Supporting Information

Injectable citrate-based polyurethane-urea as a tug-of-war-inspired bioactive self-expansive and planar-fixing screw augmented bone-tendon healing

Experimental Part

Acid value measuring method

The acid value measuring method is shown in below: a certain amount of citrate-based polyol was dried and weighed (the weight was denoted as m), dissolved in toluene/ethanol (v/v = 2/1) solution, and several drops of phenolphthalein solution in ethanol (10 g/L) was added. Then KOH solution in ethanol (0.1 mol/L) was used to titrate the citrate-based polyol solution while stirring, until the solution turned slightly red and the color was kept for at least 30 seconds. Recorded the volume of KOH/ethanol solution consumed (V_1). A blank experiment was also set to titrate pure phenolphthalein containing toluene/ethanol solution, the volume of KOH/ethanol solution consumed was recorded as V_2. The concentration of KOH in ethanol solution was denoted as C. The acid value was calculated using the following equation.

$$\text{Acid value (mg KOH/g)} = (V_1\text{-}V_2) \times C \times 56.1/m$$

Quantitative test of ALP

The cells were lysed in RIPA (Radio-Immunoprecipitation Assay) lysis buffer (Beyotime, China) for 30 minutes, and centrifuged at 4 ℃ and 10000 rpm for 10 minutes. The supernatant was collected and ALP activity was measured according to the instructions. Meanwhile, the total protein content of each sample was measured with the bicinchoninic acid (BCA) protein assay kit (Beyotime, Shanghai, China) to normalize the ALP activity at the same total protein level, n = 3.

Table S1. Primer sequences for the PCR analysis.

Gene name	Primer Sequence	
ALP	F	5'-ATGGCTCACCTGCTTCACG-3'
	R	5'-TCAGAACAGGGTGCGTAGG-3'
Runx2	F	5'-AGACCAGCAGCACTCCATAT-3'
	R	5'-CTCATCCATTCTGCCGCTAGA-3'
OCN	F	5'-AGGGCAGTAAGGTGGTGAAT-3'
	R	5'-GCATTAACCAACACGGGGTA-3'
Col1	F	5'-AACAAGGGAGGAGAGAGTGC-3'
	R	5'-AGTCTCTTGCTTCCTCCCAC-3'
SCX	F	5'-CAGCCAAGAGGTGATGCCACTAG-3'
	R	5'-GTGCTCAGATCAGGTCCAAGGTG-3'
Tnmd	F	5'-CCAGACAAGCAAGCGAGGAAGAC-3'
	R	5'-ATGACTCGACCTCCTTGGTAGCAG-3'
TnC	F	5'-CGGCACCTGCTACTGTGAAG-3'
	R	5'-CCATGGTGGTGACAGTCTGC-3'

Table S2. The grouping and corresponding components of iCSP-Scr study under different sealing conditions.

	Group	2 mL Tube	Component
1	Completely sealed group (**Sealed**)	Closed lid	0.5g CPU-NCO + 0.1g PC-HAp + 200μL water + 0.05g porogen
2	Incomplete sealed group (**Holes**)	Closed lid + 3 holes in the fixed positions	0.5g CPU-NCO + 0.1g PC-HAp + 200μL water + 0.05 g porogen
3	Completely Open group (**Open**)	Opened lid	0.5g CPU-NCO + 0.1g PC-HAp + 200μL water + 0.05g porogen
4	Squeezed group (**Squeezed**)	Closed lid + 3 holes in the fixed positions	Double amount. 1g CPU-NCO + 0.2g PC-HAp + 400μL water + 0.1g porogen

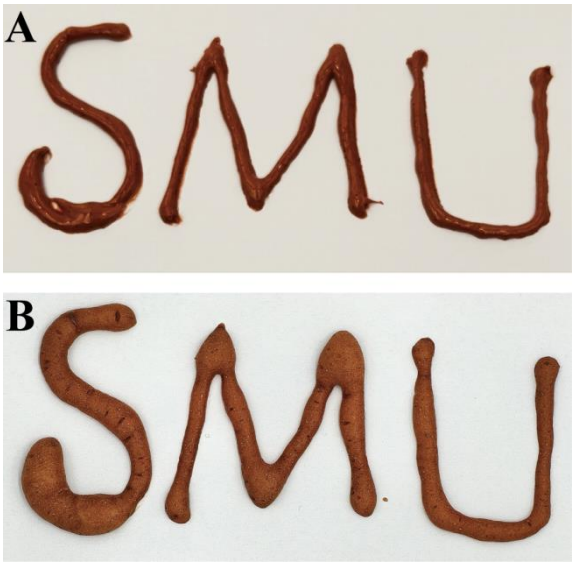

Fig. S1. The results before and after expansion of "SMU" written with the injectable iCSP-Scr. The process of writing "SMU" with the injectable iCSP-Scr can be seen in the video (Video S1).

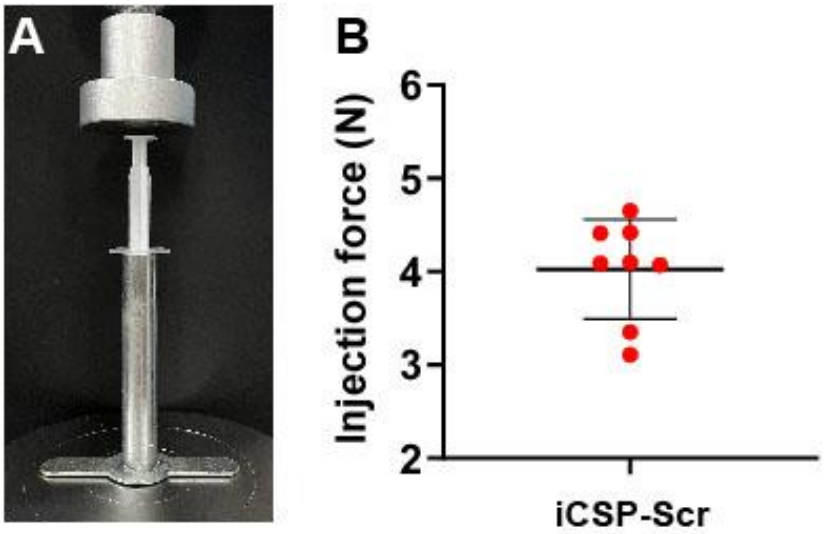

Fig. S2. The device (A) and results (B) of injection force test.

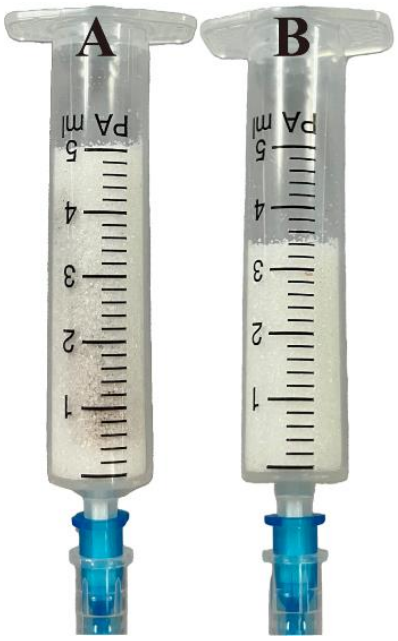

Fig. S3. The volume of crosslinked iCSP-Scr detected with 5mL syringes and salt particles. A, fill the surrounding area of the solid material with salt particles until the scale value of 5 mL. B, the salt particles were collected in another new syringe and the volume scale of the salt (V_{salt}) was recorded. $V_{crosslinked\ iCSP\text{-}Scr} = 5\text{-}V_{salt}$.

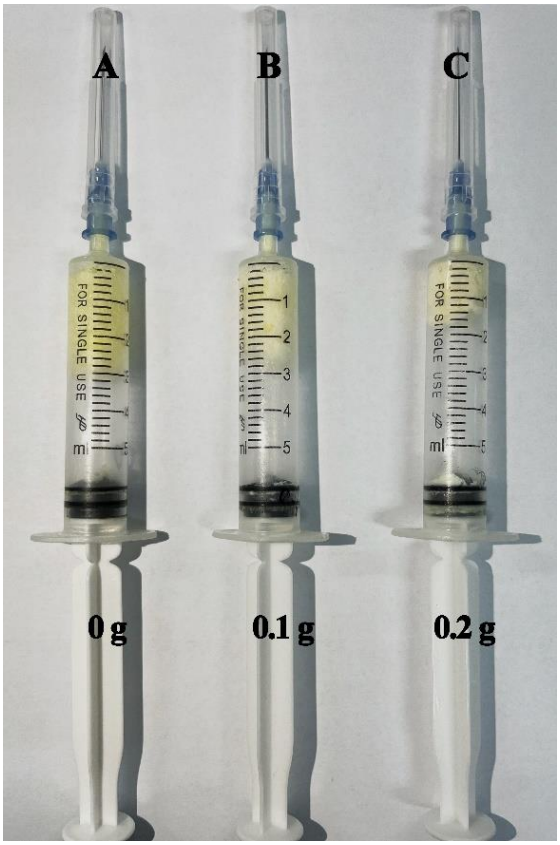

Fig. S4. The results of CPU-NCO (0.5 g), H_2O (200 μL), and HAp (0 g, 0.1 g and 0.2 g) crosslinked and expanded in 5 mL syringes.

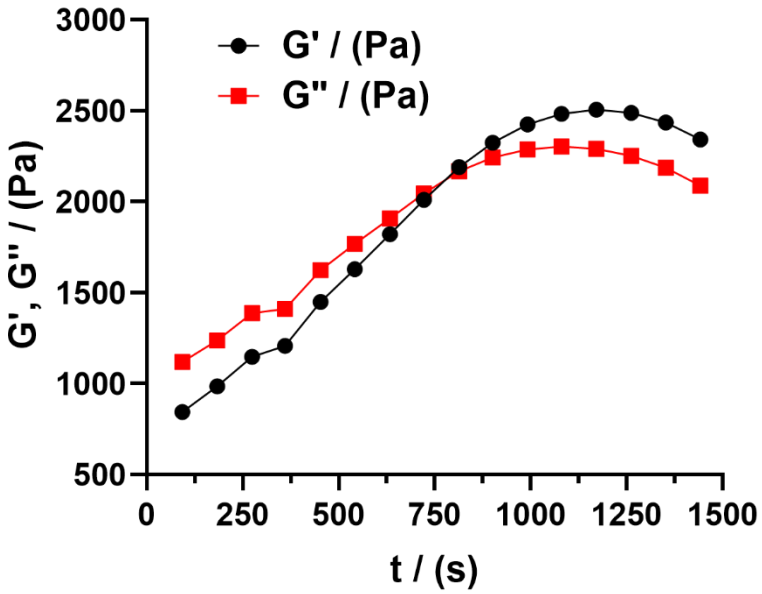

Fig. S5. The rheological result of iCSP-Scr.

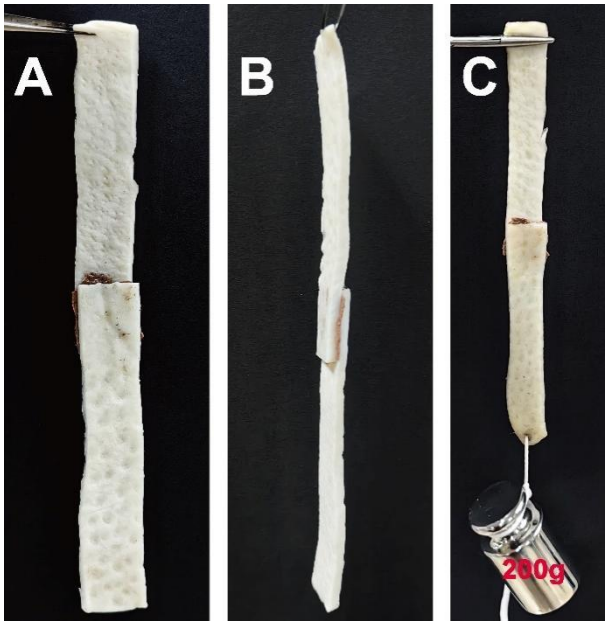

Fig. S6. The tissue adhesion performance of iCSP-Scr evaluated by lap-shear test against wet porcine skin.

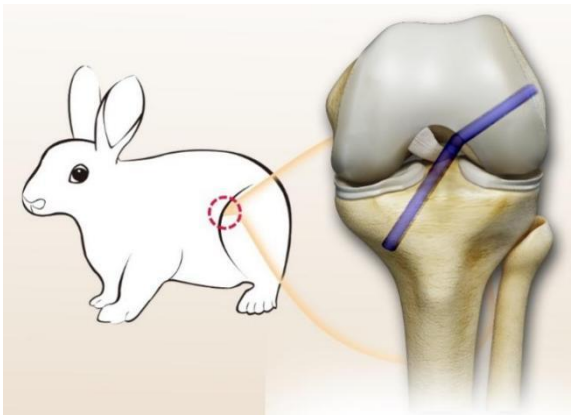

Fig. S7. The schematic diagram of ACL reconstruction in rabbits.

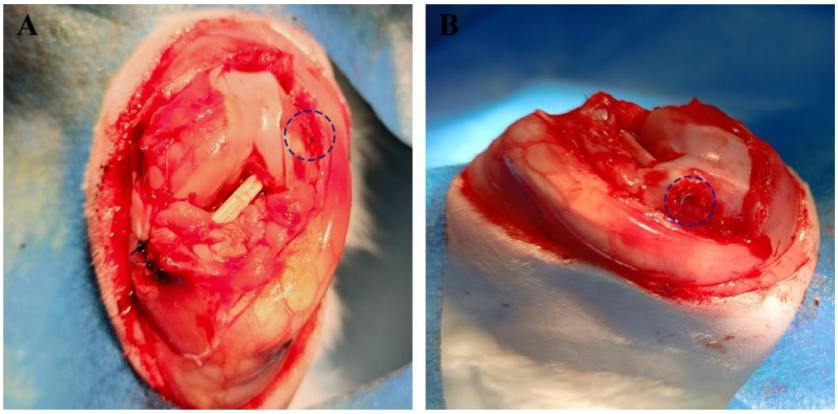

Fig. S8. In the control group of rabbit ACL reconstruction, ACL was fixed on the tissue near the opening of the tibial tunnel with knots, and on the femur with titanium screws. The blue dashed circle represents the position of the titanium screw.

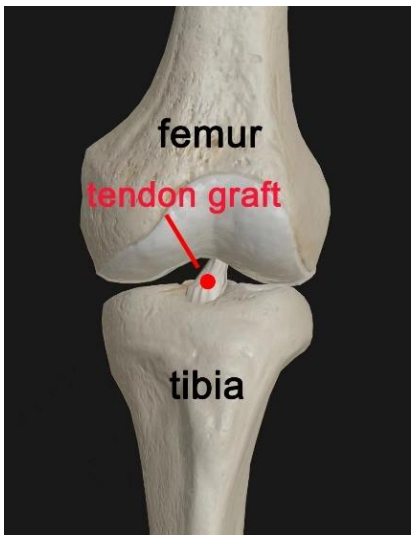

Fig. S9. The Schematic diagram of the femur-tendon graft-tibia complex.

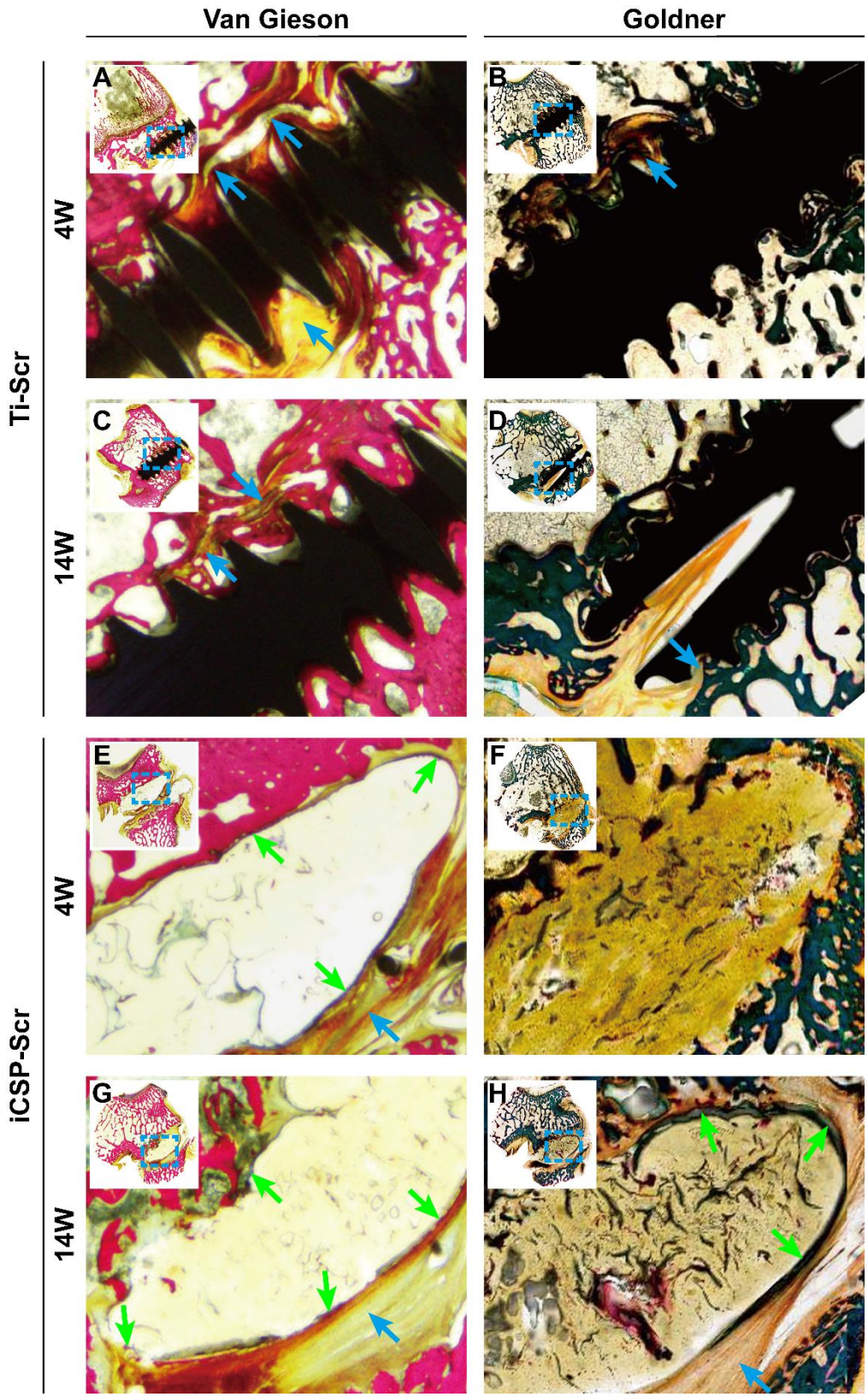

Fig. S10. The interface between titanium screws or iCSP-Scr and bone-tendon. Each image is the local magnified result of the dashed square box in its upper left corner. The blue arrow represents tendon. The green arrow represents the new bone formation.