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Supplementary information

Natural Polymer Derived Hydrogel Bioink with Enhanced Thixotropy Improves Printability and Cellular Preservation in 3D Bioprinting

Rongwei Cui[1 #], Sumei Li[1 #], Taiyi Li[1 #], Xue Gou[2], Tao Jing [2], Guowei Zhang[1, 2], Xiong Xiong[1], Guihua Wei[1], Zhongmin Jin[3], Xiong Xiong[1]*, Shuxin Qu[2]*

1. School of Life Science and Engineering, Southwest Jiaotong University, Chengdu 610031, Sichuan, China

2. Key Laboratory of Advanced Technologies of Materials, Ministry of Education, School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, Sichuan, China

3. School of Mechanical Engineering, Southwest Jiaotong University, Chengdu 610031, Sichuan, China

*Corresponding author: Prof. Shuxin Qu, Tel: +86-28-87601897, Fax: +86-28-87601371, E-mail: qushuxin@swjtu.edu.cn

*Corresponding author: Dr. Xiong Xiong, Tel: +86-28-87601897, Fax: +86-28-87601371, E-mail: xiongxiong@home.swjtu.edu.cn

[#] These authors contributed equally to this work.

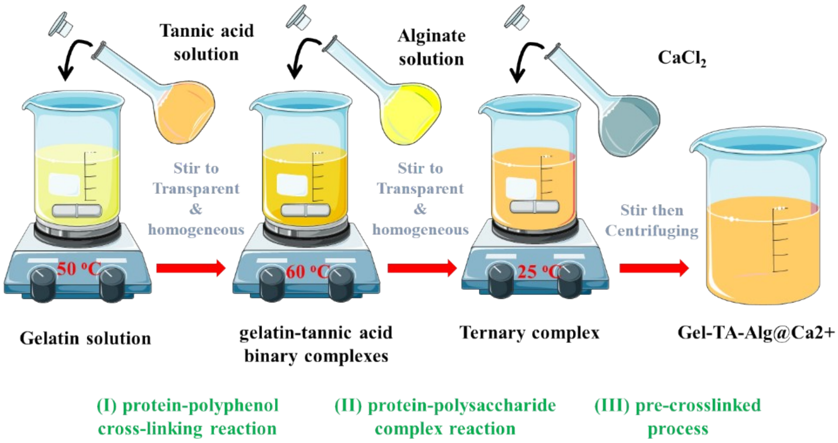

Fig. S1. Schematic of synthesis process of Gel-TA-Alg @Ca^{2+}.

Table S1 Detailed information of the printing parameters

Term	Parameter
Nozzle diameter (mm)	0.6
Extrusion width (mm)	0.72
Length* width * height (m^3)	30 *30 *30
Interior fill percentage (%)	10
X/Y axis movement speed (mm/min)	1500
Outline under speed (%)	80

Table S2 FTIR spectra characteristics of gelatin, tannic acid (TA), gelatin-TA composite (Gel-TA), sodium alginate (Alg) and Gel-TA-Alg composite

Components	Wavenumber (cm^{-1})	Assignment
Gelatin	3411	Amide A the partially overlapped stretching vibrations of O-H and N-H groups
	2937	Amide B The free amino acid O-H groups
	1654	Amide I stretching of the C=O
	1544	Amide II stretching of the N-H
	1240	Amide III stretching of the C-N and N-H groups
TA	3408	stretching vibrations O-H
	1716	stretching vibration of C=O groups of aromatic esters
	1612	aromatic C=C stretching
	1448	aromatic C-C stretching
	1323	bending vibrations for O-H
	1176	stretching vibrations for C-O
	1031	stretching vibrations C-O of polyols
	760	stretching vibrations C-H out-of-plane deformation of benzene ring
Gel-TA	3413	Amide A
	2937	Amide B
	1654	Amide I
	1541	Amide II
	1240	Amide III
Alg	3431	stretching vibrations O-H
	1611	carboxylic acid salts (RCOO-)
	1418	the C-O bond of the acid group (RCOOH)
	1029	the vibrational stretch of the C-O and C-C of the pyranose ring
Gel-TA-Alg	3418	stretching vibrations O-H
	1031	carboxylic groups (-COO)

Table S3 Different contents of protein secondary structures before and after crosslinking

Protein secondary structure	Gelatin (%)	Gel-TA (%)
Random coil	16.8	11.9
β-sheet	25.6	19.1
α-helix	11.75	9.3
β-corner	37.0	48.5

Table S4 Detailed information for characterizing of injectability

Group	Nozzle shape	Needle diameter(μm)	The needle type(G)
Co N	Cone	410	22
Cy N1	cylinder	410	22
Cy N2	cylinder	260	25
Cy N3	cylinder	600	20

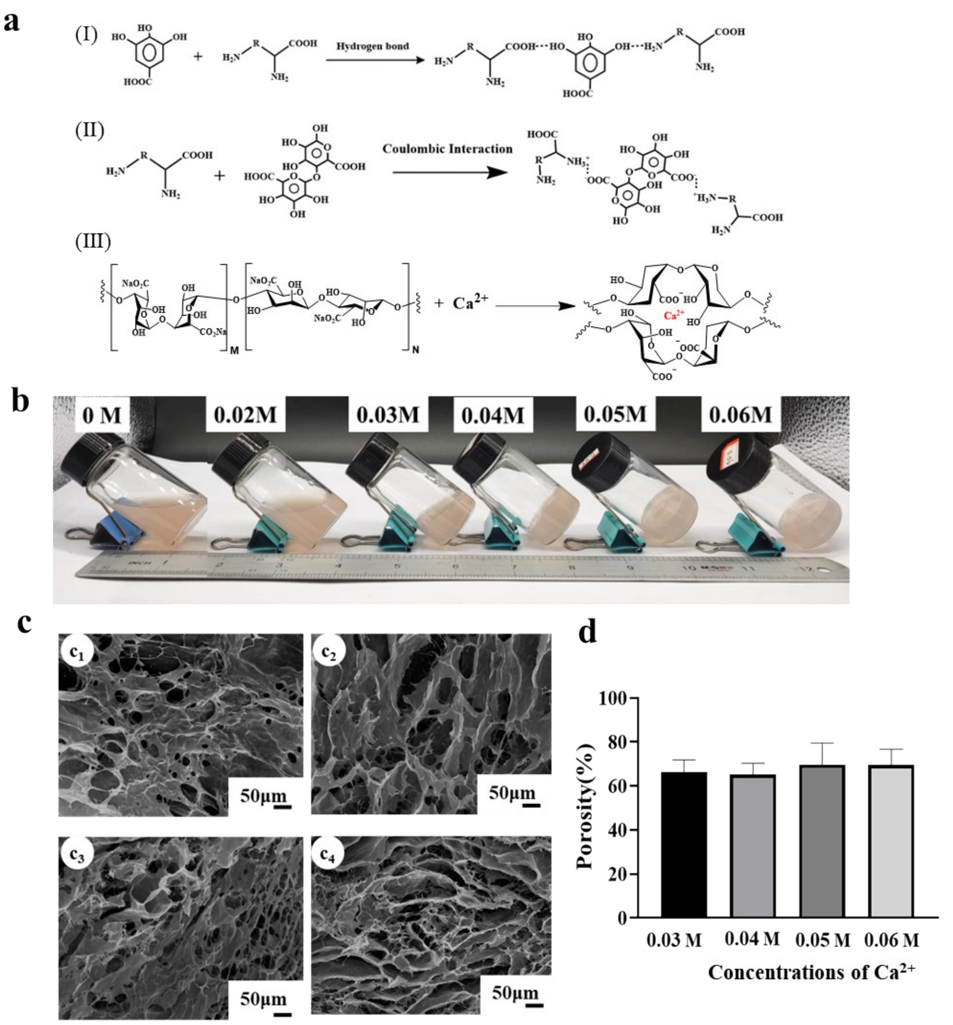

Fig. S2. Synthesis and characterization of Gel-TA-Alg@Ca^{2+}. (a) The hypothesized chemical reaction equation of Gel-TA-Alg@Ca^{2+} according to the infrared results and literatures；(b) Images of Gel-TA-Alg@Ca^{2+} with different concentrations of Ca^{2+} before and after gelling; (c) The micromorphology and porosity of Gel-TA-Alg@Ca^{2+} with pre-crosslinking of different concentrations of Ca^{2+}; (d) Porosity of hydrogels with different Ca^{2+}.

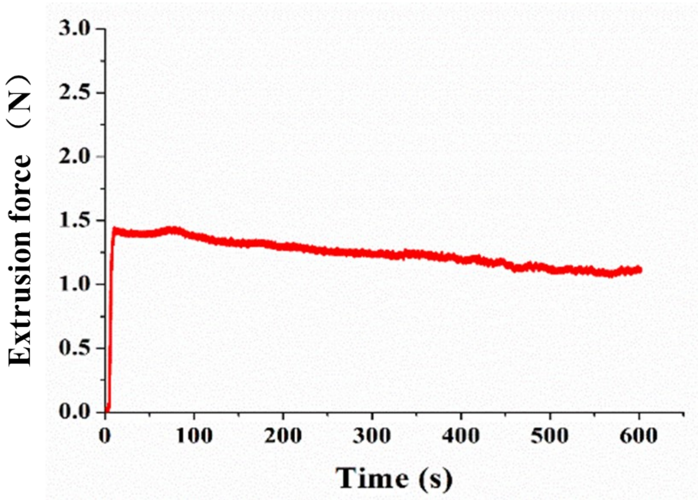

Fig. S3 The curve of extrusion force versus time to extrude water at the speed of 1.5 mm/s by a needle with the diameter of 410 µm.

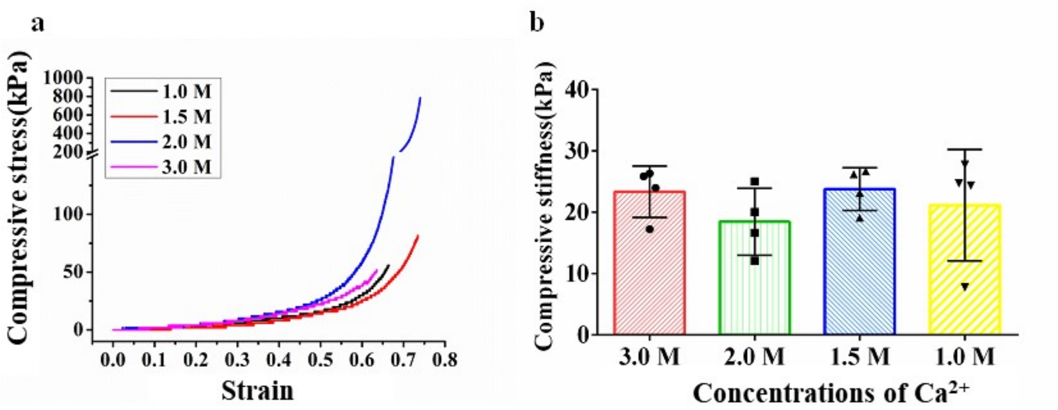

Fig. S4 The mechanical properties of Gel-TA-Alg@Ca^{2+} using a universal mechanical testing machine. (a) Stress-strain curves of Gel-TA-Alg@Ca^{2+} after post-crosslinking with different concentrations of Ca^{2+} for 24 h；(b) Compression modulus results of 5%-15% of Gel-TA-Alg@Ca^{2+} in the linear strain region.