Supplementary Material (ESI) for Lab on a Chip
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Microfluidic generation of hollow Ca-alginate microfibers

Supplementary material

Zhi-Jun Meng,[a] Wei Wang,*[a] Rui Xie,[a] Xiao-Jie Ju,[a] Zhuang Liu[a] and Liang-Yin Chu*[a,b,c]

[a] *School of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, China*
E-mail: chuly@scu.edu.cn (L.-Y. Chu), wangwei512@scu.edu.cn (W. Wang); Tel. & Fax: +86 28 8546 0682

[b] *State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, Sichuan, 610065, China*

[c] *Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing, Jiangsu 211816, China*

Part I. Supplementary Experimentals

Microfluidic generation of hollow chitosan, PVA and PLGA microfibers

Chitosan (M_n=100000, degree of deacetylation = 85 %) was obtained from Ji'nan Haidebei Marine Bioengineering Co., Ltd. Poly(lactic-*co*-glycolic acid) (PLGA, 50:50, M_w=40000) was obtained from Chengdu Dikang Pharmaceutical Co., Ltd. Poly(vinyl alcohol)1799 (PVA1799), acetic acid (HAc), glycerol, sodium tripolyphosphate (STPP), Na_2SO_4, $CuSO_4{\cdot}5H_2O$, NaOH, and *N*-methylpyrro lidone (NMP) were obtained from Chengdu Kelong Chemical Reagents.

For generation of hollow chitosan microfibers, four aqueous solutions were used as follows. Core phase: 2 % (w/v) PEG20000 + DI water; sheath phase: 2 % (w/v) chitosan + 2 % (v/v) HAc + 0.1 % (w/v) methylene blue + DI water; buffer phase: 20 % (w/v) glycerol + DI water; outmost phase: 10 % (w/v) STPP + DI water. The $P_3O_{10}^{5-}$ ions in the outmost phase could diffuse across the buffer phase and crosslink the chitosan in the sheath phase to form hollow chitosan microfibers. 2 % (w/v) STPP solution was used as the collection solution for collecting and completely crosslinking the hollow chitosan microfibers.

For generation of hollow PVA microfibers, four aqueous solutions were used as follows. Core phase: 2 % (w/v) PEG20000 + DI water; sheath phase: 5 % (w/v) PVA1799 + 0.5 % (~~v~~w/v) $CuSO_4{\cdot}5H_2O$ + DI water; buffer phase: 20 % (w/v) glycerol + DI water; outmost phase: 8 % (w/v) NaOH + DI water. The OH^- ions could diffuse across the buffer solution and react with the Cu^{2+} in the sheath phase to form $Cu(OH)_2$, leading to solidification of the PVA for formation of the hollow PVA microfibers. 20 % (w/v) Na_2SO_4 solution was used as the collection solution for collecting and completely solidifying the hollow PVA microfiber.

For generation of hollow PLGA microfibers, four solutions were used as follows. Core phase: NMP; sheath phase: 20 % (w/v) PLGA + NMP; buffer phase: NMP; outmost phase: 10 % (w/v) PEG20000 + DI water. Since the NMP in the sheath phase was soluble with water in outmost phase, the PLGA gradually solidified in the sheath phase upon contacting with water to form hollow PLGA microfibers. DI water was used as the collection solution for collecting and completely solidifying the hollow PLGA microfibers.

The morphologies of the hollow chitosan, PVA and PLGA microfibers were characterized by optical microscope (Dmil LED, Leica).

Part II. Supplementary Figures S1-S16

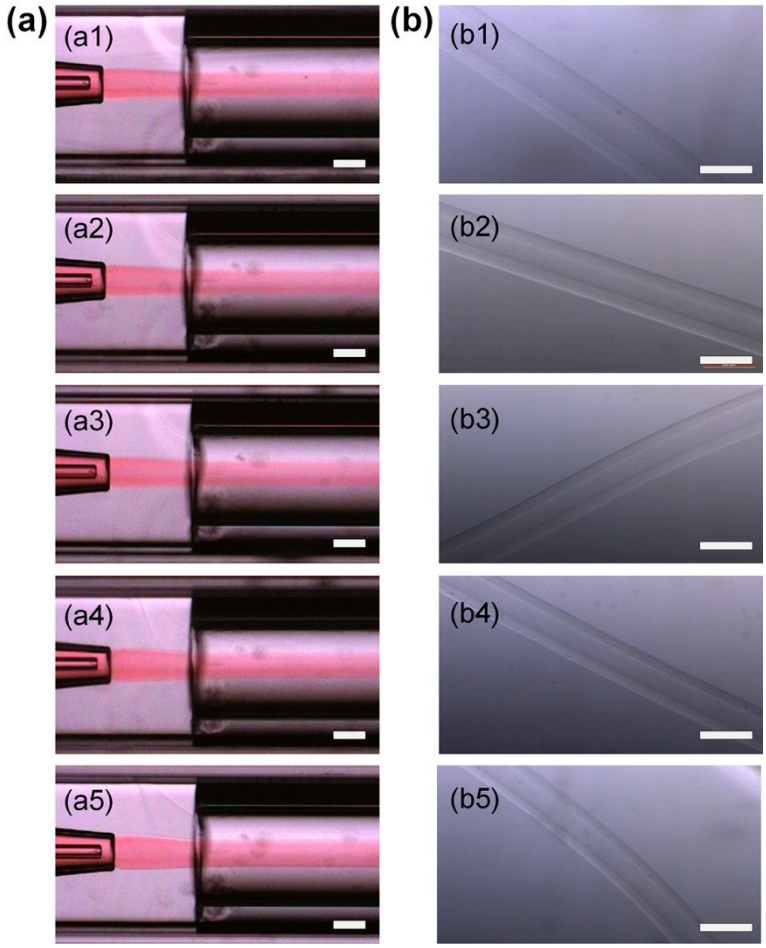


Fig. S1 Effect of PEG20000 concentration in the buffer phase on the morphology of hollow Ca-alginate microfibers. (a) High-speed snapshots showing the microfiber generation process in microfluidic device. (b) Optical micrographs of the obtained hollow Ca-alginate microfibers. The PEG20000 concentrations are 0 % (w/v) (a1,b1), 0.5 % (w/v) (a2,b2), 1 % (w/v) (a3,b3), 2 % (w/v) (a4,b4) and 4 % (w/v) (a5,b5). The Q_{W1}, Q_{W2}, Q_{W3}, and Q_{W4} are fixed at 150 μL h^{-1}, 300 μL h^{-1}, 2500 μL h^{-1}, and 1000 μL h^{-1} respectively. Scale bars are 200 μm.

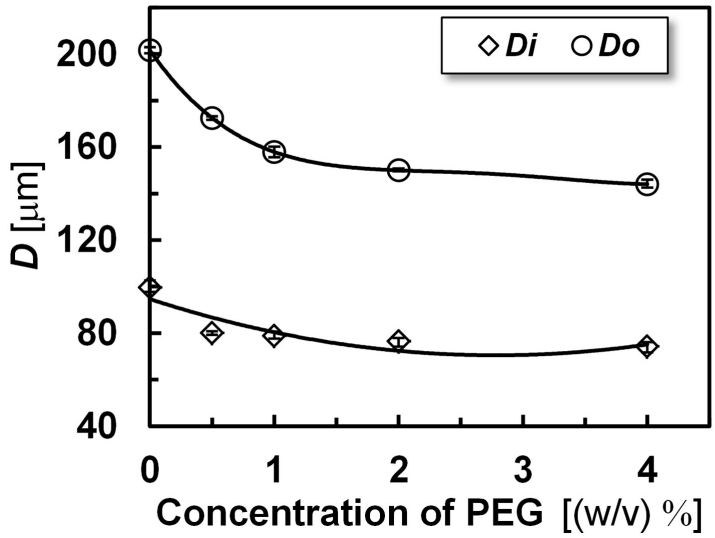


Fig. S2 Effect of the concentration of PEG20000 on the structure of hollow Ca-alginate microfibers. All the microfibers are fabricated under the same flow condition: Q_{W1} = 150 μL h^{-1}, Q_{W2} = 300 μL h^{-1}, Q_{W3} = 2500 μL h^{-1}, and Q_{W4} = 1000 μL h^{-1}.

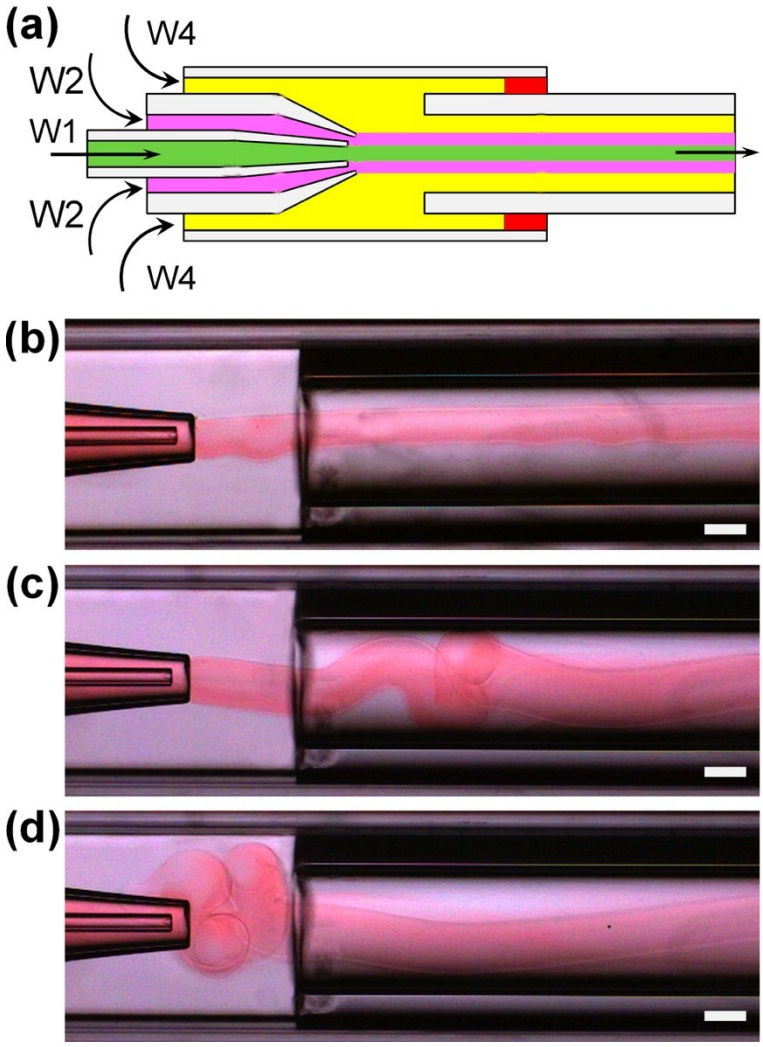


Fig. S3 (a) Schematic illustration of microfluidic gengeration of hollow Ca-alginate microfibers using traditional three-aqueous-phase flow templates. (b-d) High-speed snapshots showing the clogging of microchannels in the outlet tube (c) and at the orifice of the injection tube (d) during the the microfiber fabrication (b). Scale bars are 200 μm.

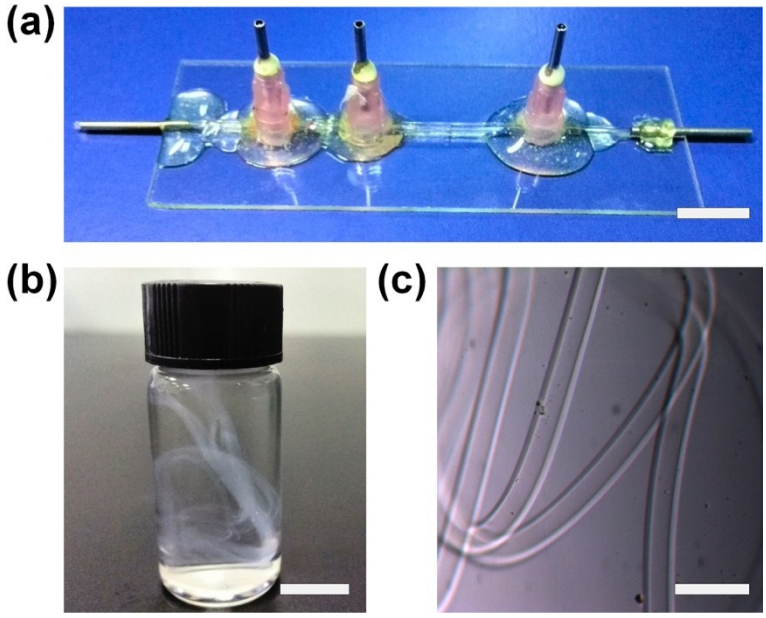


Figure. S4 (a-b) Digital photos of the coaxial microfluidic device (a) and the poduced hollow Ca-alginate microfibers in a water-containing vessel (b). (c) Optical micrograph of the hollow Ca-alginate microfibers. Scale bars are 1 cm in (a) and (b), and 200 μm in (c).

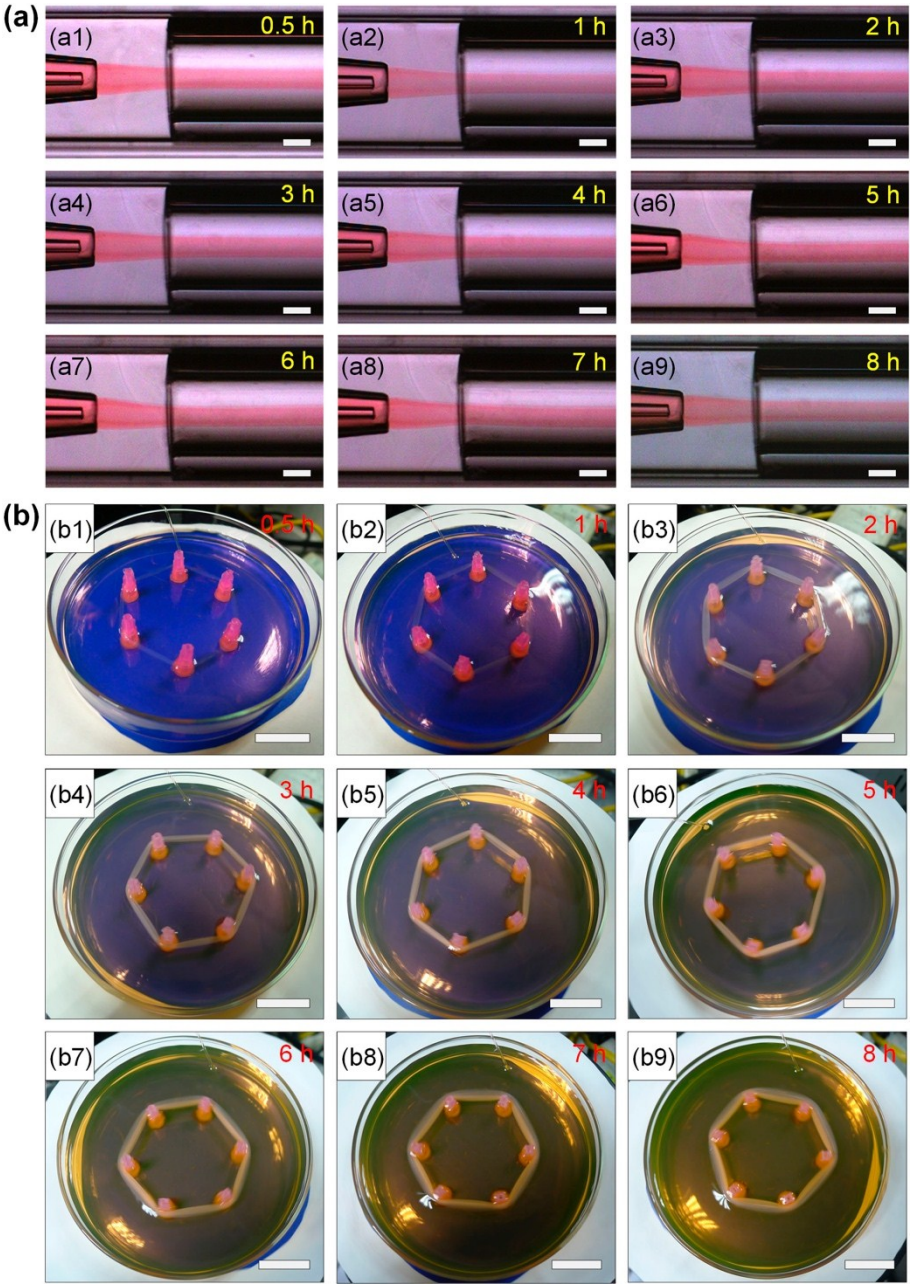


Fig. S5 Continuous microfluidic generation of hollow Ca-alginate microfibers. (a) High-speed snapshots showing the continuous generation of hollow Ca-alginate microfibers in microfluidic device for 8h. The Q_{W1}, Q_{W2}, Q_{W3} and Q_{W4} are fixed at 200 μL h^{-1}, 400 μL h^{-1}, 3000 μL h^{-1} and 2000 μL h^{-1}, respectively. (b) Digital photos showing the rotatory collection of the continuously generated hollow Ca-alginate microfibers in a Petri dish for 8 h. The rotatory speed is set at 8 rpm and the length of a circle is ~0.15 m, thus the lenth of the hollow Ca-alginate microfiber after continuous generation for 8 h is ~576.0 m. Scale bars are 200 μm in (a), and 2 cm in (b).

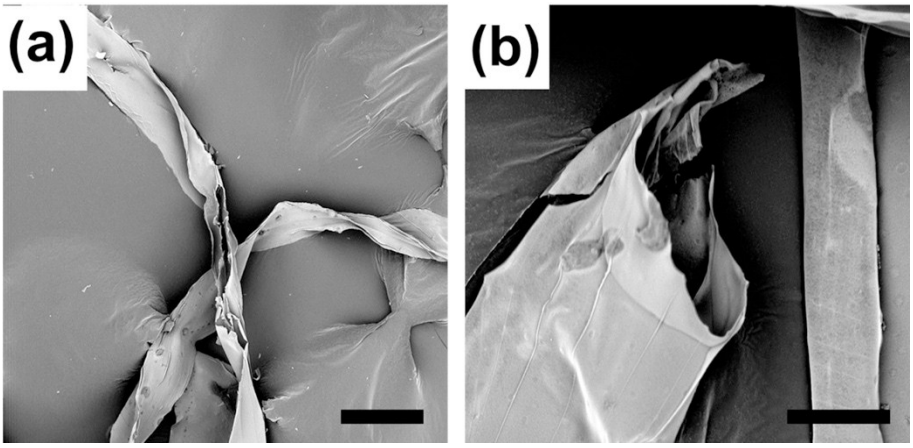


Fig. S6 SEM images of dried and ruptured hollow Ca-alginate microfibers. The scale bar is 100 μm in (a), and 30 μm in (b).

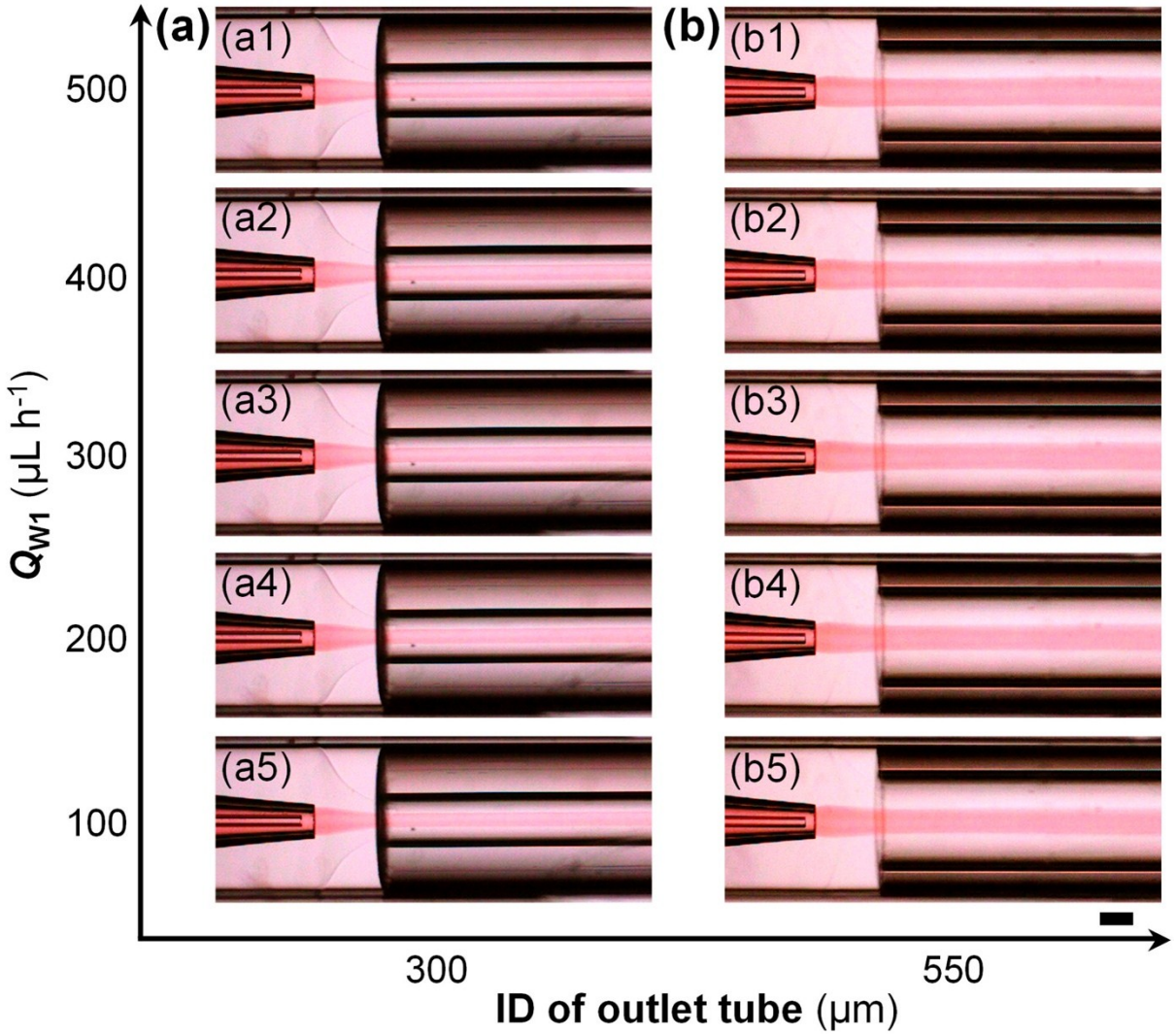


Fig. S7 High-speed snapshots of the hollow Ca-alginate microfibers fabricated from coaxial microfluidic device containing outlet tubes with inner diameters (ID) of 300 μm (a) and 550 μm (b) by changing Q_{W1}. The Q_{W2}, Q_{W3} and Q_{W4} are fixed at 300 μL h^{-1}, 2000 μL h^{-1} and 1500 μL h^{-1}, respectively. The scale bar is 200 μm.

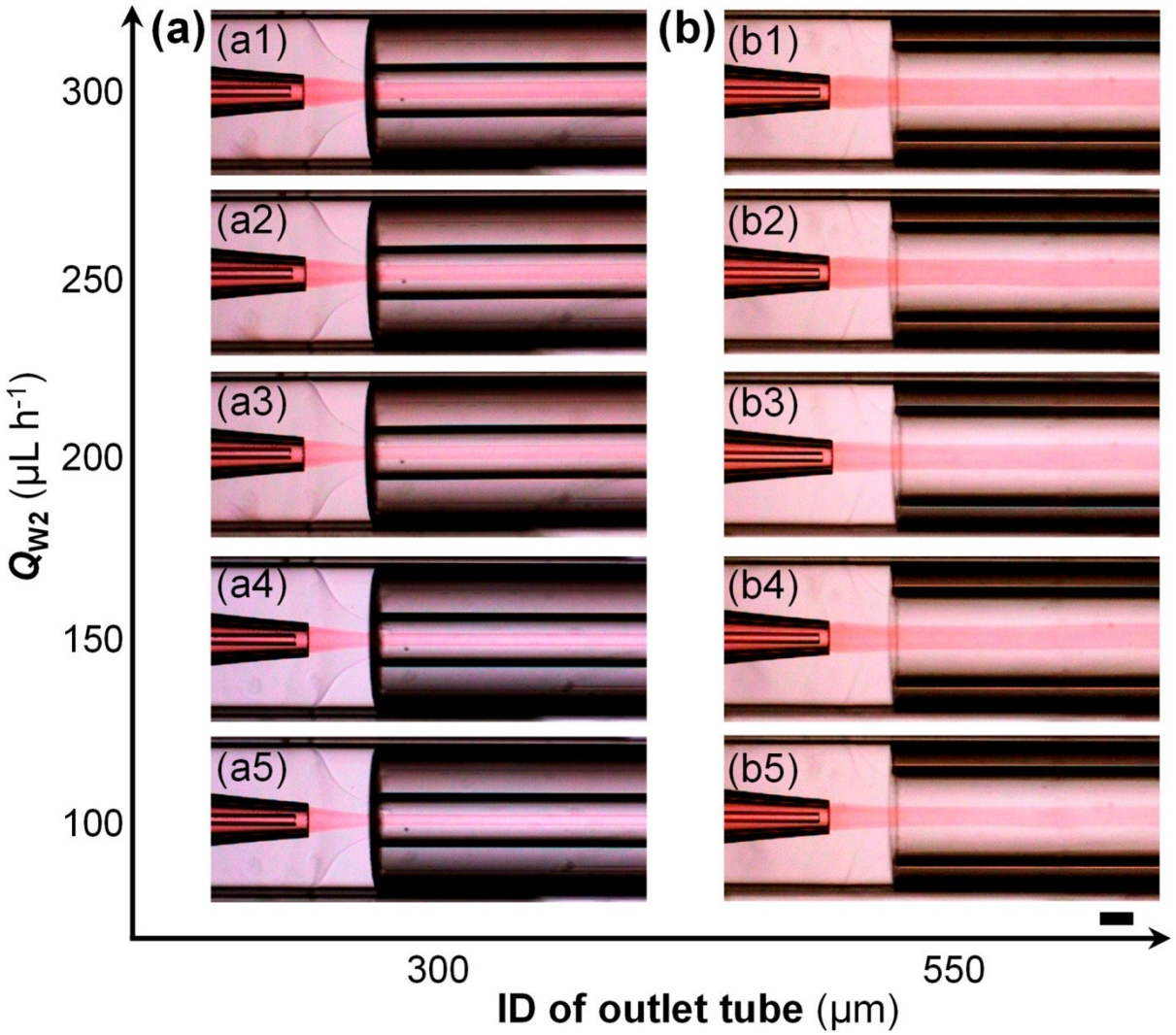


Fig. S8 High-speed snapshots of the hollow Ca-alginate microfibers fabricated from coaxial microfluidic device containing outlet tubes with inner diameters (ID) of 300 μm (a) and 550 μm (b) by changing Q_{W2}. The Q_{W1}, Q_{W3} and Q_{W4} are fixed at 100 μL h^{-1}, 1500 μL h^{-1} and 1000 μL h^{-1}, respectively. The scale bars is 200 μm.

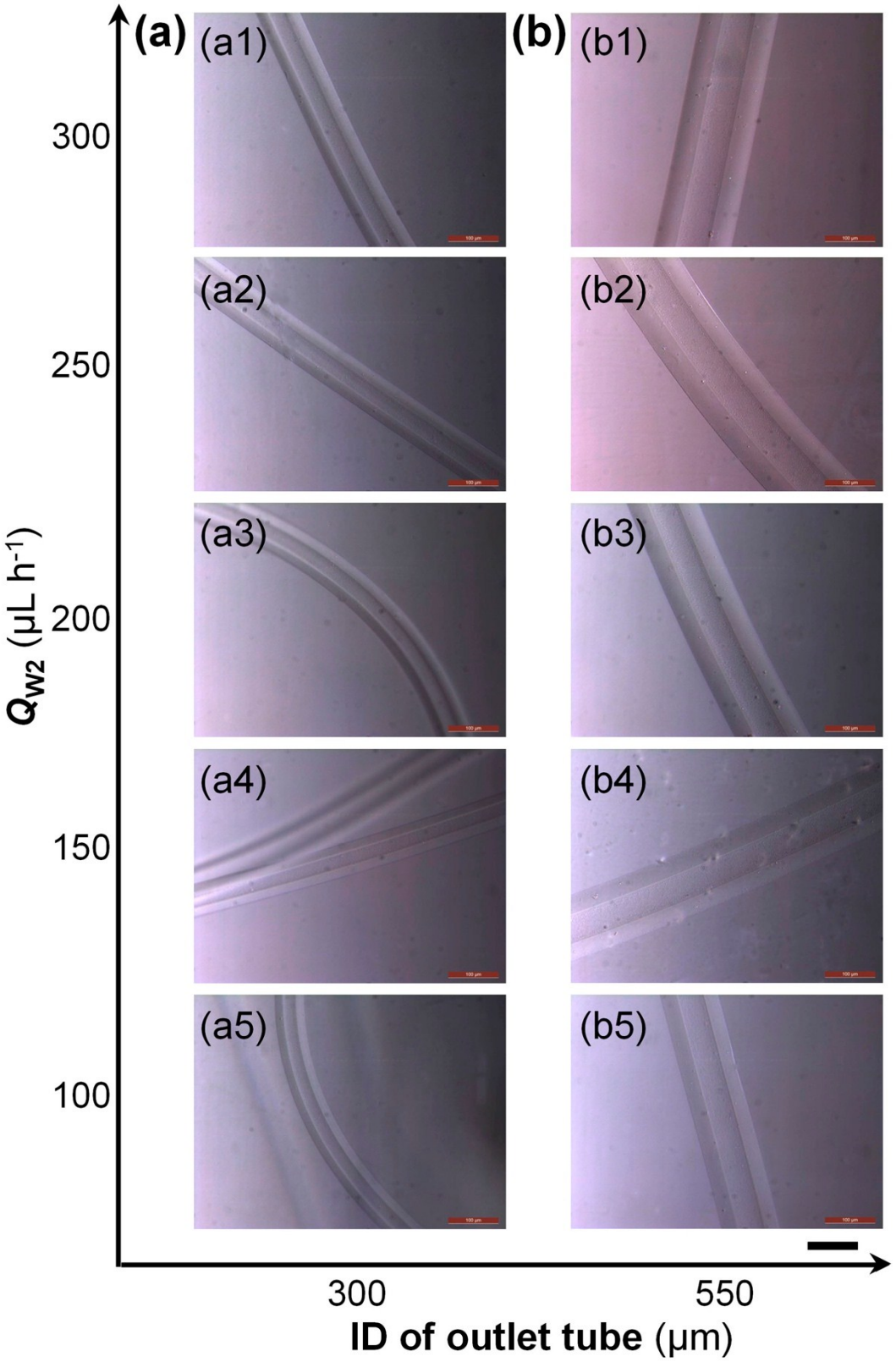


Fig. S9 Optical micrographs of the hollow Ca-alginate microfibers fabricated from coaxial microfluidic device containing outlet tubes with inner diameters (ID) of 300 μm (a) and 550 μm (b) by changing Q_{W2}. The Q_{W1}, Q_{W3} and Q_{W4} are fixed at 100 μL h^{-1}, 1500 μL h^{-1} and 1000 μL h^{-1}, respectively. Scale bars are 100 μm.

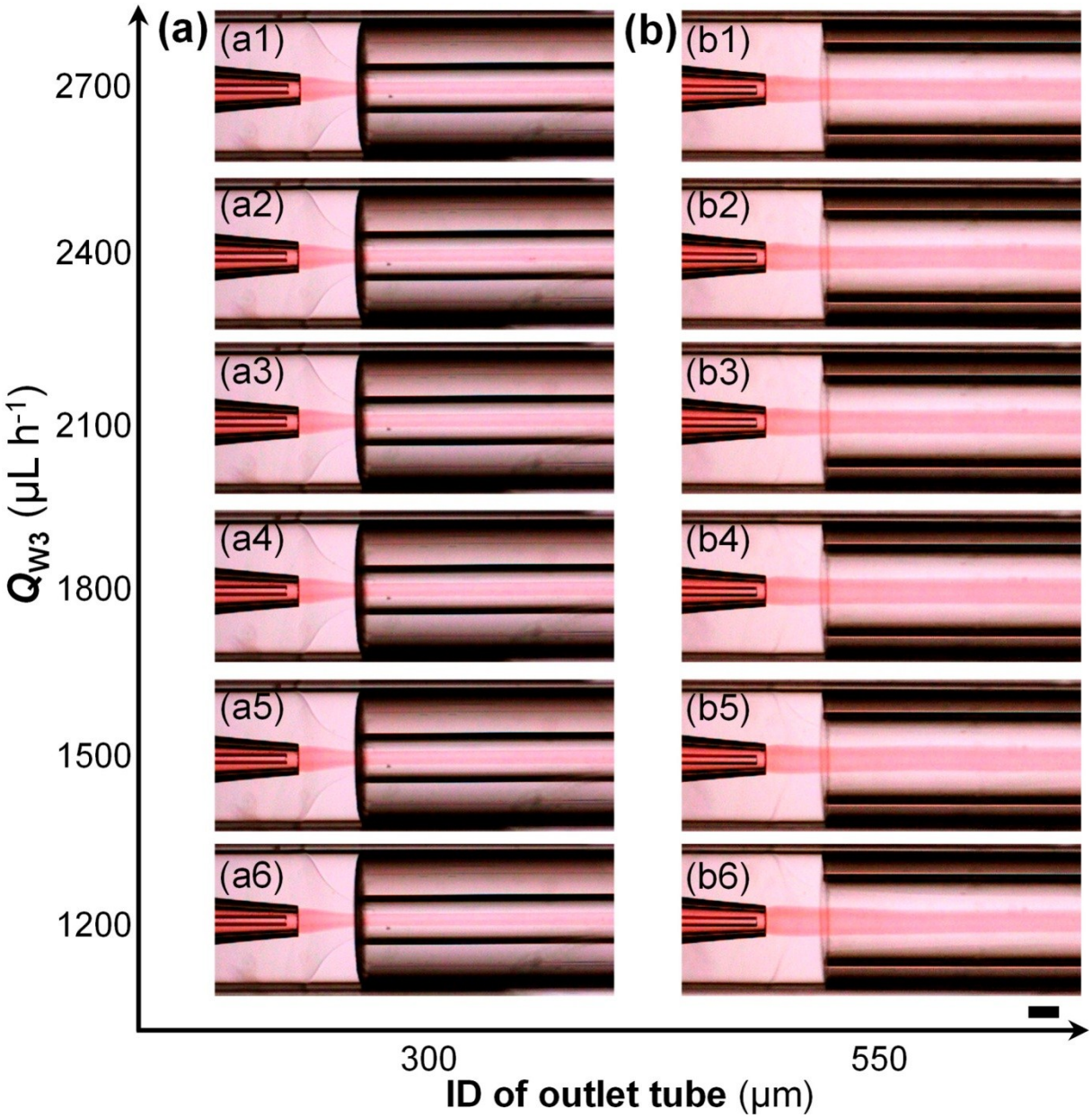


Fig. S10 High-speed snapshots of the hollow Ca-alginate microfibers fabricated from coaxial microfluidic device containing outlet tubes with inner diameters (ID) of 300 μm (a) and 550 μm (b) by changing Q_{W3}. The Q_{W1}, Q_{W2} and Q_{W4} are fixed at 100 μL h^{-1}, 300 μL h^{-1} and 1500 μL h^{-1}, respectively. The scale bar is 200 μm.

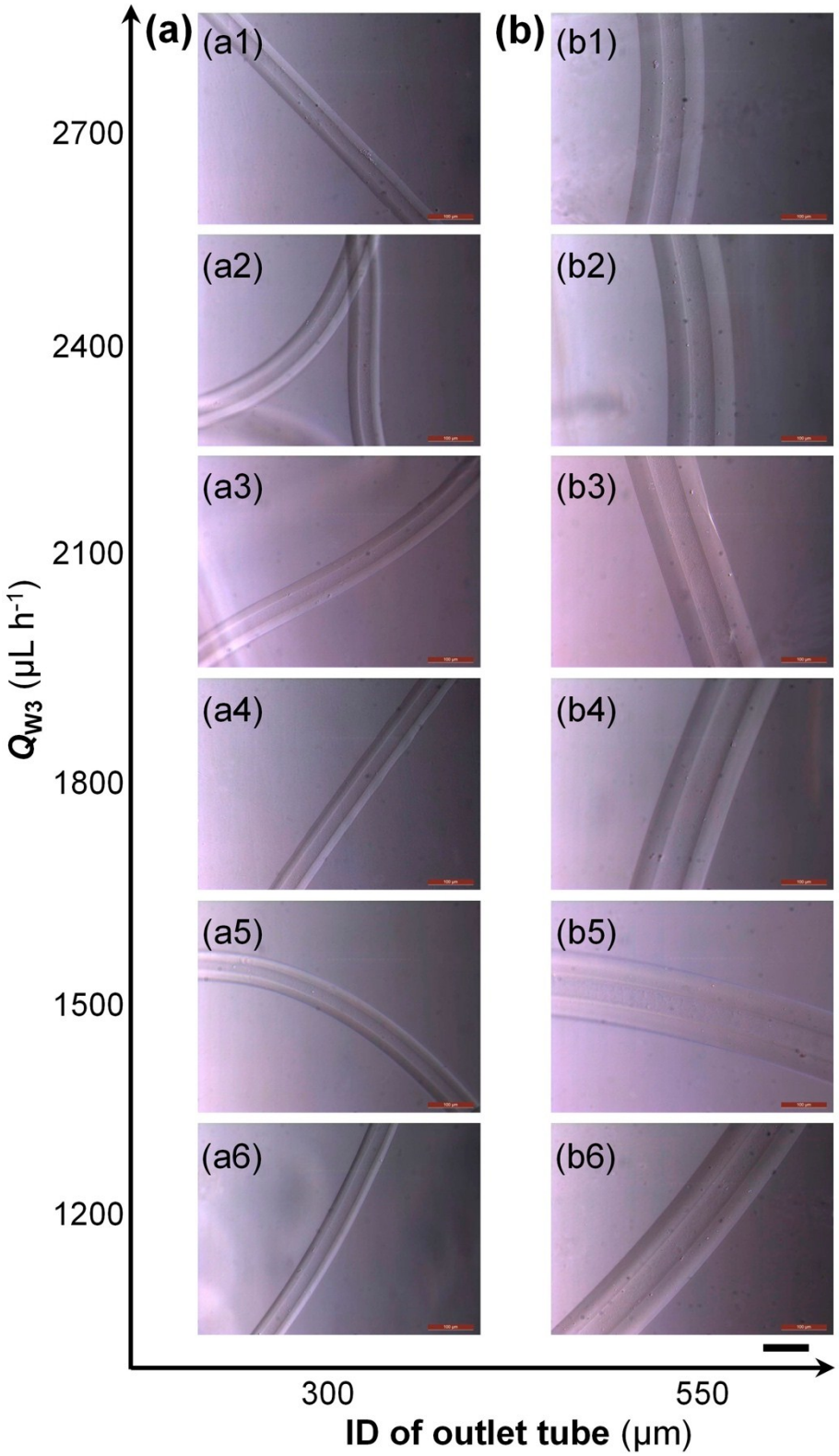


Fig. S11 Optical micrographs of the hollow Ca-alginate microfibers fabricated from coaxial microfluidic device containing outlet tubes with inner diameters (ID) of 300 μm (a) and 550 μm (b) by changing Q_{W3}. The Q_{W1}, Q_{W2} and Q_{W4} are fixed at 100 μL h^{-1}, 300 μL h^{-1} and 1500 μL h^{-1}, respectively. Scale bars are 100 μm.

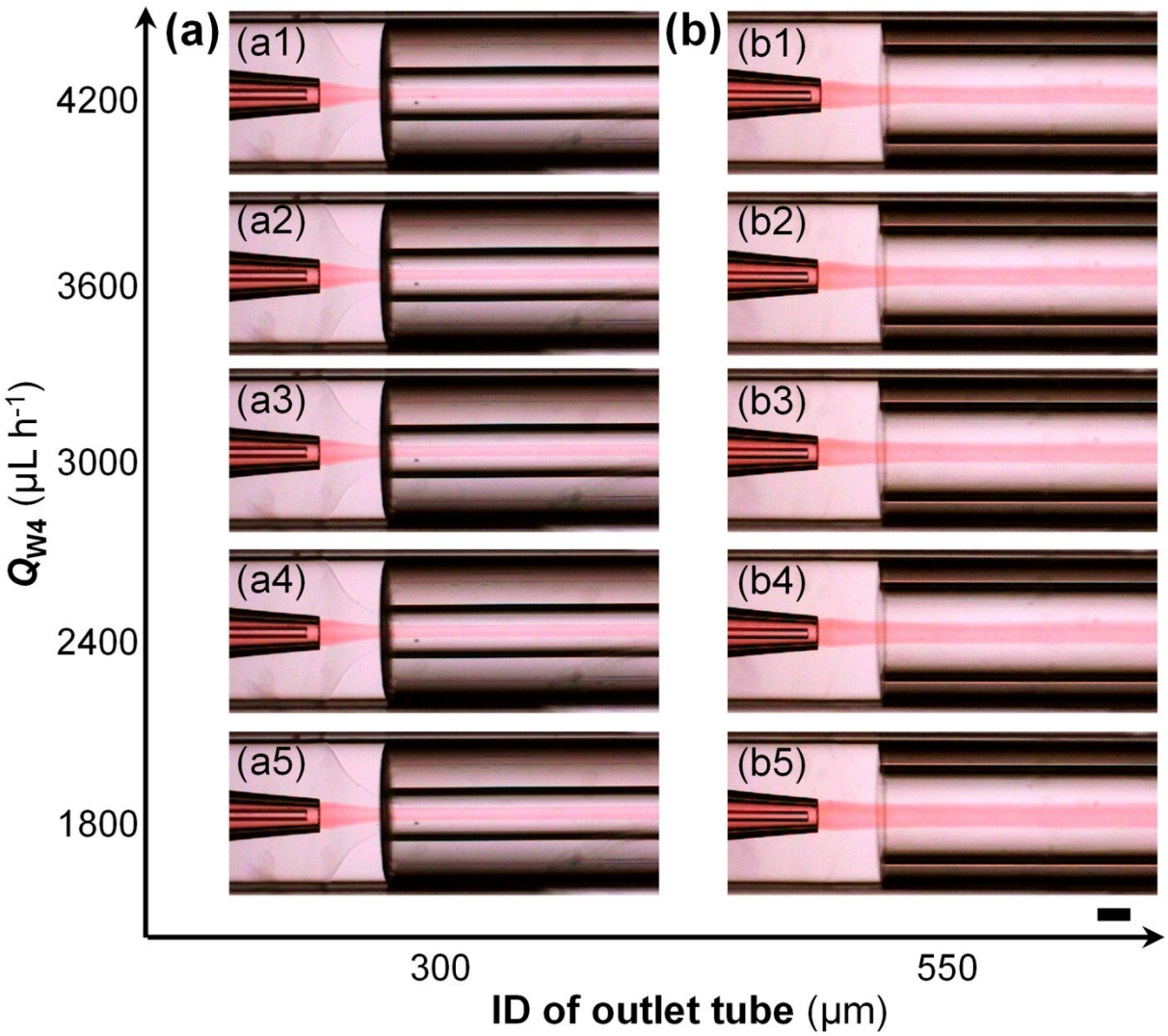


Fig. S12 High-speed snapshots of the hollow Ca-alginate microfibers fabricated from coaxial microfluidic device containing outlet tubes with inner diameters (ID) of 300 μm (a) and 550 μm (b) by changing Q_{W4}. The Q_{W1}, Q_{W2} and Q_{W3} are fixed at 100 μL h^{-1}, 300 μL h^{-1} and 2500 μL h^{-1}, respectively. The scale bar is 200 μm.

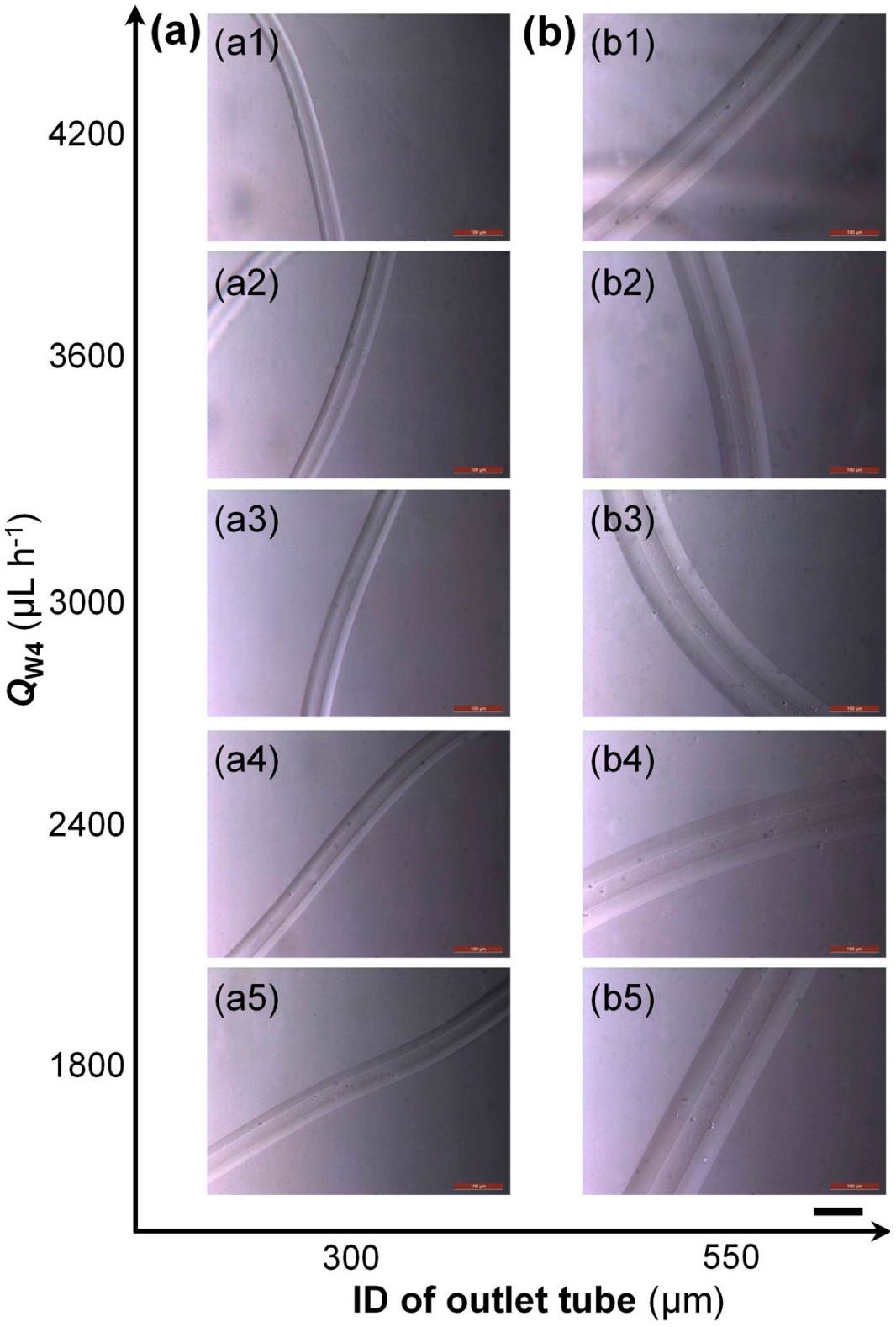


Fig. S13 Optical micrographs of the hollow Ca-alginate microfibers fabricated from coaxial microfluidic device containing outlet tubes with inner diameters (ID) of 300 μm (a) and 550 μm (b) by changing Q_{W4}. The Q_{W1}, Q_{W2} and Q_{W3} are fixed at 100 μL h^{-1}, 300 μL h^{-1} and 2500 μL h^{-1}, respectively. Scale bars are 100 μm.

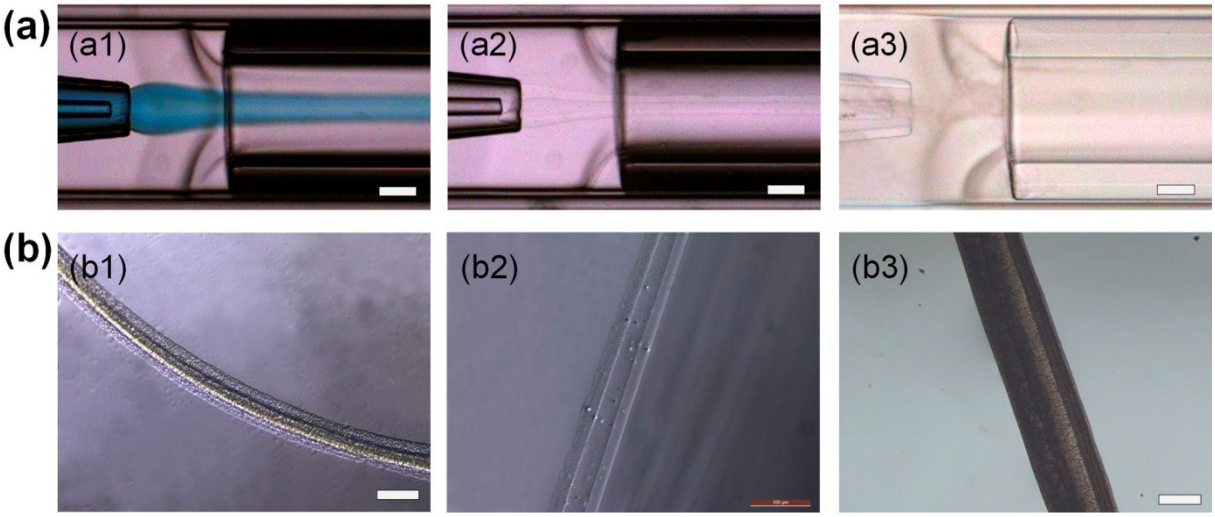


Fig. S14 High-speed snapshots (a) and optical micrographs (b) showing the continuous microfluidic generation of hollow chitosan microfibers (a1, b1), hollow PVA microfibers (a2, b2) and hollow PLGA microfibers (a3, b3). Scale bars are 200 μm in (a), and 100 μm in (b).

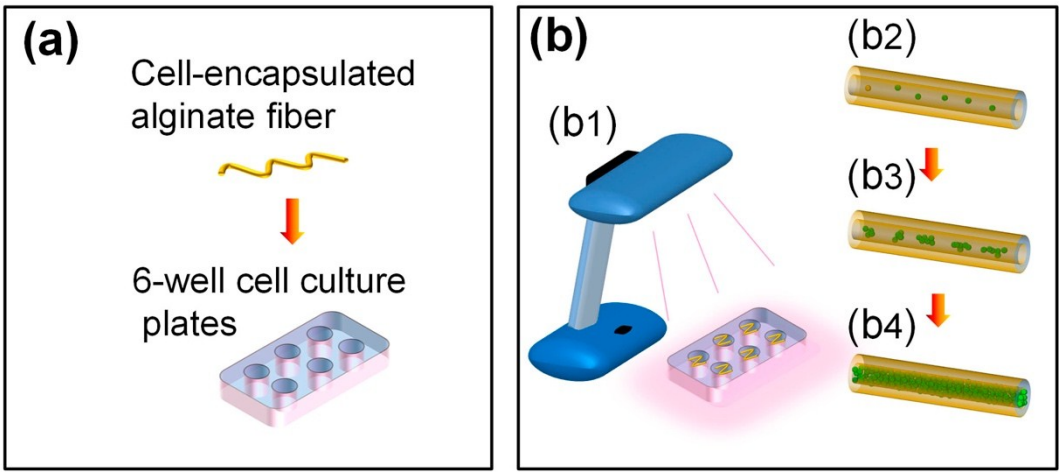


Fig. S15 Schematic illustration of the confined growth of chlorella pyrenoidosa cells in the hollow internal of hollow Ca-alginate microfibers. (a) Cell-laden hollow Ca-alginate microfibers are placed in the wells of cell culture plates for cell growth. (b) Confined growth of the chlorella pyrenoidosa cells inside the hollow internals of microfibers under lamp light.

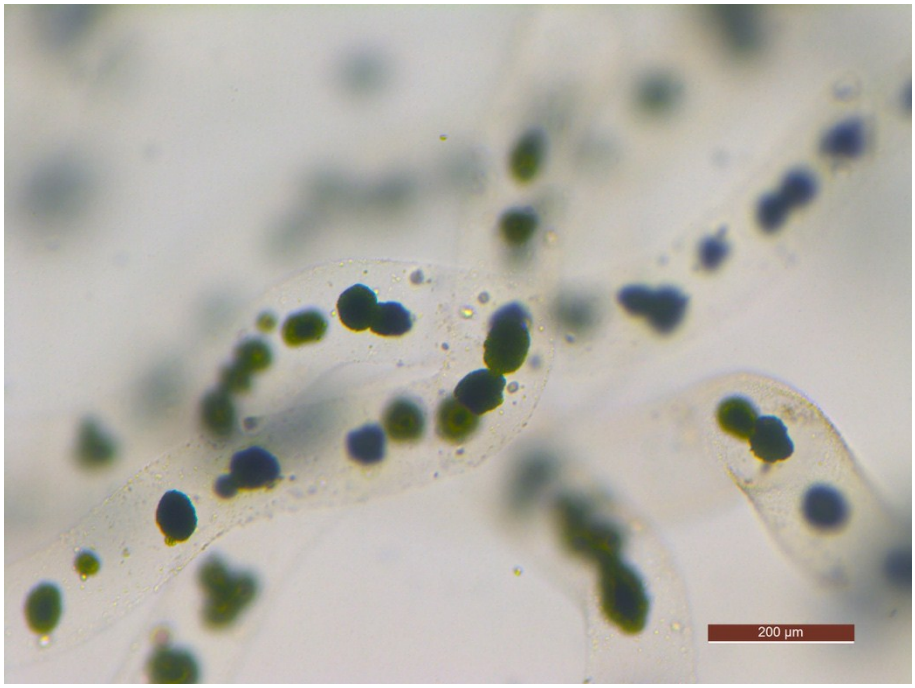


Fig. S16 Optical micrographs of chlorella pyrenoidosa cells in solid Ca-alginate microfibers after growth for 7 days. The scale bar is 200 µm.

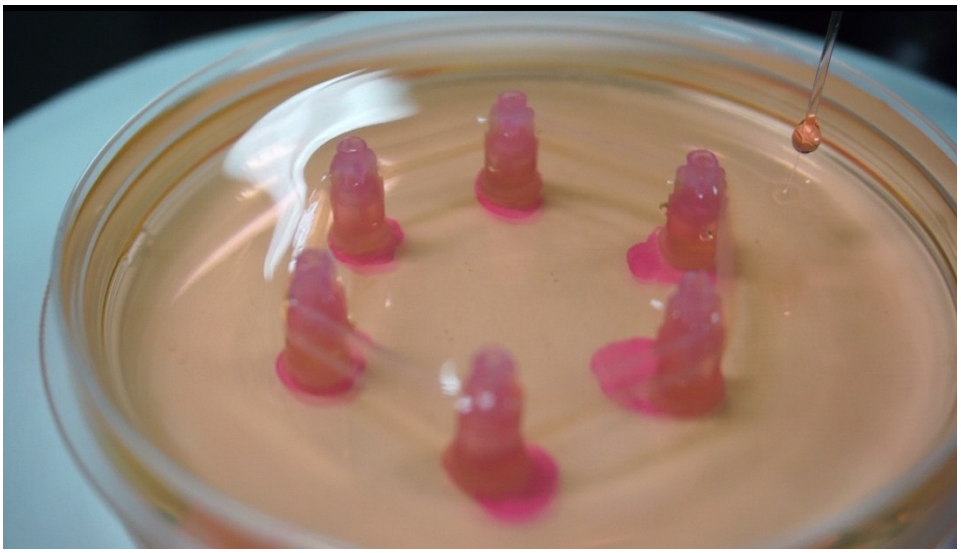
Part III. Supplementary Table S1

Table S1 Effect of PEG20000 concentration on the changes of viscosity of the buffer solution and the diffusion coefficient of Ca^{2+}.

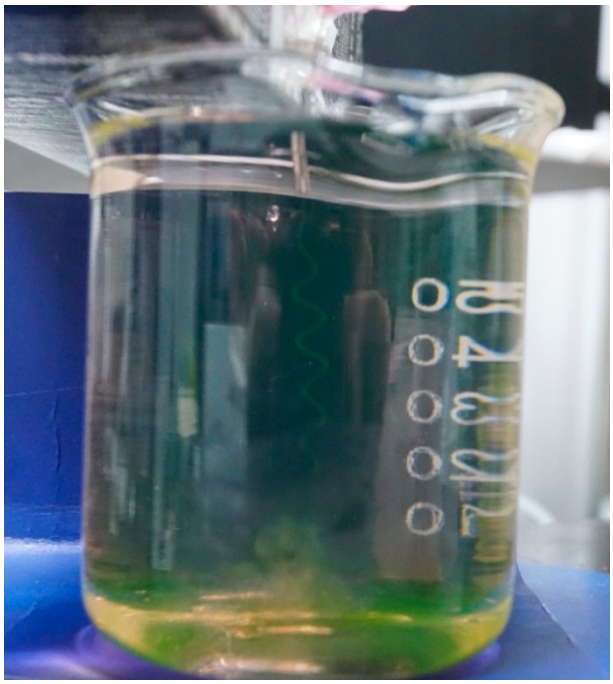
No.	C_{PEG} / %	μ / mPa·s	(D_i/D_0) / %
1	0	0.87±0.02	100
2	0.5	1.04±0.03	83.7
3	1	1.26±0.05	69.0
4	2	1.77±0.05	49.2
5	4	3.19±0.09	27.3
6	8	7.42±0.11	11.7
7	16	21.88±0.21	4.0

Note: The symbol "C_{PEG}" represents the PEG20000 concentration; "μ" represents the viscosity of the buffer solution, measured by a viscometer (DV2T, Brookfiled) at 25.8 ^{o}C; "D_0" represents the diffusion coefficient of Ca^{2+} ions in DI water, "D_i" (i=1, 2, 3, 4, 5, 6 and 7) represents the diffusion coefficient of Ca^{2+} ions in the buffer solutions with different PEG20000 concentrations.

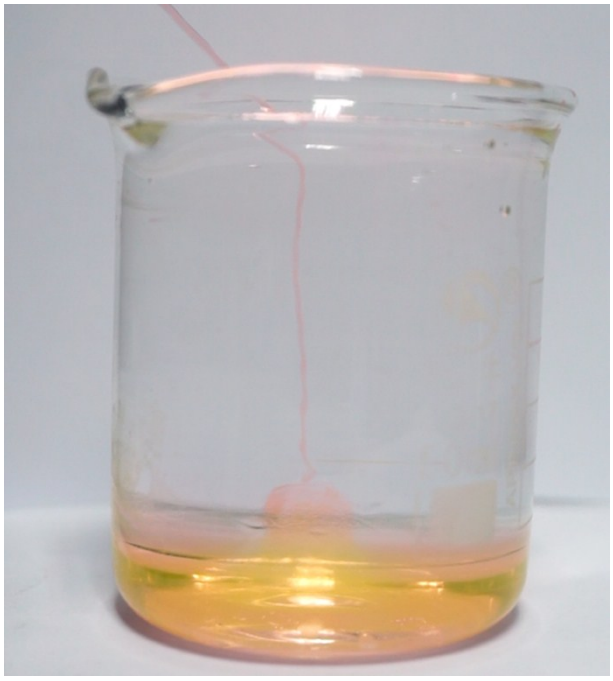
Part IV. Supplementary Movies S1-S3



Movie S1 Rotary collection process of hollow Ca-alginate microfibers from the coaxial microfluidic device.



Movie S2 Rotator-free collection of continuously generated hollow Ca-alginate microfibers from vertically fixed microfluidic device.



Movie S3 Rotator-free collection of continuously generated hollow Ca-alginate microfibers from horizontaly fixed microfluidic device as shown in Fig.2a. The orifice of the collection microcapillary is immersed in the collection solution for microfiber collection.