

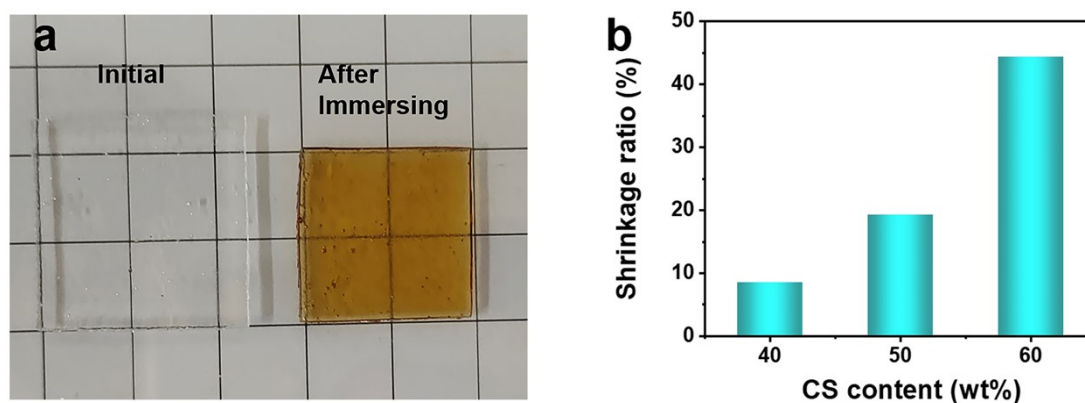
## Electronic Supplementary Information

### Strong and tough self-wrinkling polyelectrolyte hydrogels constructed via diffusion-complexation strategy

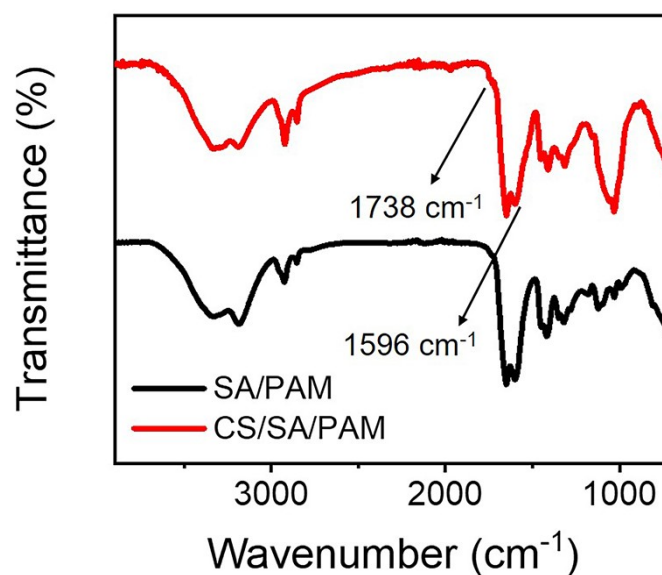
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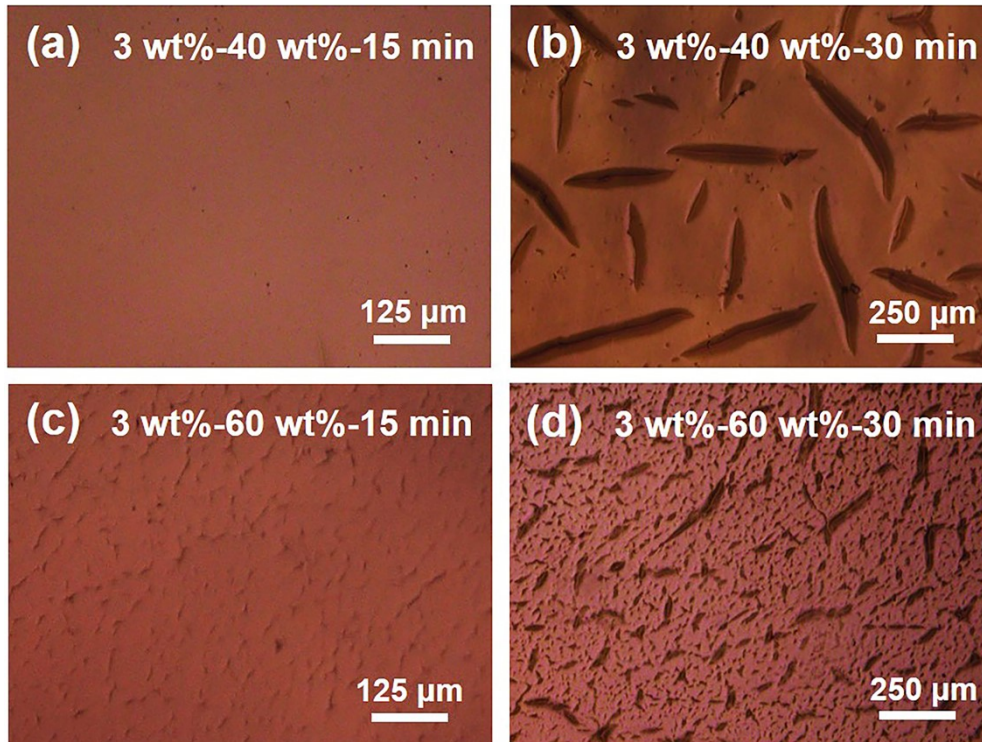
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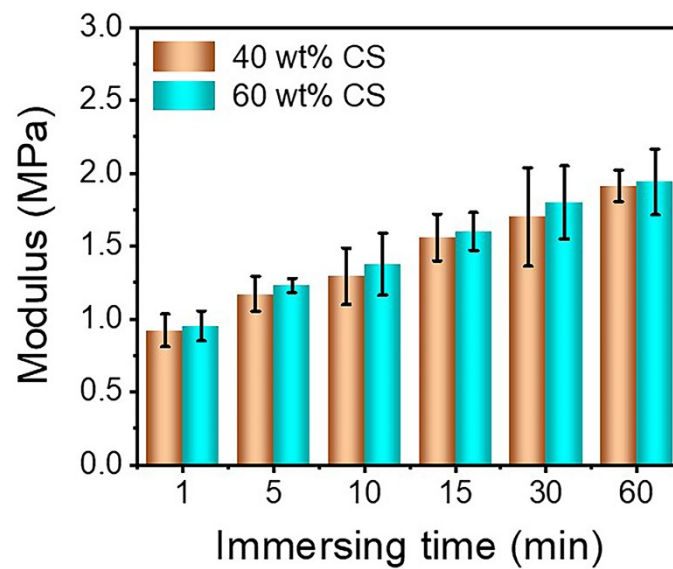
**Fig. S1** SA/PAM hydrogels shrink in CS solution. (a) Optical image. (b) The shrinkage ratio of SA/PAM hydrogels at different CS solution concentrations.



**Fig. S2** FTIR spectra of initial SA/PAM hydrogel and self-wrinkling SA/PAM hydrogel.



**Fig. S3** Optical images of the surfaces of SA/PAM hydrogels in 40 wt% (a,b) and 60 wt% (c,d) CS solutions as a function of immersion time. The doping concentration of SA in the SA/PAM hydrogels is 3 wt%.



**Fig. S4** Surface modulus ( $\bar{E}_s$ ) of SA/PAM hydrogels in 40 wt% and 60 wt% CS solutions as a function of immersion time. The doping concentration of SA in the SA/PAM hydrogels is 3 wt%.

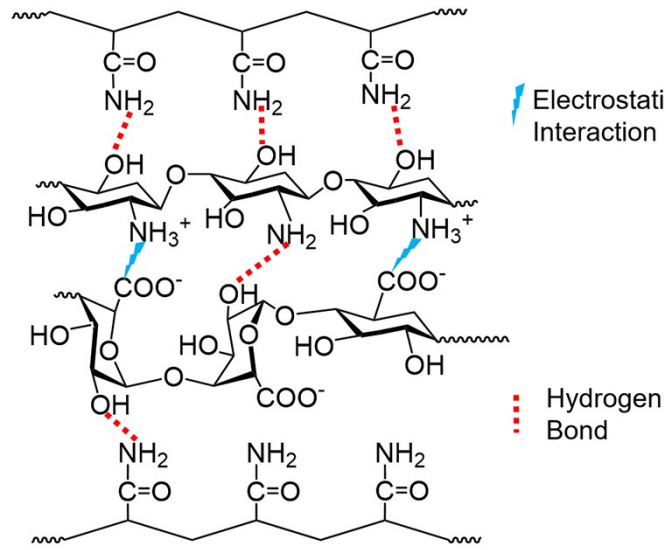


Fig. S5 Schematic illustration of electrostatic interactions and the hydrogen bonds within self-wrinkled hydrogels.

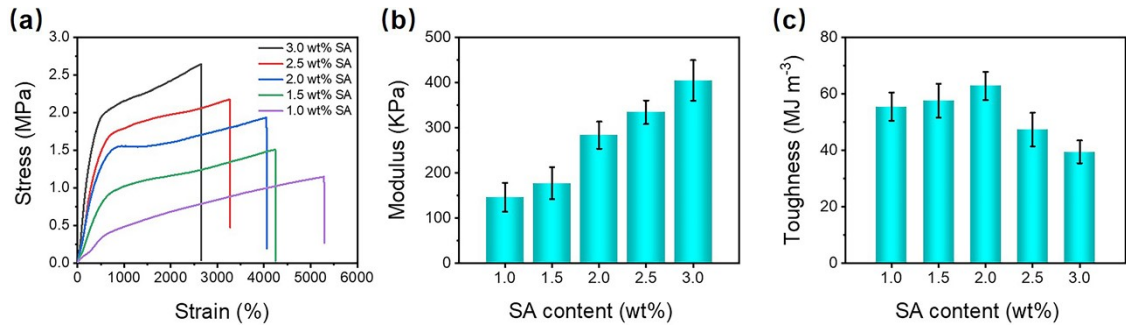


Fig. S6 Mechanical properties of self-wrinkling hydrogels prepared by approach I. (a) Stress-strain curves of the SA/PAM hydrogels with different SA contents before and after being immersed into 60 wt% CS solution for 24 h. (b) Modulus and (c) toughness of self-wrinkling SA/PAM hydrogels prepared with different prestretching multiples in 60 wt% CS solutions.

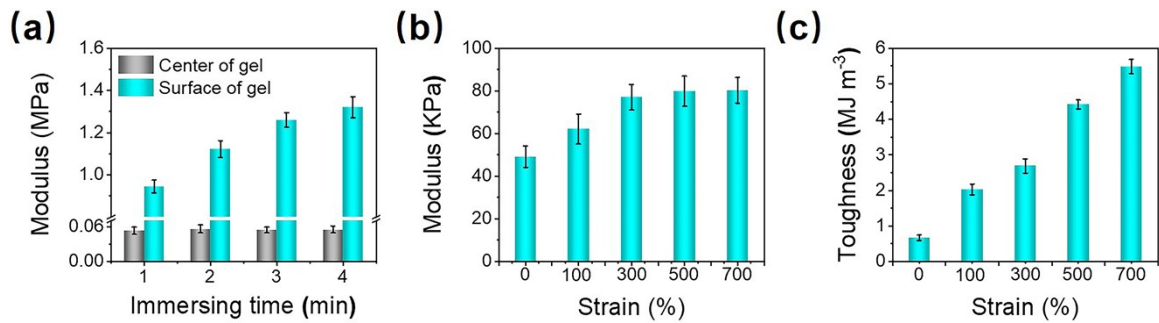
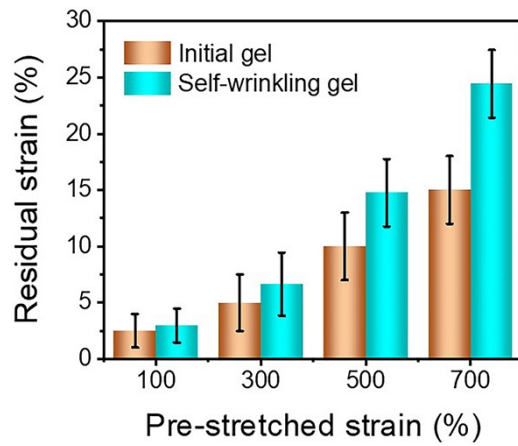
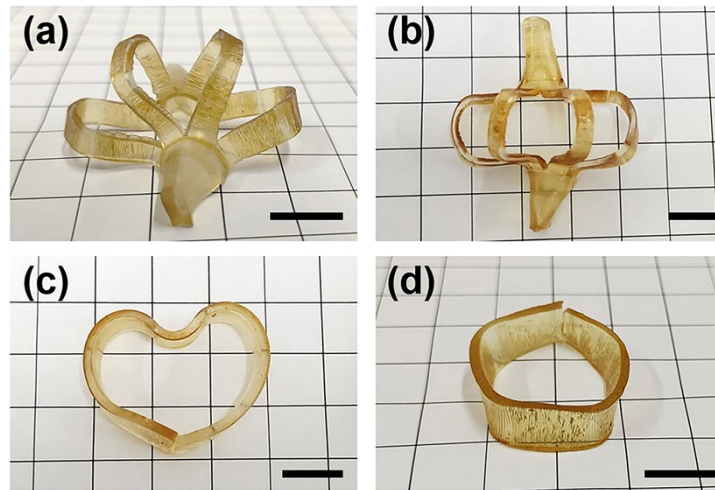


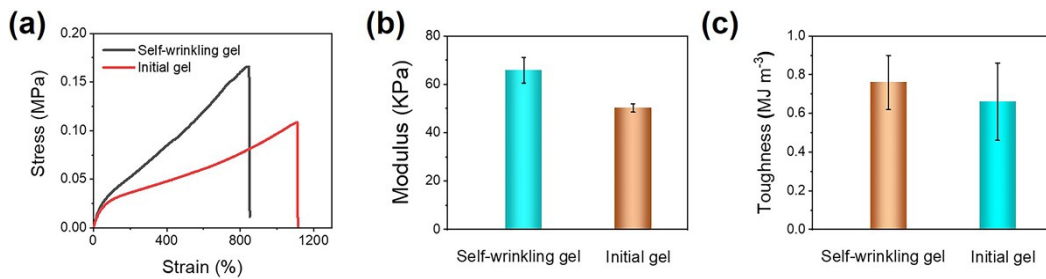
Fig. S7 (a) Comparison of internal and surface modulus of SA/PAM hydrogels in 60 wt% CS solutions. (b) Modulus and (c) toughness of self-wrinkling SA/PAM hydrogels prepared with different prestretching multiples in 60 wt% CS solutions. The doping concentration of SA in the SA/PAM hydrogels is 3 wt%.



**Fig. S8** Comparison of residual strains between the initial hydrogels and self-wrinkling hydrogels prepared under different pre-stretched strains.



**Fig. S9** Different 3D hydrogels with ordered wrinkled surfaces constructed by the approach III, including (a,b) cage-shaped, (c) heart-shaped, and (d) pentagram-shaped self-wrinkling hydrogels. All scale bars are 1cm.



**Fig. S10** (a) Stress-strain curves, (b) toughness and (c) modulus of initial SA/PAM hydrogels and self-wrinkling SA/PAM hydrogels prepared by the approach III.