

# Intrafibrillar growth of hydroxyapatite nanocrystals in multiscale collagen

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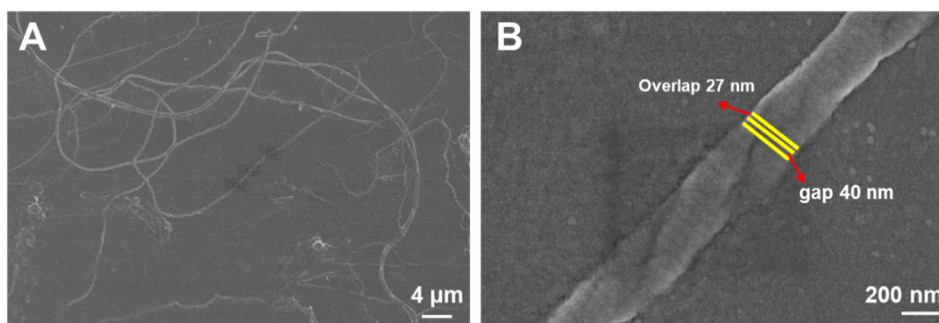
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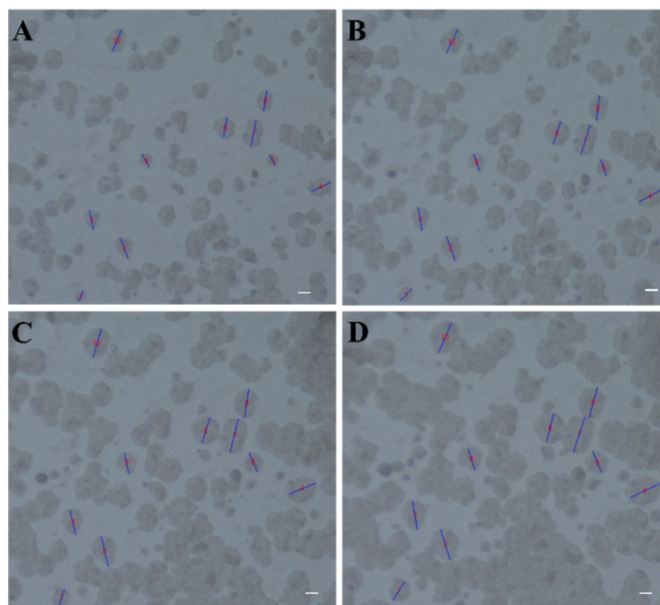
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## Supplementary Information



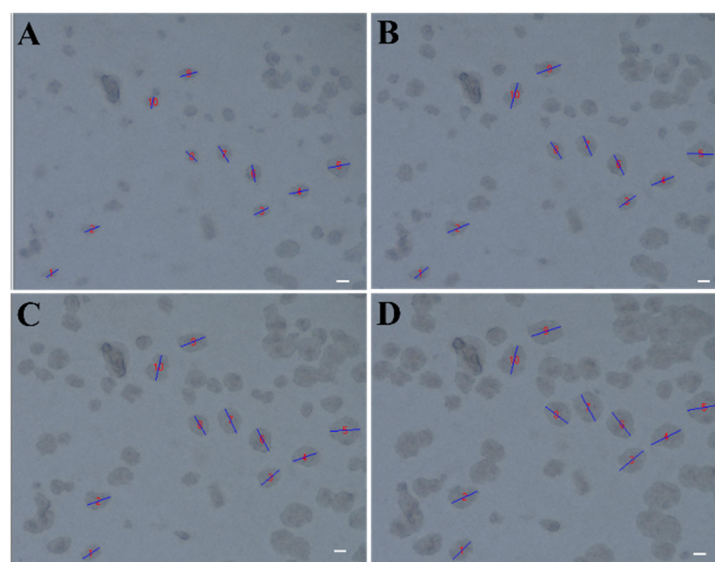
**Figure S1.** The original collagen fibril.



**Figure S2.** Monitoring of areas with HAP of film in the growth solution (50  $\mu\text{g/ml}$  PAA, pH 7.5), images(A-D) were taken at 120 min, 150 min, 180 min, and 210 min, respectively (scale bar 20 $\mu\text{m}$ ).

**Table S1** The size ( $\mu\text{m}$ ) of selected areas of film in the solution (50  $\mu\text{g/ml}$  PAA, pH 7.5), data were collected at 120 min, 150 min, 180 min, and 210 min, respectively

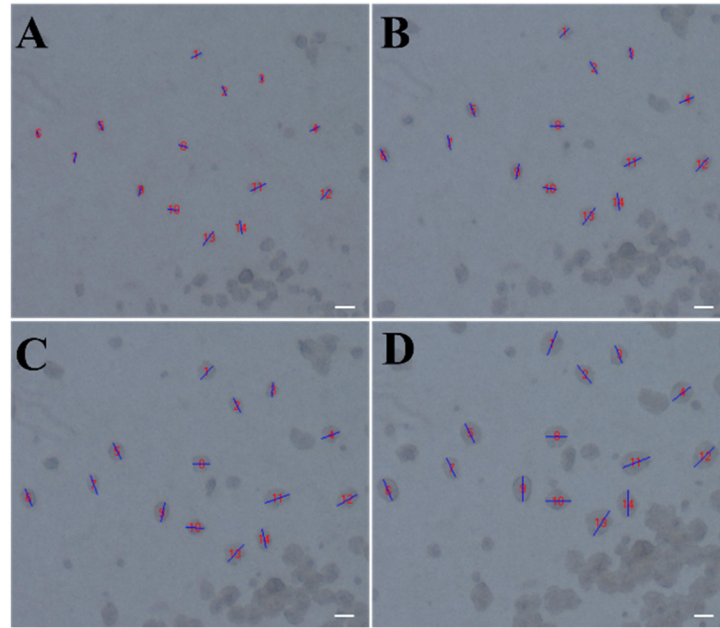
	1	2	3	4	5	6	7	8	9	10
120min	17.36	37.2	33.11	34.04	20.14	33.11	44.27	35.07	25.04	38.95
150min	25.87	44.12	39.43	47.82	30.01	40.02	51.72	41.01	33.59	47.97
180min	32.44	50.84	45.85	56.28	35.01	46.37	56.85	48.04	37.61	51.91
210min	40.61	58.61	54.97	67.9	44.02	55.32	67.64	55.18	44.82	61.65



**Figure S3.** Monitoring of areas with HAP of film in the growth solution (**100 µg/ml PAA, pH 8.0**), images(A-D) were taken at 120 min, 150 min, 180 min, and 210 min, respectively (scale bar 20µm).

**Table S2** The size (µm) of selected areas of film in the solution (**100 µg/ml PAA, pH 8.0**), data were collected at 120 min, 150 min, 180 min, and 210 min, respectively

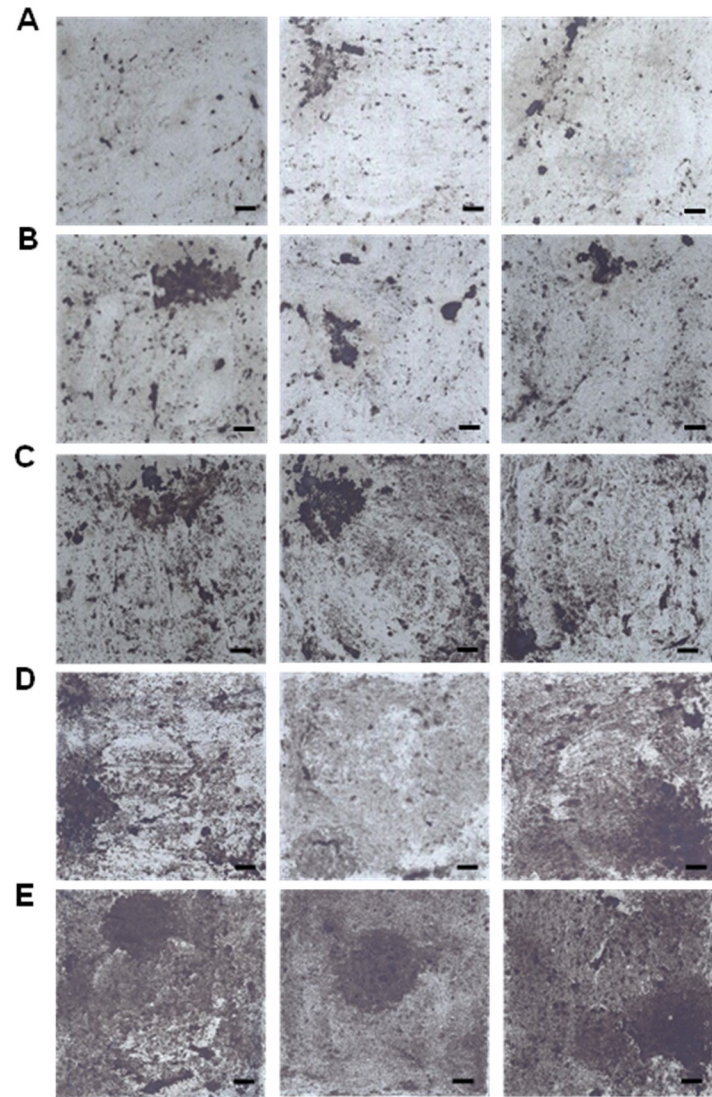
	1	2	3	4	5	6	7	8	9	10
120min	19.89	22.46	21.71	27.12	29.99	23.23	26.32	21.35	23.64	17.18
150min	27.33	29.1	26.48	30.91	34.34	27.89	31.68	26.66	31.91	32.3
180min	34.06	35.44	33.41	37.6	39.62	33.66	35.06	31.35	38.01	35.11
210min	36.49	39.15	39.77	41.00	43.54	39.21	39.17	37.97	42.86	41.63



**Figure S4.** Monitoring of areas with HAP of film in the growth solution (100µg/ml PAA, pH 7.5), images(A-D) were taken at 120 min, 150 min, 180 min, and 210 min, respectively (scale bar 20µm).

**Table S3** The size (µm) of selected areas of film in the solution (100 µg/ml PAA, pH 7.5), data were collected at 120 min, 150 min, 180 min, and 210 min, respectively

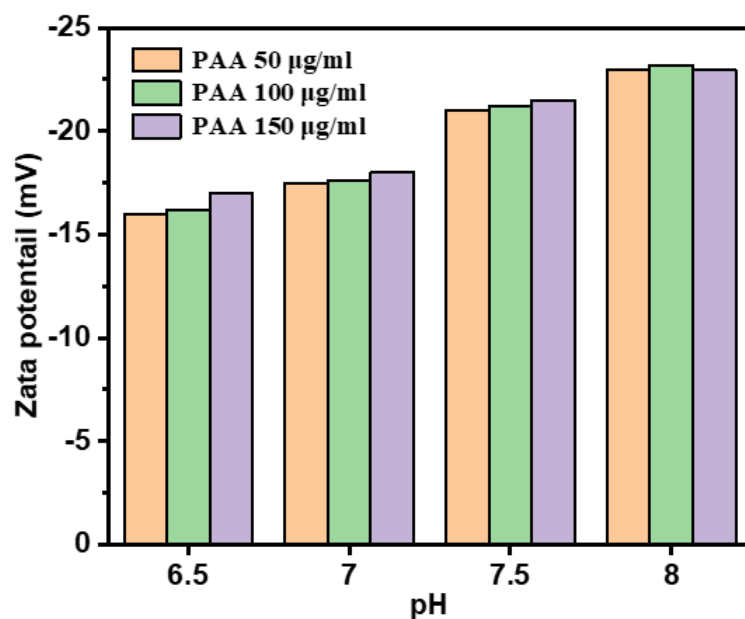
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
120	13.	11.	5.6	12.	11.	6.6	11.	11.	10.	11.	18.	15.	19.	15.
min	83	44	5	38	91	5	88	05	9	9	88	98	74	41
150	15.	16.	13.	18.	16.	16.	16.	17.	18.	16.	23.	21.	24.	20
min	84	47	58	09	58	56	8	35	51	11	03	58	75	
180	20.	21.	17.	21.	20.	22.	21.	17.	22.	21.	29.	25.	23.	22.
min	83	17	79	61	24	33	85	79	68	14	84	16	93	8
210	29.	25.	21.	26.	23.	25.	23.	23.	28.	27.	32.	31.	33.	29.
min	27	97	19	19	82	8	83	38	08	7	13	81	34	51



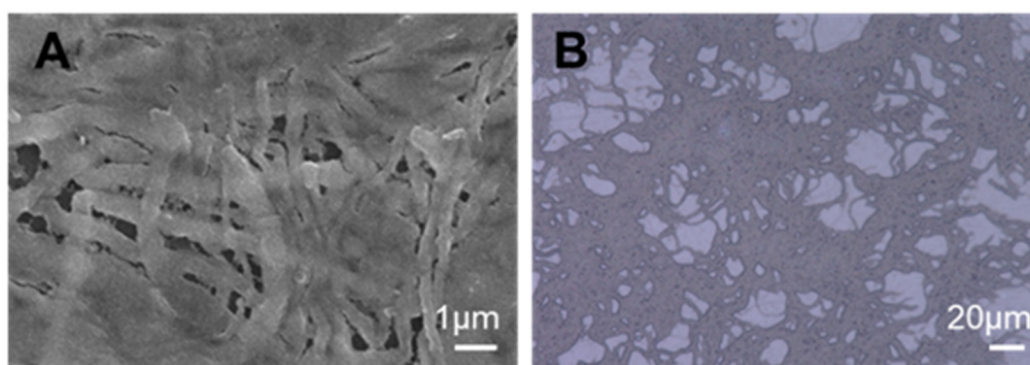
**Figure S5.** The collagen films reacted in the solution of different conditions, three experiments were conducted under each condition of solution. (A) The condition of solution of 150  $\mu\text{g/ml}$  PAA, pH 7.5, (B) the condition of solution of 150  $\mu\text{g/ml}$  PAA, pH 8.0, (C) the condition of solution of 100  $\mu\text{g/ml}$  PAA, pH 7.5, (D) the condition of solution of 100  $\mu\text{g/ml}$  PAA, pH 8, (E) the condition of solution of 50  $\mu\text{g/ml}$  PAA, pH 7.5

**Table S4** the growth area ratio of each specimen in Fig. S5.

	Specimen 1	Specimen 2	Specimen 3
150 $\mu\text{g/ml}$ PAA, pH 7.5	6.1%	8.5%	7.3%
150 $\mu\text{g/ml}$ PAA, pH 8.0	14.9%	14.7%	10.3%
100 $\mu\text{g/ml}$ PAA, pH 7.5	30.9%	38%	28.7%
100 $\mu\text{g/ml}$ PAA, pH 8.0	49.61%	46.4%	59.3%
50 $\mu\text{g/ml}$ PAA, pH 7.5	73.8%	76.2%	82.4%



**Figure S6.** Zeta potential of precursors in different growth solutions.



**Figure S7.** The extrafibrillar growth of HAP of the films in a growth solution of 50 µg/ml PAA, pH 8. (A) The SEM image. (B) The optical image.