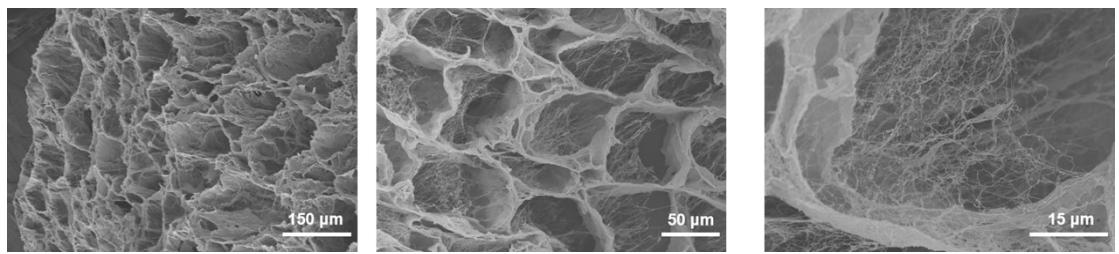


## Supporting information

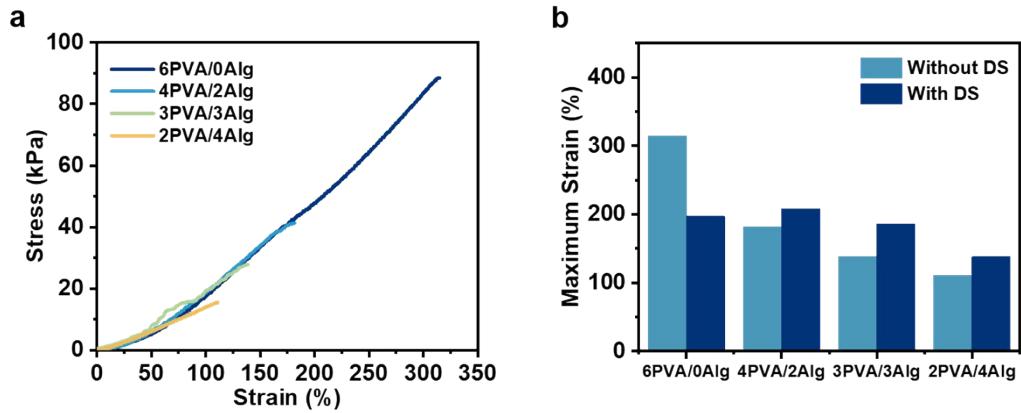
### Hierarchical hydrogel scaffolds with clustered and oriented structure

Jian Cheng<sup>1,2</sup>, Jiangtao Xue<sup>2,4</sup>, Yuan Yang<sup>2</sup>, Dengjie Yu<sup>2,5</sup>, Zhuo Liu<sup>2,3\*</sup>, Zhou Li<sup>1,2\*</sup>

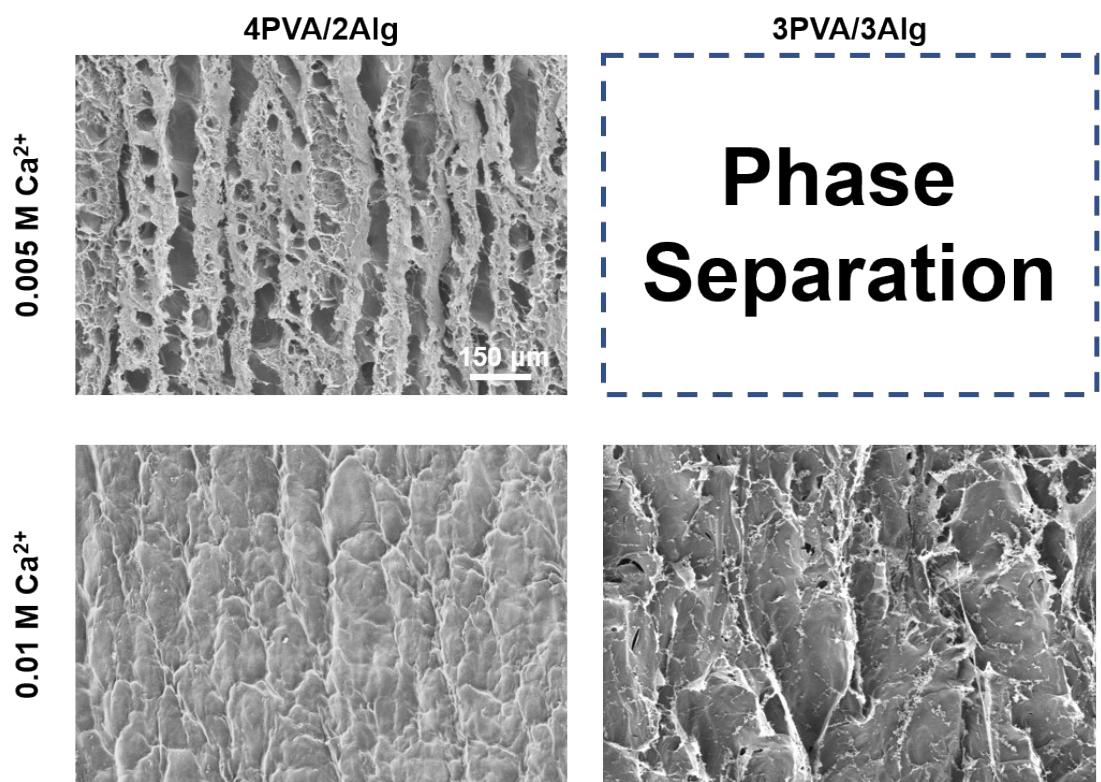
\*Corresponding authors. Email: [liuzhuo@buaa.edu.cn](mailto:liuzhuo@buaa.edu.cn) (Z. Liu); [zli@binn.cas.cn](mailto:zli@binn.cas.cn) (Z. Li)



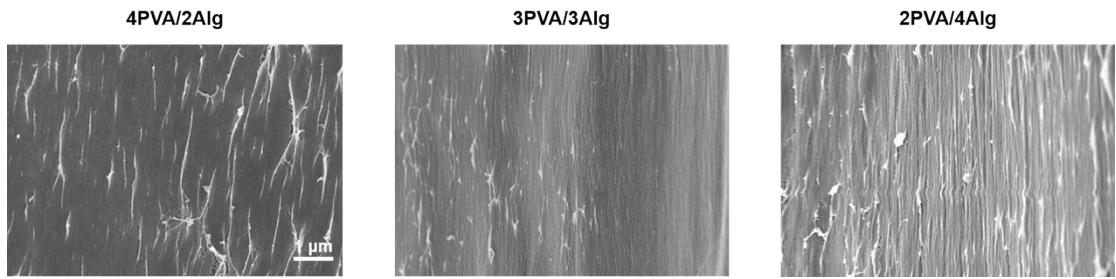
**Fig. S1** SEM images of cross sections of COS-3PVA/3Alg hydrogels.



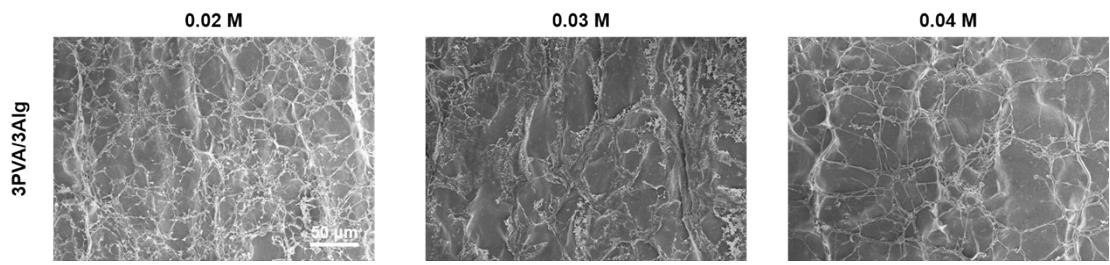
**Fig. S2** **a**, Tensile stress-strain curve of COS-PVA/Alg hydrogels without DS in different polymer proportions. **b**, Maximum Strain of COS-PVA/Alg hydrogels with and without DS in different polymer proportions.



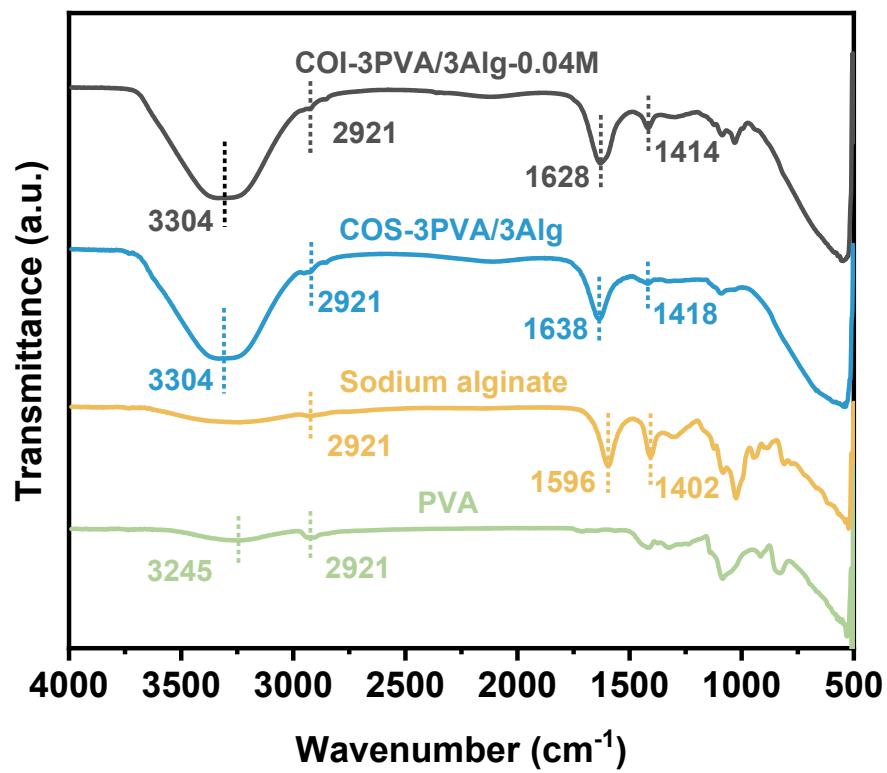
**Fig. S3** SEM images showing the structure of COI-PVA/Alg hydrogels crosslinked with 0.005 M and 0.01 M  $\text{Ca}^{2+}$ .



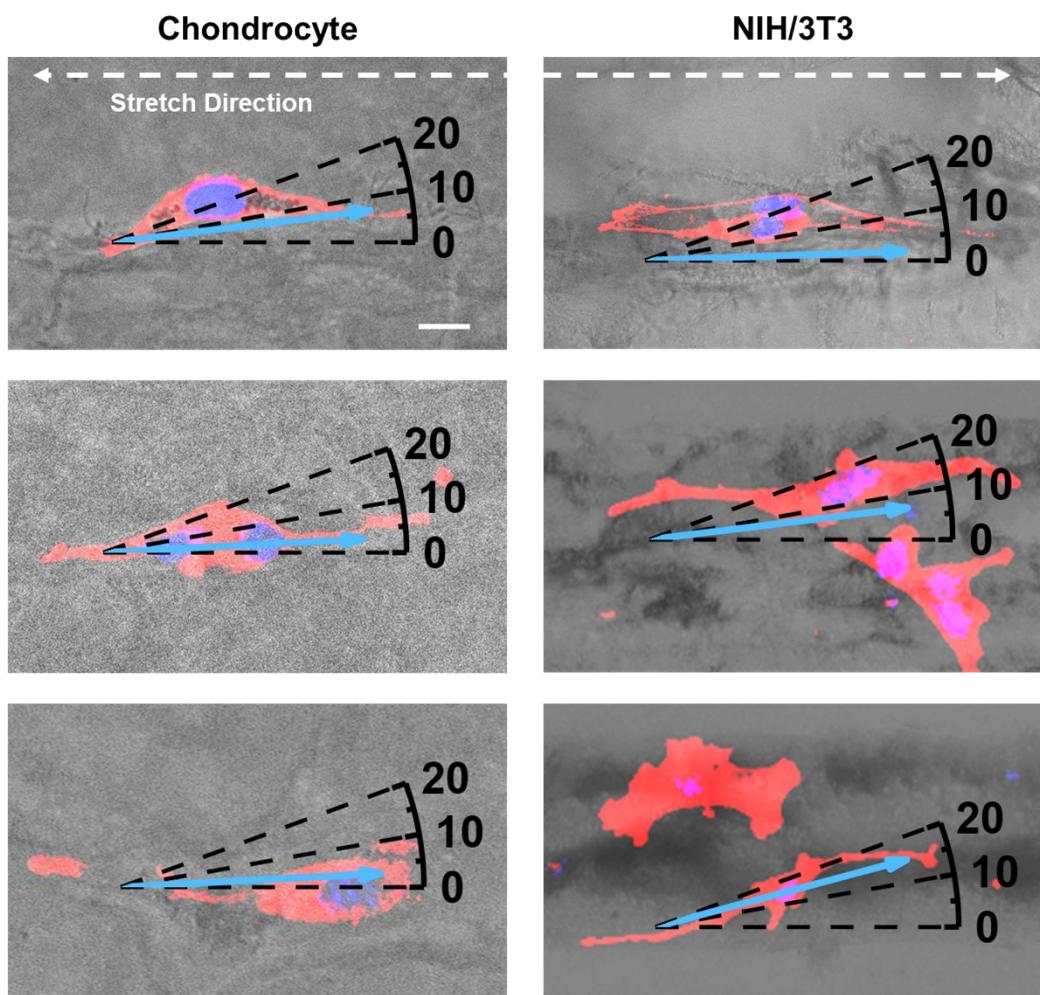
**Fig. S4** SEM images showing the clustered and oriented structure of COI-PVA/Alg hydrogels crosslinked with 0.04 M  $\text{Ca}^{2+}$ .



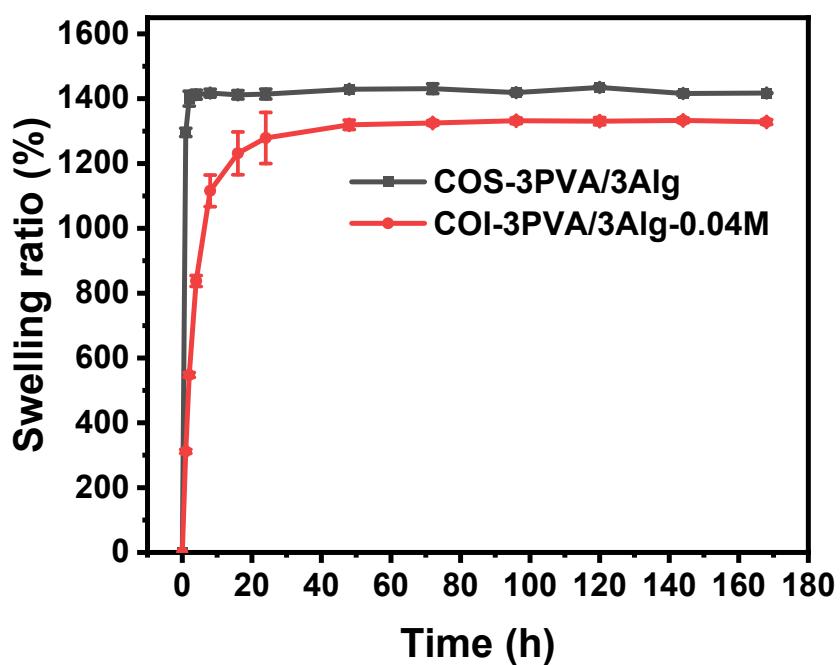
**Fig. S5** SEM images of 3PVA/3Alg hydrogels crosslinked with  $\text{Ca}^{2+}$  without DS.



**Fig. S6** Typical FT-IR spectra of COI-3PVA/3Alg-0.04 M hydrogel, COS-3PVA/3Alg hydrogel, sodium alginate and PVA.

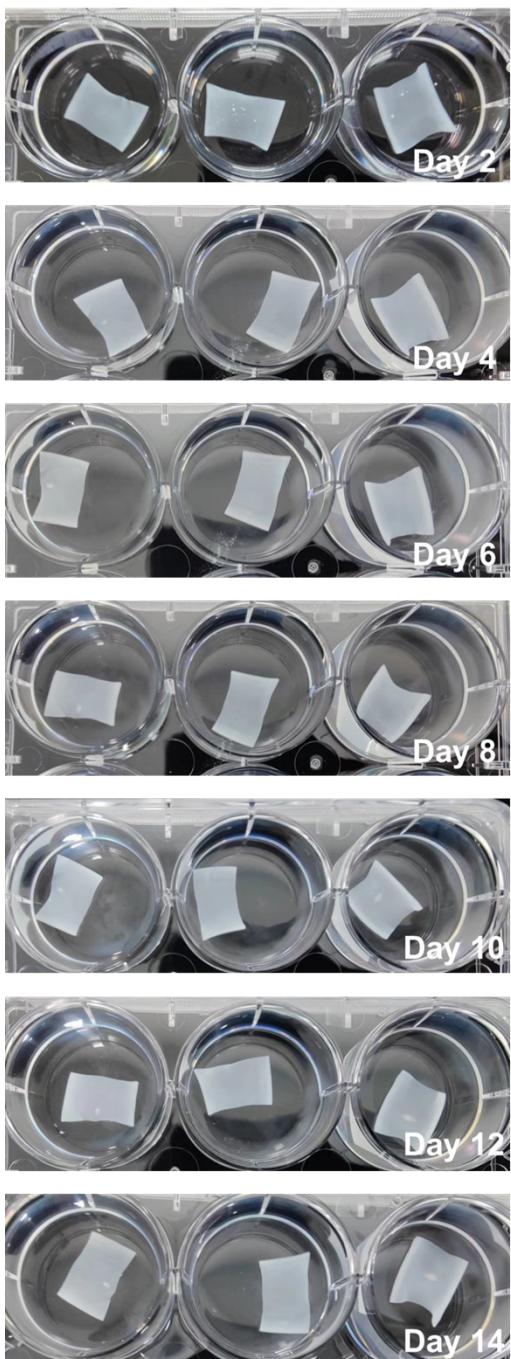


**Fig. S7** Typical oriented fibroblasts on COS-3PVA/3Alg hydrogels and chondrocytes on COI-3PVA/3Alg-0.04 M hydrogels.

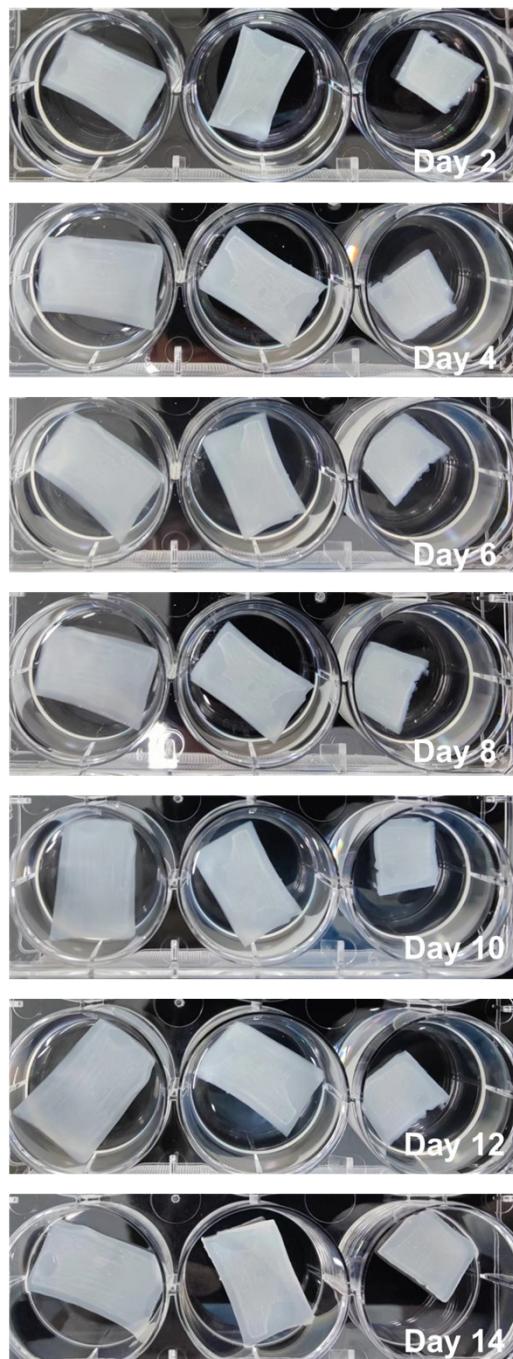


**Fig. S8** Swelling properties of COS-3PVA/3Alg hydrogels and COI-3PVA/3Alg-0.04 M hydrogels in PBS.

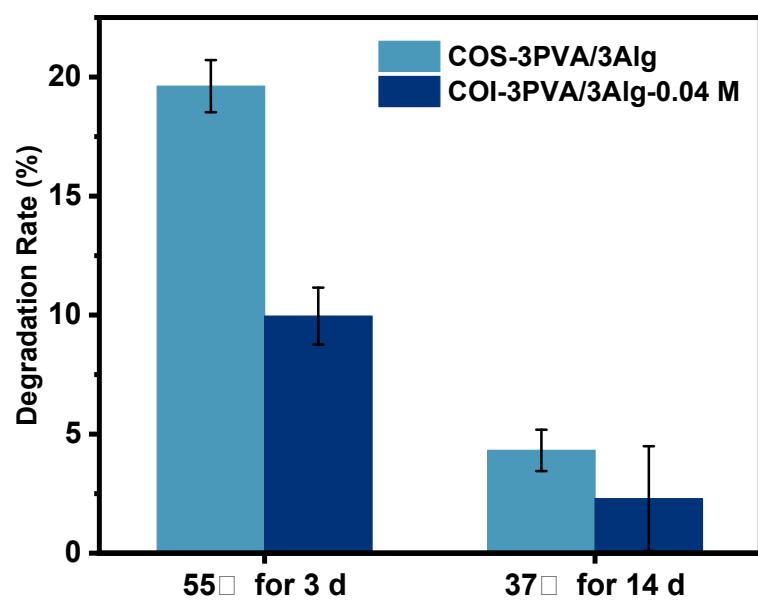
**COS-3PVA/3Alg**



**COI-3PVA/3Alg-0.04M**



**Fig. S9** Images of COS-3PVA/3Alg hydrogels and COI-3PVA/3Alg-0.04 M hydrogels degradation at 37°C for 14 days.



**Fig. S10** Degradation rate of COS-3PVA/3Alg and COI-3PVA/3Alg-0.04 M at 55°C for 3 days and 37°C for 14 days, respectively.

**Table. S1** Mechanical Properties and Microstructure Comparison of Various Hydrogels

Ref No.	Materials	Methods	Young Modulus	Water Content	Biocompatibility	Microstructure
Our work	PVA/Alg	Direction freezing; Drying under stretch	50 kPa-20 MPa	60%-95%	Good	Hierarchical; Oriented and Clustered
<sup>1</sup>	Silk	Lyophilization	2.05 MPa	--	Good	Aligned microfibers
<sup>2</sup>	PVA	Freeze-thawed; salting out	24-2500 kPa	85%	--	Continuous networks of nanofibrils
<sup>3</sup>	HPC/PVA	Freeze-thawed	15-900 kPa	--	--	Porous wrinkle structure
<sup>4</sup>	NaCl/SA/ PAM	One-pot free-radical polymerization	0.75 MPa	--	--	Supramolecular nanofibrils
<sup>5</sup>	AMD-QCS	UV-polymerization; One-pot method	1.5 MPa	--	Good	Homogeneous pore microstructure
<sup>6</sup>	Al-NC	UV-polymerization	52.3 MPa	62.3%	Poor	Lotus-leaf-like microstructure
<sup>7</sup>	B-DN	UV-polymerization	2 MPa	42%	--	Isotropic structure
<sup>8</sup>	PVA/PA M/NaCl	One-pot method	595-872 kPa	--	--	3D porous and dense microstructure

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