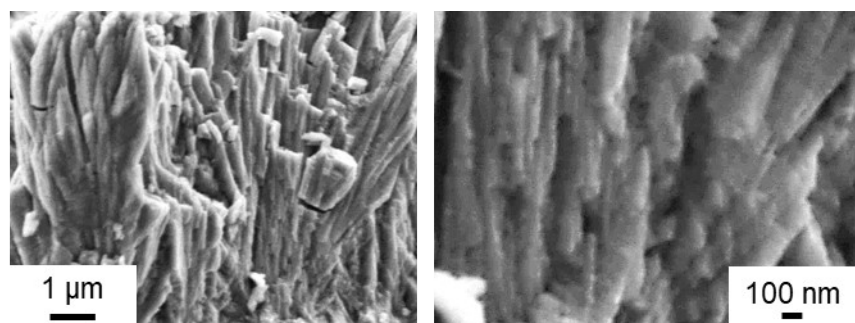


Fig. S6 Cross-sectional SEM images of aragonite films grown in a solution supersaturated by the introduction of  $\text{CO}_2$  that was generated by the decomposition of  $(\text{NH}_4)_2\text{CO}_3$ .<sup>3</sup> We prepared the films on the seed layer consisting of aragonite nanoparticles in a mother solution at  $[\text{Ca}^{2+}] = 10 \text{ mmol dm}^{-3}$  without putrescine.

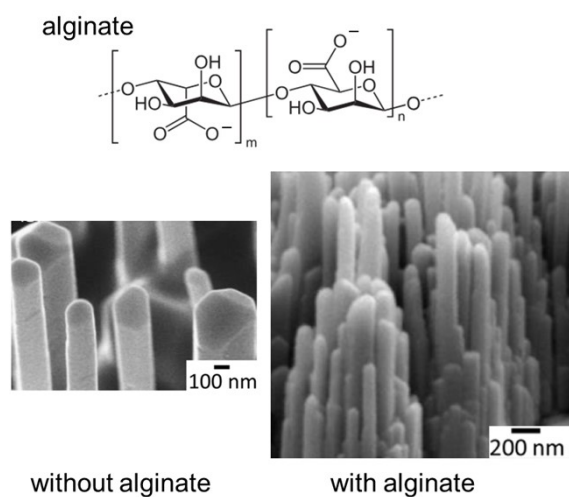


Fig. S7 Molecular formula of alginate and SEM images of aragonite rods with and without alginate.<sup>4</sup> Reprinted with permission from ref. 3. Copyright 2016 American Chemical Society.

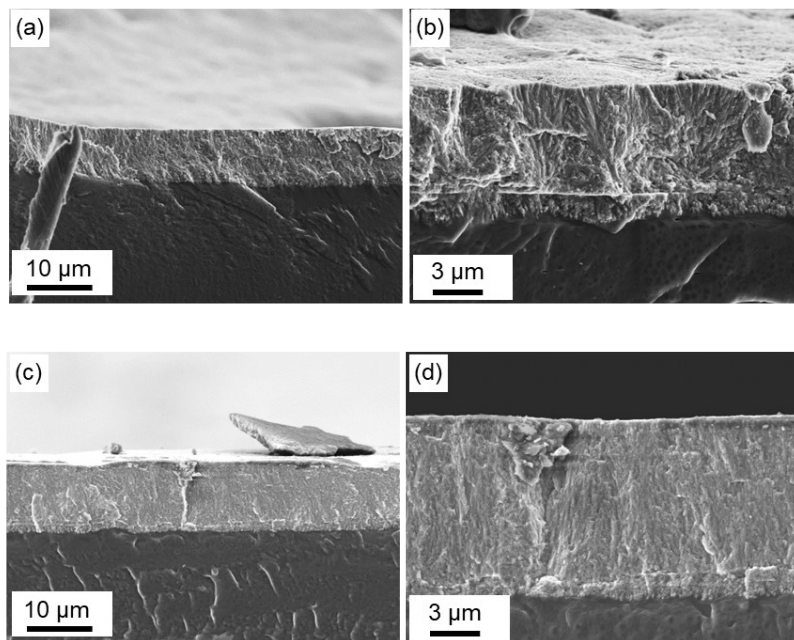
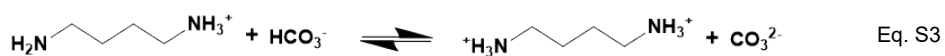
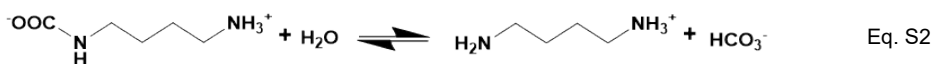
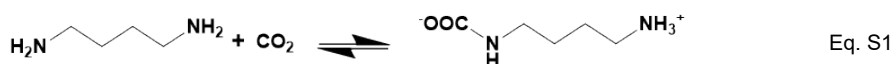


Fig. S8 Cross-sectional SEM images of aragonite films with addition of alginate. Homogeneous films consisting of aragonite nanorods were obtained in the solutions at  $[\text{COO}^-_{\text{alginate}}] = 0.15$  (a, b) and  $0.5 \text{ mol dm}^{-3}$  (c, d).



Equations S1–S3 indicate chemical reactions of putrescine with  $\text{CO}_2$  in water.<sup>5</sup>

## References

1. Y. Ohno, A. Iguchi, C. Shinzato, M. Inoue, A. Suzuki, K. Sakai and T. Nakamura, *Sci. Rep.*, 2017, **7**, 40324.
2. M. Sugiura, K. Yasumoto, M. Iijima, Y. Oaki, H. Imai, *CrystEngComm*, 2021, **23**, 3693.
3. Y. Nagai, Y. Oaki and H. Imai, *CrystEngComm*, 2018, **20**, 1656.
4. M. Suzuki, Y. Oaki, H. Imai, *Cryst. Growth Des.*, 2016, **16**, 3741.
5. K. Yasumoto, M. Yasumoto-Hirose, J. Yasumoto, R. Murata, S. Sato, M. Baba, K. Mori-Yasumoto, M. Jimbo, Y. Oshima, T. Kusumi, S. Watabe, *Mar. Biotechnol.*, 2014, **16**, 465.