Electronic supplementary information

Crystal growth-induced reconfiguration of the biopolymer framework in shell biomineralization

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Experimental details of X-ray diffraction (XRD) analysis

After freeze-dried, the shell fragments near the shell's edge (marked position in Fig. 1a) were mechanically separated. Then the periostraca were gently removed with a scalpel to expose the spherulitic layer (Fig. 1b) with a characteristic silver color.

The samples of the spherulitic layer for XRD analysis (about 1g in weight) were obtained by scraping the spherulitic layer with a scalpel. The scraped loose materials were collected and finally ground into powder with a mortar and pestle.

The samples of the crossed-lamellar layer were obtained as follows. First, the as-prepared shell fragments were ground with 400-grit SiC paper to remove the spherulitic layer. Then the fragments were crushed and ground into powder with a mortar and pestle.

Finally, all XRD patterns were recorded with a diffractometer (Rigaku D/max-2500) using Cu Kα radiation (λ = 0.15406 nm).

Fig. S1

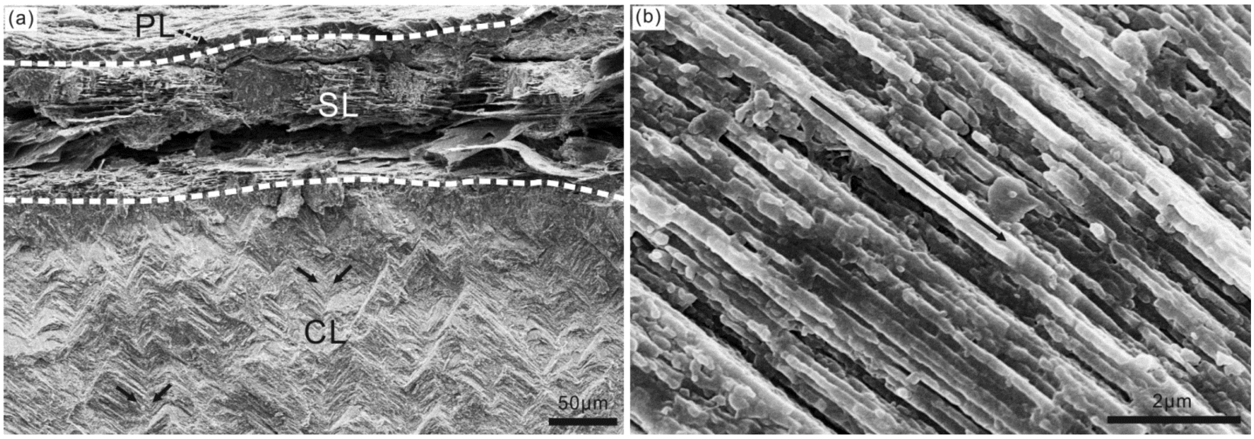


Fig. S1 Cross-sectional views of the shell fragment (about 2cm away from the shell's growing edge). Black arrows indicate the long axes of aragonite fibers. (a) The shell consists of an extremely thin periostracum layer (PL), a thin, porous spherulitic layer (SL), and a thick, dense crossed-lamellar layer (CL). The CL often displays a chevron pattern caused by two groups of aragonite fibers with alternating orientations. (b) Close-up of one group of fibers in the CL with the same orientation.

Fig. S2

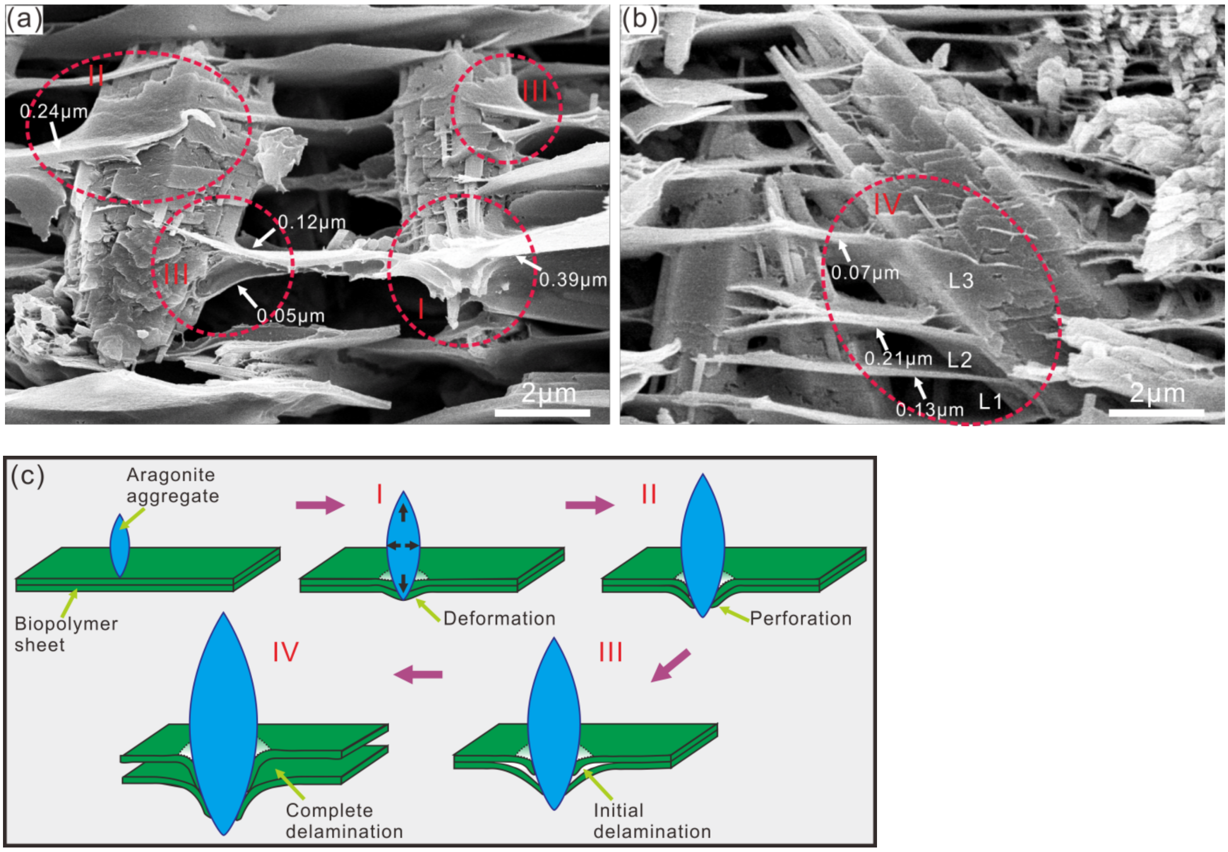


Fig. S2 (a-b) Cross-sectional views of the mineralized area (MA) with spindle-shaped aragonite aggregates. White arrows indicate where the sheet thickness (*t*) is measured and marked, while the circled areas highlight the delamination stages of a thick sheets induced by the spindle's growth. (c) Schematic diagram showing how a thick sheet is delaminated with the spindle's growth (not scaled). The delamination stage marked with the Roman numerals corresponds to that marked in the circled areas of (a) and (b). In addition, short black arrows indicate the spindle's growth directions.

Notes:

The delamination process of a thick sheet can be roughly divided into four sequential stages:

I—The deformation. The initial thick sheet seems sticky and looks like a hydrogel (circled area I in a). When it is being penetrated by a spindle, it clearly thickens and slightly bends.

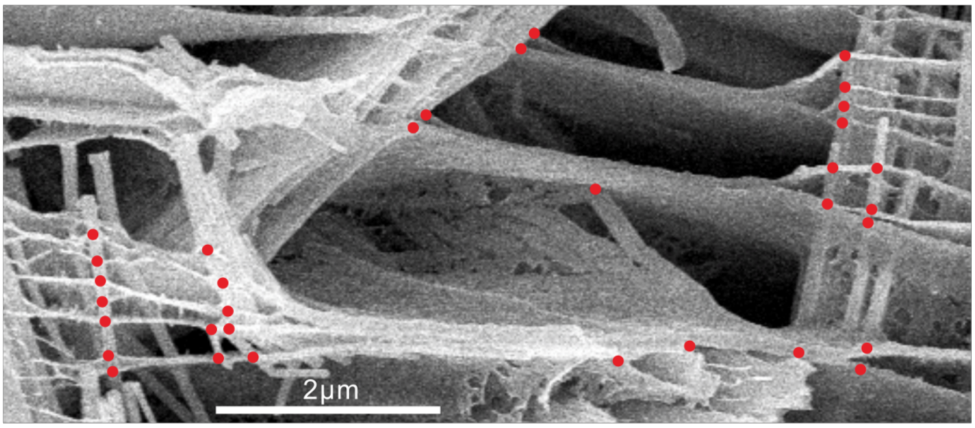
II—The perforation. The thick sheet is totally perforated by the spindle; meanwhile, part of the sheet is firmly attached to the spindle's surface (circled area II in a).

III—The initial delamination. The thick sheet near the spindle's surface begins to delaminate (circled area III in a). The forces causing this delamination should originate from the spindle's growth. That is, the axial and lateral growth of the spindle will result in the axial and lateral compressive forces, which will act on the sheets.

IV—The complete delamination. The thick sheet is delaminated into separate and parallel thin sheets (circled area IV in b). During this stage, the adjacent aragonite aggregates may work cooperatively to cause the sheet's delamination.

Electronic Supplementary Material (ESI) for CrystEngComm

Fig. S3



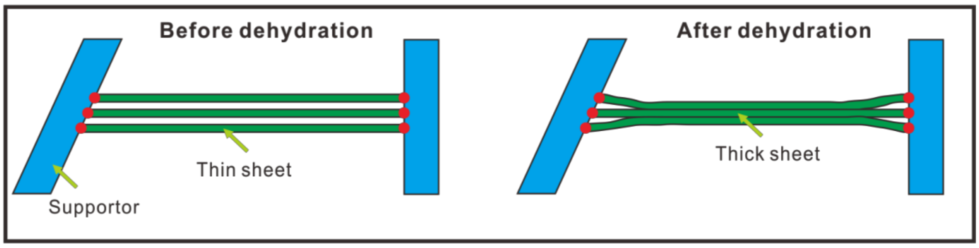


Fig. S3 Top: Cross-sectional view of the spherulitic layer. The viewing area corresponds to that between Fig. 3d and 3e in the communication. Bottom: Schematic diagram showing that if a thick sheet is resulted from the fusion of adjacent thin sheets on dehydration of samples, its two ends should have equal number of nodes. In both images, red dots indicate the nodes at which the sheets are attached to the supporters (other sheets or aragonite crystals).

Notes:

(1) All sheets, no matter how thick they are, are supported by other sheets or aragonite fibers (or aggregates).

(2) During dehydration of samples, the nodes should be immovable; otherwise the whole structure of the spherulitic layer will collapse.

(3) For a relatively thick sheet, its two ends often have different number of nodes (as shown in top image), which indicates the thick sheet is not resulted from the fusion of adjacent thin sheets on dehydration of samples. The reason is as follows: if we assume the thick sheet is resulted from the fusion of adjacent thin sheets, we must first assume these thin sheets are separated from each other before dehydration, as shown in the left side of the bottom image. Therefore, after dehydration, the fused thick sheet should have equal nodes at its two ends, as shown in the right side of the bottom image.