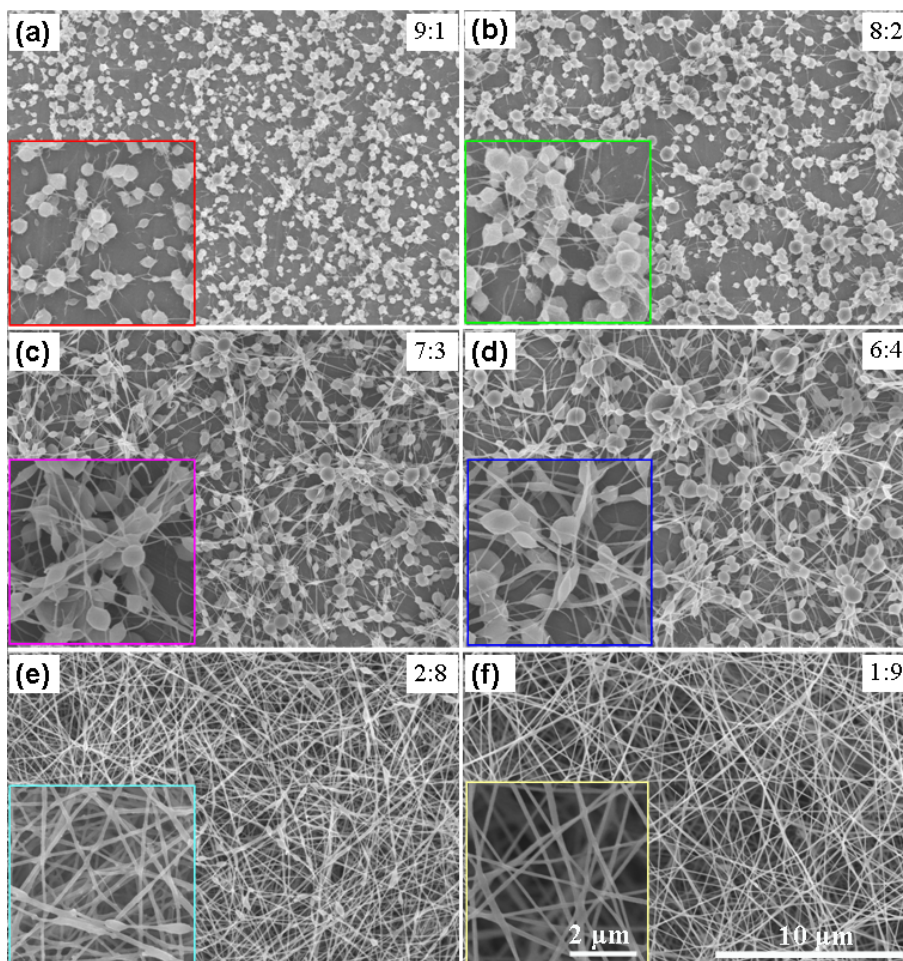


Electronic Supplementary Information



5 **Figure S1.** SEM images of electrospun CHI-PEO products with different CHI/PEO ratio. Insets in (a–f) are magnification of SEM images (bottom-left) and CHI/PEO ratio (top-right), respectively. It was observed that the fiber-free droplets produced when CHI/PEO ratio was 9:1 (CHI/PEO=2.7%/0.3 % [w/v]) (**Fig. S1a**). As a rule, along with the increase of proportion in weight of PEO, the productions of electrospinning became continuous, and generated short fibers and a “bead on the string” morphology (CHI/PEO=2.4%/0.6 % [w/v]) (**Fig. S1b**), but fiber which was totally smooth are not found (**Fig. S1c–e**) until the CHI/PEO ratio of 1:9 (CHI/PEO=0.3%/2.7 % [w/v]) (**Fig. S1f**), at the random electrospinning condition (i.e., voltage: 10 kV; collection distance: 10 cm; syringe pump rate: 0.2 mL.h⁻¹).

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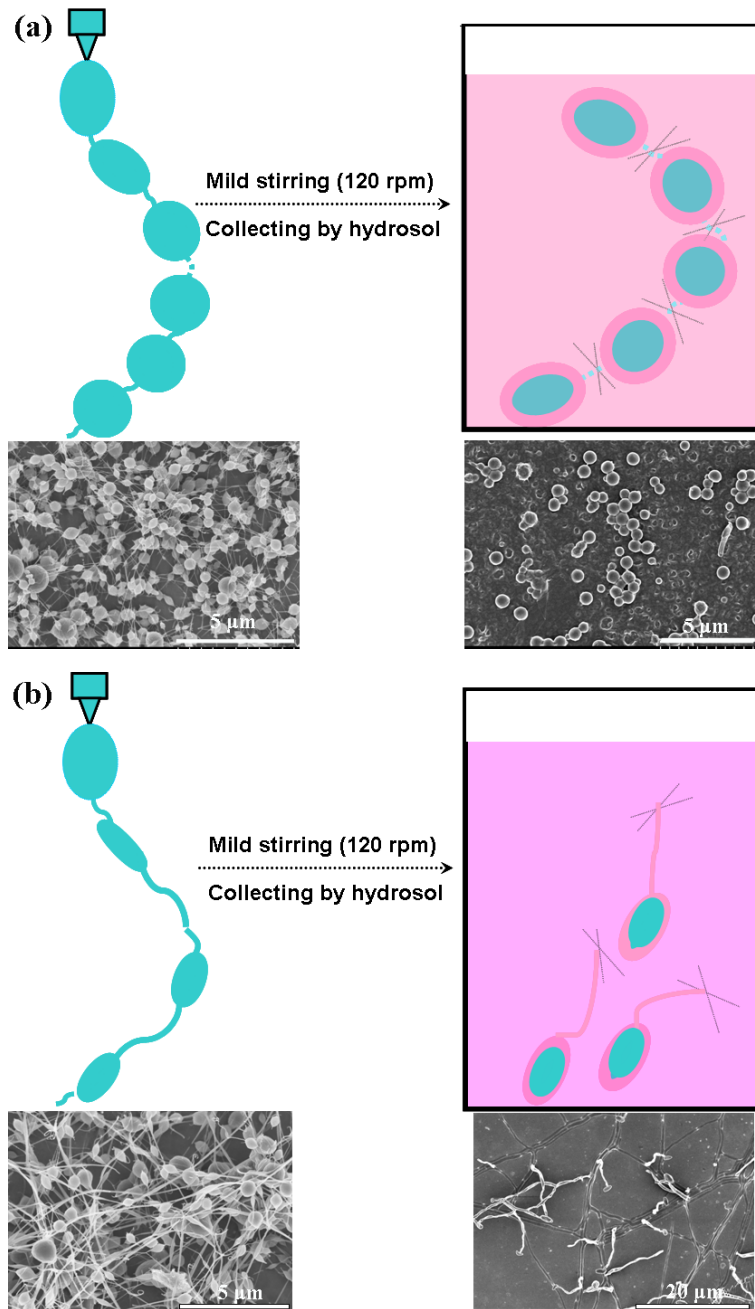


Figure S2. Schematic illustration of the core-shell-structured microcapsule and bean-sprout-like fiber formation by electrospinning the bead-rich nanofibers with CHI/PEO of 2.4%/0.6 % **(a)** and 1.8%/1.2% **(b)** [w/v] into the biologically active counterionic hydrosols under mild magnetic stirring, together with the SEM images of the bead-rich nanofibers (collecting by aluminum foil) and beads (collected by counterionic hydrosol). It is reasonable to postulate that the continuous short nanofiber (~50 nm in diameter) between the two beads (~1000 nm in diameter) would break due to the hydrosol disturbance by the mild magnetic stirring; thus the isolated beads may be capped by the counterionic polyelectrolytes to form core-shell microcapsules. However, with the increase of fiber-diameter/bead-diameter ratio, the fiber break at the head of bead to produce bean-sprout-like structure.

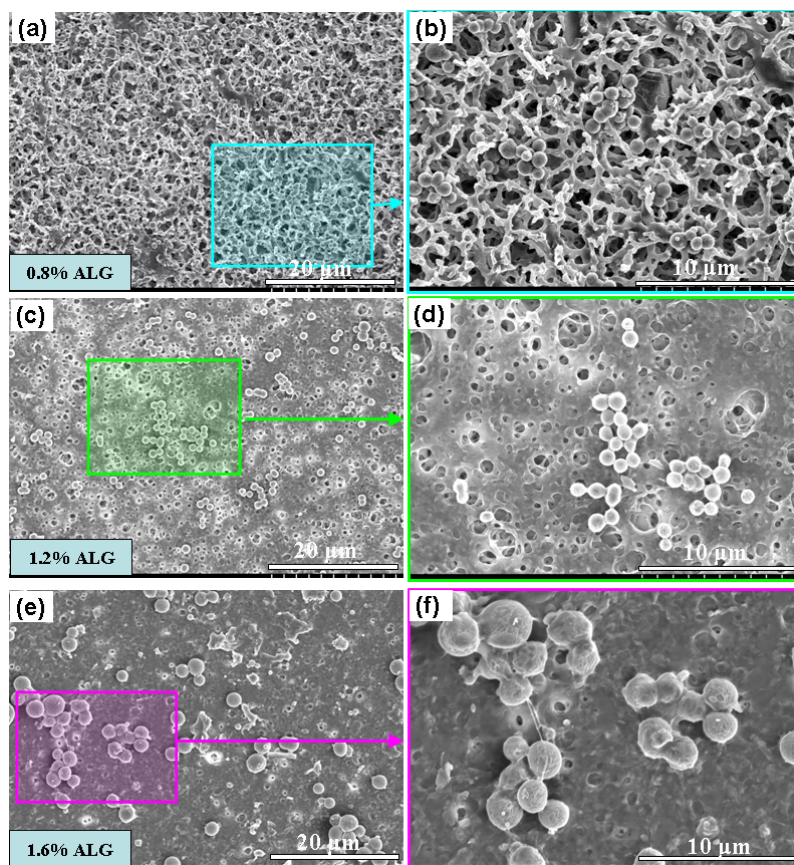


Figure S3. SEM images of electrospun microcapsules from CHI-PEO blends under different ALG hydrosol concentration conditions. (a) 0.8% ALG solution, (b) 1.2 % ALG solution, (c) 1.6% ALG solution.

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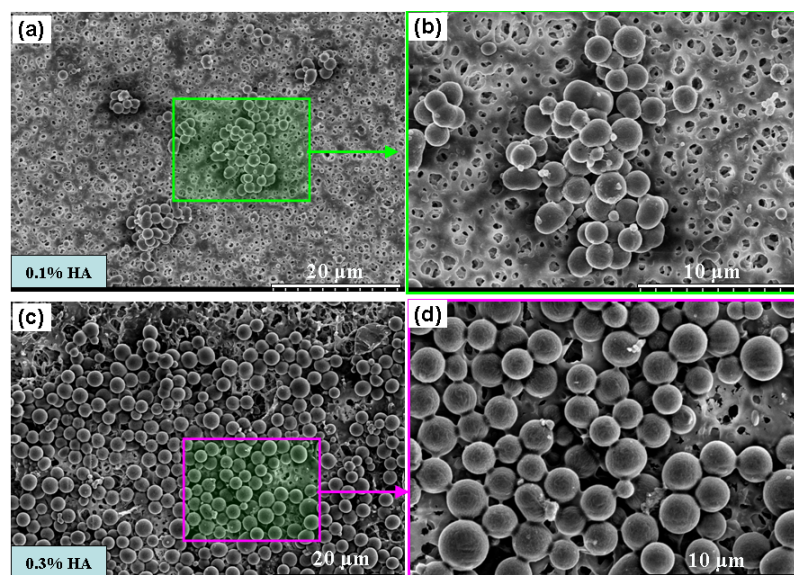


Figure S4. SEM images of electrospun microcapsules from CHI-PEO blends under different HA hydrosol concentration conditions. (a, b) 0.1% HA solution, (c, d) 0.3 % HA solution.

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