

**Preparation of a “Branch-Fruit” structure chitosan  
nanofiber/Hyaluronic acid/ $\beta$ -glycerophosphate disodium physical  
hydrogels with high mechanical strength and pH-responsive  
controlled drug release properties**

Table S1 Composition of CSNF/HA/ $\beta$ -GP composite hydrogels.

Hydrogel name	Chitosan solution (C)			$\beta$ -GP/HA solution (G-A)		$V_C:V_{G-A}^a$
	CSP (w/v)	CSNFs (w/v)	Acetic acid (mol/l)	$\beta$ -GP (w/v)	HA (w/v)	
HG <sub>0</sub>	2.0%	—				
HG <sub>1</sub>	—	1.0%				
HG <sub>2</sub>	—	1.5%	0.03	10%	1.5%	4:1
HG <sub>3</sub>	—	2.0%				

<sup>a</sup> $V_C:V_{G-A}$ : the volume ratio of Chitosan solution to  $\beta$ -GP/HA solution

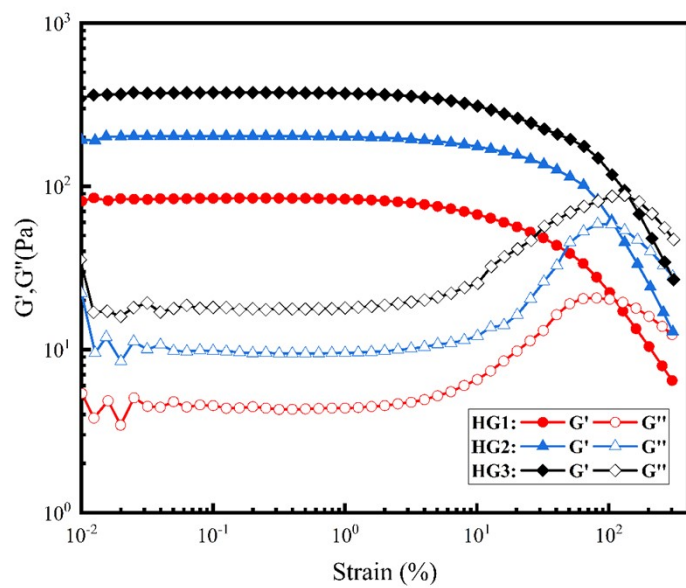


Figure S1. The rheological curves of HG<sub>1</sub>, HG<sub>2</sub> and HG<sub>3</sub> in the strain mode.

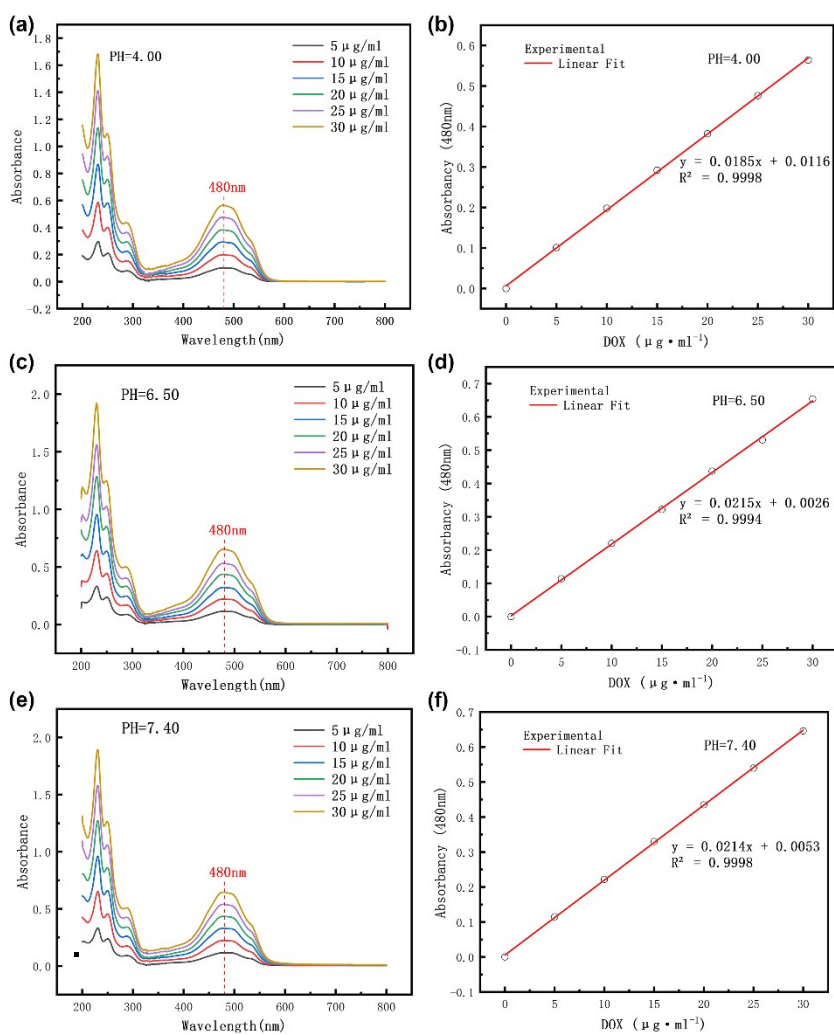


Figure S2. UV absorption spectra of DOX in PBS at different pH (a, c, e) and calibration curves for absorbance of DOX concentration at 480 nm (b, d, f). Figure b) pH=7.40, the calibration curve equation is  $y=0.0214x+0.0053(R^2=0.9998)$ ; d) pH=6.50, the calibration curve equation is  $y=0.0215x+0.0026(R^2=0.9994)$ ; f) pH=4.00, the calibration curve equation is  $y=0.0185x+0.0116$  ( $R^2=0.9998$ )

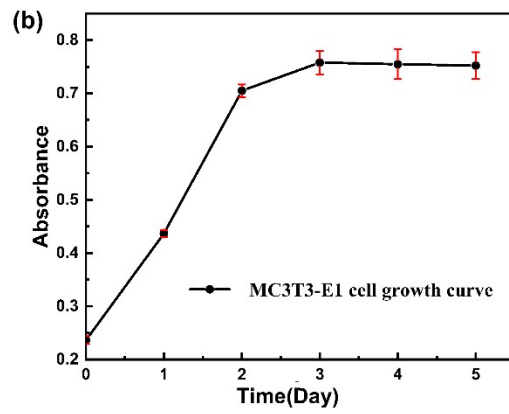
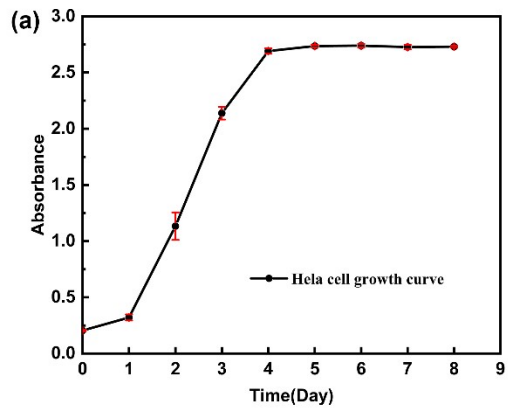


Figure S3. a) HeLa cell and b) MC3T3-E1 cell growth curve

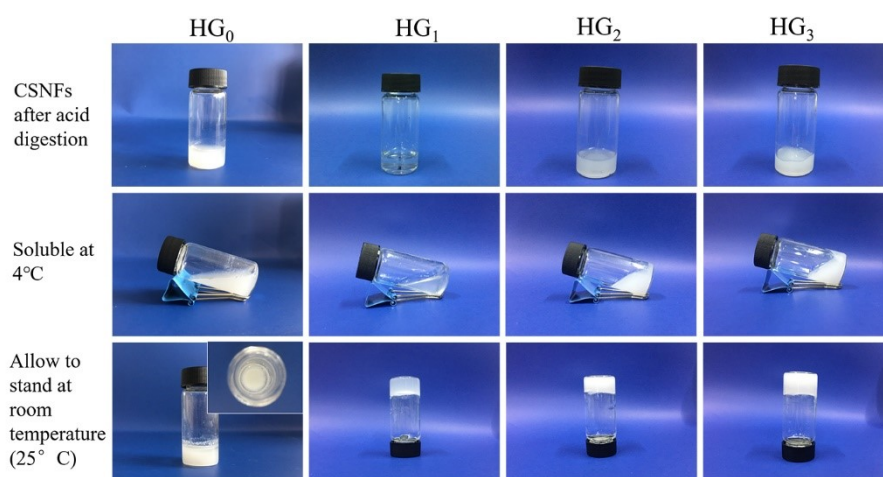


Figure S4. Gelation diagram of different CSNFs concentration gel system from sol to gel

Table S2. Fitting parameter values of different models for DOX release in HG<sub>1</sub> at different pHs

pH	parameter values	Zero-order	First-order	Huguchi	Ritger-Peppas
		$F=kt+b$	$F=1-b(e^{-kt})$	$F=kt^{1/2}+b$	$F=kt^n+b$
pH=7.4	k	0.1804	0.0027	2.04218	37758
	b	23.326	76.96	19.02914	-37739
	n	-	-	-	0.0000967
	R <sup>2</sup>	0.3172	0.331	0.52815	0.8575
pH=6.5	k	0.7659	0.0456	8.04516	7128.1
	b	44.432	70.867	28.77339	-7095.1
	n	-	-	-	0.0018
	R <sup>2</sup>	0.5197	0.743	0.74538	0.9367
pH=4.0	k	0.8107	0.2441	8.73221	-196.23
	b	61.874	82.973	44.40403	245.32
	n	-	-	-	-0.0806
	R <sup>2</sup>	0.4501	0.9914	0.67863	0.9413

Table S3 Fitting parameter values of different models for DOX release in HG<sub>2</sub> at different pHs

pH	parameter values	Zero-order	First-order	Huguchi	Ritger-Peppas
		$F=kt+b$	$F=1-b(e^{-kt})$	$F=kt^{1/2}+b$	$F=kt^n+b$
pH=7.4	k	0.19495	0.00276	2.14744	35811.27
	b	20.7529	79.55177	16.33363	-35794.66
	n	-	-	-	0.000105
	R <sup>2</sup>	0.36474	0.37998	0.58059	0.90088
pH=6.5	k	0.56253	0.01876	6.10135	73516.64325
	b	42.58558	62.97613	30.28787	-73484.56193
	n	-	-	-	0.000139
	R <sup>2</sup>	0.42566	0.50652	0.65084	0.928005
pH=4.0	k	0.95361	0.1512	9.9833	773.849
	b	50.6603	87.55781	31.30365	-737.227
	n	-	-	-	0.01957
	R <sup>2</sup>	0.53217	0.97723	0.75806	0.93376

Table S4 Fitting parameter values of different models for DOX release in HG<sub>3</sub> at different pHs

pH	parameter values	Zero-order	First-order	Huguchi	Ritger-Peppas
		$F=kt+b$	$F=1-b(e^{-kt})$	$F=kt^{1/2}+b$	$F=kt^n+b$
pH=7.4	k	0.21369	0.00302	2.38584	35039.1874
	b	19.17771	81.19365	14.22419	-35024.677
	n	-	-	-	0.000119
	R <sup>2</sup>	0.33966	0.35545	0.55029	0.85728
pH=6.5	k	0.56661	0.01268	5.96334	8256.11655
	b	29.04593	74.63911	17.41417	-8235.64359
	n	-	-	-	0.00114
	R <sup>2</sup>	0.51258	0.59586	0.73794	0.93494
pH=4.0	k	0.82562	0.12901	8.72524	31683.13
	b	50.86211	82.25877	33.76434	-31645.25
	n	-	-	-	0.0004399
	R <sup>2</sup>	0.50453	0.88579	0.73237	0.95005