Wire-templated electrodeposition of vessel-like structured chitosan hydrogel by using a pulsed electrical signal
(Supporting Information)

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1. Moving front model for chitosan hydrogel growth during the ON-step

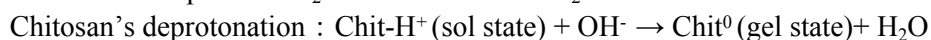As illustrated in **Fig. S1**, the moving is based on several fundamental assumptions:

(i) Chitosan is defined into two mainly states: fully deprotonated (Chit^0) and fully protonated (Chit-H$^+$);

Chitosan's primary amines conferring a unique pH-responsiveness (pKa~6.3): at low pH the protonated amines make chitosan a soluble polyelectrolyte (as a fully deprotonated chitosan gel state) while at high pH the amines become deprotonated allowing chitosan self-assemble into a hydrogel network (as a fully protonated sol state).

(ii) Chitosan's neutralization is responsible for gelation and gelation is rapid such that the growing pH-front and growing gelation-front are co-localized;

(iii) The charge transfer associated with proton consumption at the electrode is equated to chitosan's deprotonation;

The proton consumption at the electrode is equated to the chitosan's deprotonation (i.e., no other buffering species are present to influence the proton consumption).

Proton consumption : $2H_2O + 2e^- \rightarrow 2OH^- + H_2$
Chitosan's deprotonation : Chit-H$^+$ (sol state) + OH$^- \rightarrow$ Chit^0 (gel state)+ H$_2$O

(iv) Chitosan chains undergo no net migration in response to the electrical component of ON-signal and the chains concentration (Chit^{total} = Chit^0 + Chit-H$^+$) is the same everywhere within the deposition cell.
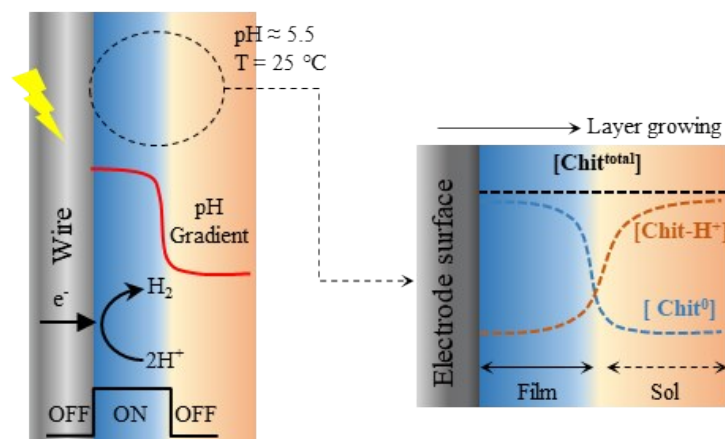
2. Characterizations.

Fig. S1 Schematically illustrated the assumptive concentration profiles of the fully deprotonated and fully protonated chitosan chains during deposition process.
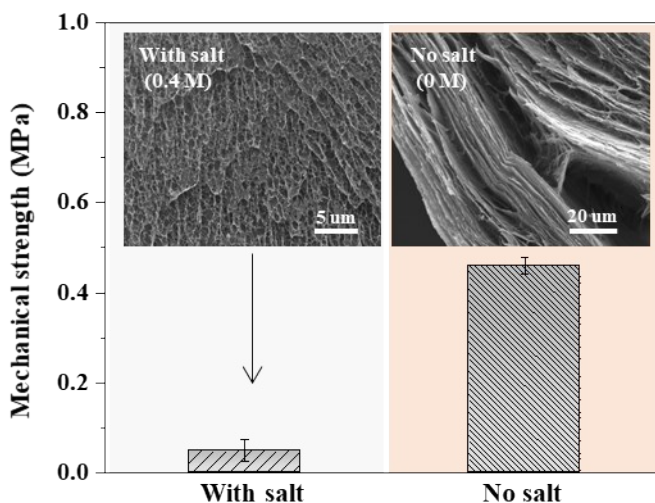

Fig. S2 Mechanical properties and microstructural observations of the chitosan films deposited from different salt conditions.