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Mussel Byssus Cuticle-Inspired Ultrastiff and Stretchable Triple-crosslinked Hydrogels

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Content

1. Supporting Tables

Table S1. The pH values of solutions in the formation of TC hydrogels.

Metal ion	Sample name	0 h*	12 h	24 h
Cu(Ⅱ)	TC100-Cu	3.55	1.92	1.91
	TC200-Cu	3.26	1.65	1.66
Fe(Ⅲ)	TC100-Fe	1.56	1.36	1.33
	TC200-Fe	1.30	1.10	1.08
Al(Ⅲ)	TC100-Al	3.32	3.28	3.28
	TC200-Al	3.13	3.11	3.10
Zr(Ⅳ)	TC100-Zr	0.80	0.80	0.81
	TC200-Zr	0.52	0.50	0.50

* pH of initial metal salt solutions before soaking

Table S2. The pH values of solutions during the annealing process.

Sample name	Fresh Water	After 1st day's annealing	After 2nd day's annealing	After 3rd day's annealing	After 4th day's annealing	After 5th day's annealing
TC100-Cu	6.35	2.67	3.85	4.29	5.07	5.40
TC200-Cu	6.35	2.26	3.16	4.44	4.84	4.95
TC100-Fe	6.35	2.70	4.18	4.57	4.97	5.09
TC200-Fe	6.35	2.52	3.81	4.05	4.20	4.32
TC100-Al	6.35	3.51	4.70	5.20	5.05	5.11
TC200-Al	6.35	3.83	4.15	5.25	4.89	5.15
TC100-Zr	6.35	2.19	3.74	4.37	5.18	5.50
TC200-Zr	6.35	1.96	3.49	4.75	5.02	5.11

Table S3. The weight percentages of PAAm, metal ions, water, and TA in various TC hydrogels.

Ion type	Sample name	PAAm (wt. %)	M^{n+} (wt. %)	H_2O (wt. %)	TA (wt. %)
-	DC100	24.65±2.57	-	35.85±2.10	39.50±2.30
	DC200	21.78±3.01	-	36.24±2.98	41.98±3.10
Cu(Ⅱ)	TC100-Cu	33.01±1.86	0.38±0.10	33.02±3.07	33.16
	TC200-Cu	28.83±2.45	0.48±0.11	32.54±2.71	37.62
Fe(Ⅲ)	TC100-Fe	34.41±3.06	0.41±0.11	32.85±2.88	31.56
	TC200-Fe	30.78±1.82	0.48±0.12	31.94±2.63	35.88
Al(Ⅲ)	TC100-Al	33.47±2.37	0.27±0.09	32.89±1.86	32.31
	TC200-Al	29.18±2.23	0.35±0.10	31.54±1.49	37.54
Zr(Ⅳ)	TC100-Zr	36.91±2.09	1.91±0.14	30.60±2.78	27.60
	TC200-Zr	35.86±1.44	2.11±0.16	28.88±1.88	29.86

1. The weight percentage of PAAm was defined as:

$$W_{PAAm}(\%) = \frac{m_{PAAm}}{m_{hydrogel}} \times 100\%$$

where $m_{hydrogel}$ and m_{PAAm} were the weight of the TC hydrogel and neat PAAm aerogel samples, respectively.

2. The weight percentage of metal ion (M^{n+}) was defined as:

$$W_{M^{n+}}(\%) = \frac{m_1 - m_2}{m_{hydrogel}} \times 100\%$$

where m_1 was the metal ion weight in the original solution, and m_2 was the metal ion weight in the solution after soaking hydrogels.

3. The weight percentage of water (H_2O) was defined as:

$$W_{H_2O}(\%) = \frac{m_{hydrogel} - m_{aerogel}}{m_{hydrogel}} \times 100\%$$

where $m_{aerogel}$ was the weight of the freeze-dried aerogel samples.

4. The weight percentage of TA was defined as:

$W_{TA}(\%) = 100\%\text{-}W_{PAAm}(\%)\text{-}W_{MClx}(\%)\text{-}W_{H_2O}(\%)$

Because the weight percentage of TA in TC hydrogels couldn't be measured directly, it was calculated through subtraction.

Table S4. The comparison of the binding energy (B. E.) (eV) of metal ions in their chlorides and their corresponding TC hydrogels based on XPS characterizations.[1-8]

	Cu(Ⅱ) $2p_{3/2}$	Fe(Ⅲ) $2p_{3/2}$	Al(Ⅲ) 2p	Zr(Ⅳ) $3d_{5/2}$
B.E. of M^{n+} in chloride (eV)	935.80	711.50	74.90	183.70
B.E. of M^{n+} in TC hydrogels (eV)	933.00	710.70	74.16	182.70

2. Supporting Figures

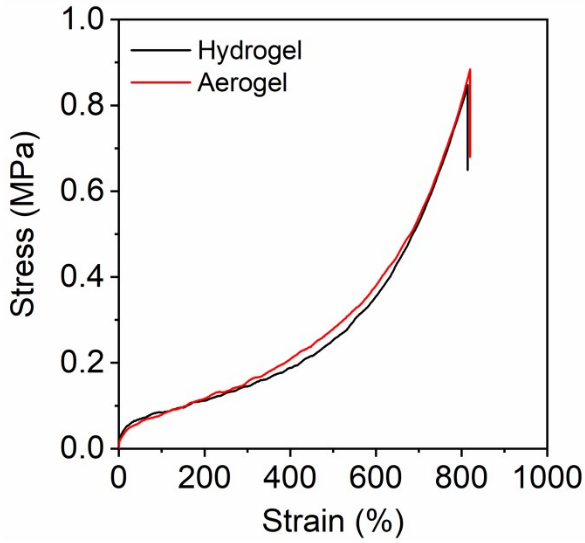


Figure S1. The comparison of tensile stress-strain curves of DC100 hydrogels produced by directly immersing the PAAm hydrogels or PAAm aerogels in TA solution.

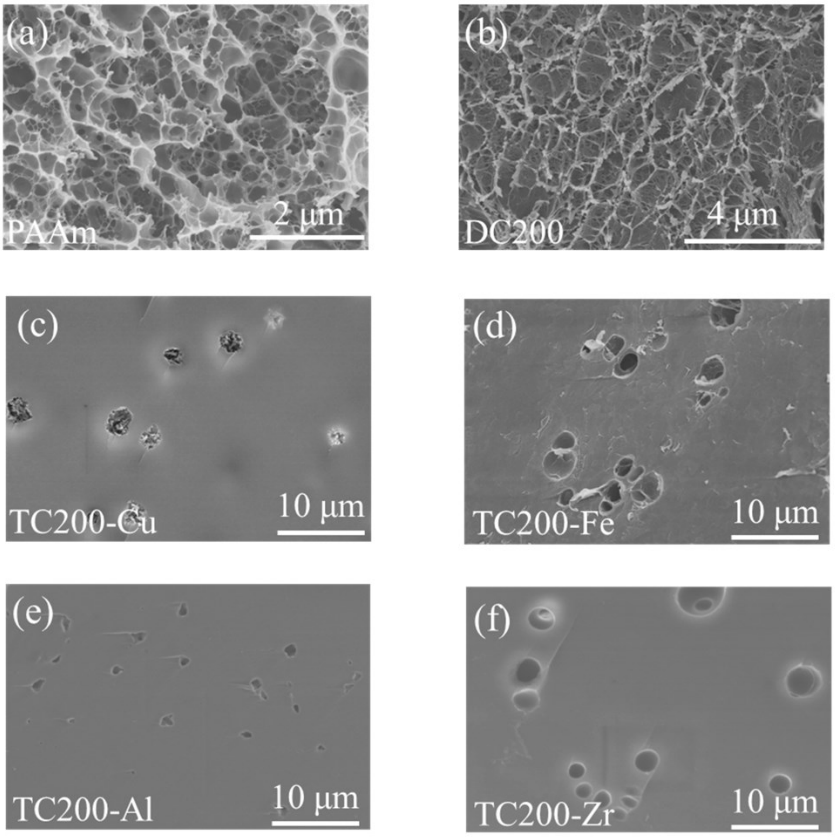


Figure S2. SEM images of the fractured sections of PAAm, DC, and TC hydrogels.

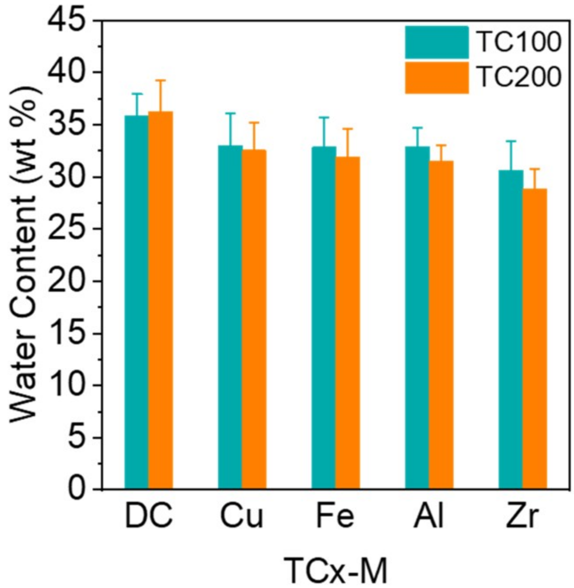


Figure S3. The water content of DC and TC hydrogels.

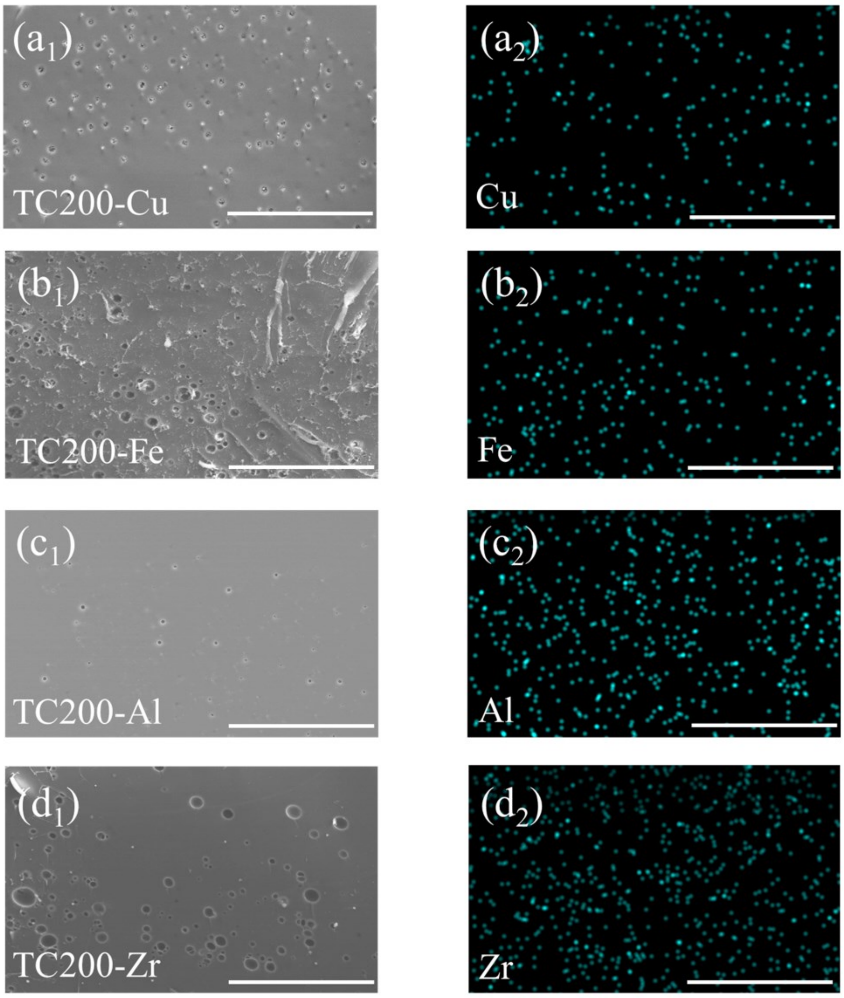


Figure S4. SEM images with related EDS mapping of the distribution of Cu(II), Fe(III), Al(III), and Zr(IV) within TC hydrogels. The scale bar is 100 µm.

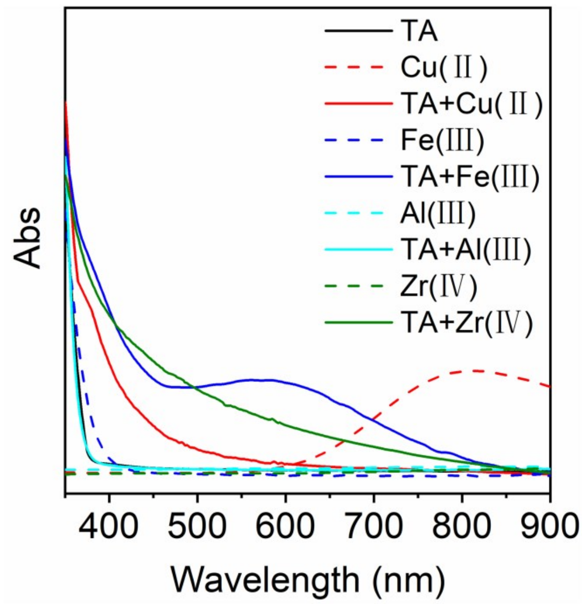


Figure S5. UV-vis absorption spectra of TA solution, different metal ion solutions, and TA-metal coordination compounds.

Figure S6. The photographs of DC100 and TC100-M hydrogels. The scale bar is 5 mm.

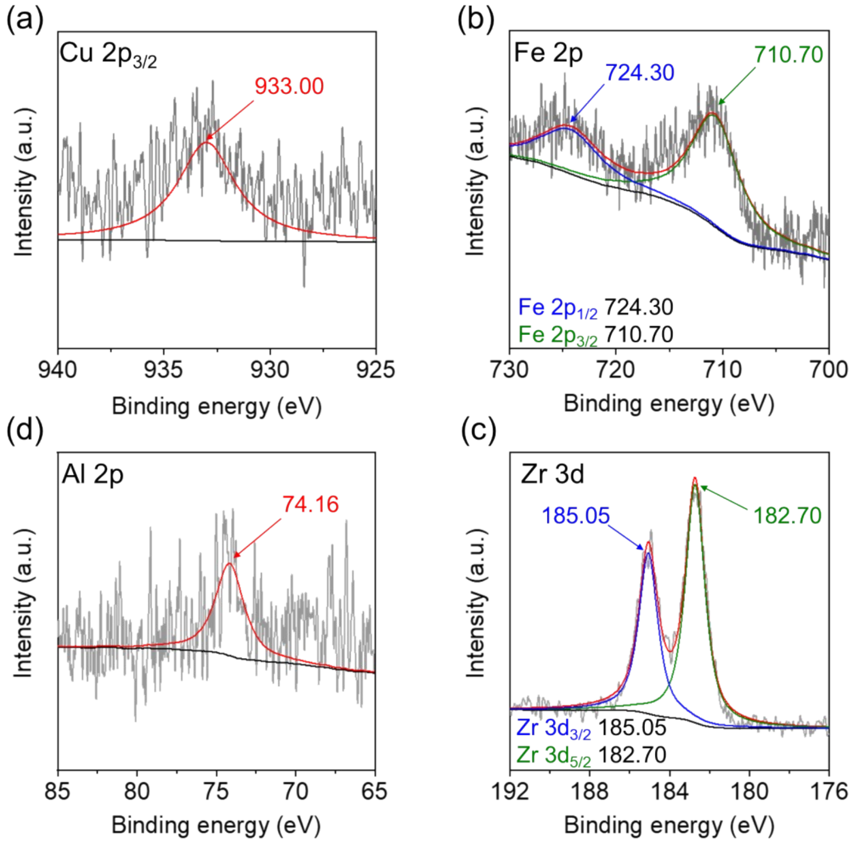


Figure S7. XPS high-resolution spectra of Cu $2p_{3/2}$ (a), Fe 2p (b), Al 2p (c) and Zr 3d (d) in TC hydrogels.

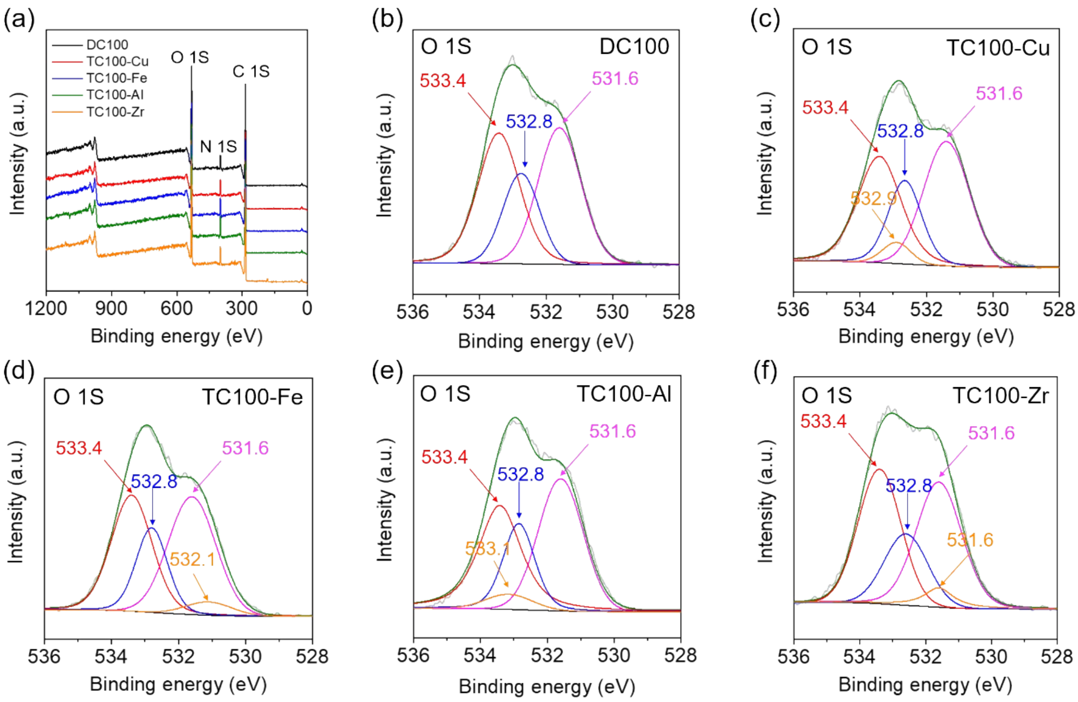


Figure S8. (a) XPS survey of DC100 hydrogels and TC100-M hydrogels. XPS high-resolution spectra of O 1S for DC100 (b), TC100-Cu (c), TC100-Fe (d), TC100-Al (e), and TC100-Zr (f) hydrogels.

The high-resolution O 1s spectra also confirmed the coordination between metal ions and TA. The high-resolution O 1s spectrum of DC100 hydrogels can be deconvoluted into three peaks, ~531.6 eV for C=O in the acrylamide group, ~532.8 eV for hydroxyl group (-OH) in TA, ~533.4 eV for C=O in TA according to literature (Figure S8b).[9-11] After coordination with metal ions, new peaks at ~532.9 eV for TA-Cu(II) (Figure S8c),[11] ~531.1 eV for TA-Fe(III) (Figure S8d),[12] ~533.1 eV for TA-Al(III) (Figure S8e)[13] and ~531.6 eV for TA-Zr(IV) (Figure S8f)[6] appeared. It should be noted that the binding energy at ~531.6 eV of TA-Zr(IV) coordination and C=O of TA is overlapped. In the O1s spectrum of TC100-Zr-S hydrogels, if the peak at 531.6 eV was assigned to C=O of TA, it's percentage will be larger than that in original DC100 hydrogels. So, we divided it into two parts, i.e. TA-Zr(IV) coordination bond and C=O of TA.

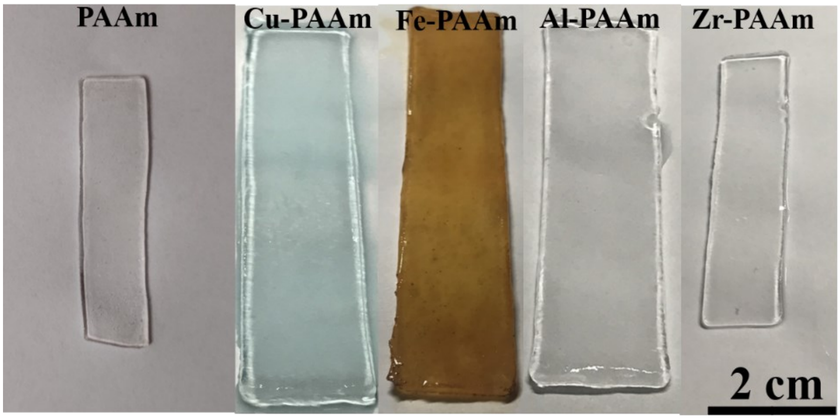


Figure S9. The photographs of neat PAAm, Cu-PAAm, Fe-PAAm, Al-PAAm, and Zr-PAAm hydrogels.

The PAAm aerogels were immersed in metal ion solutions at 60 °C for 24 h to construct M-PAAm hydrogels, keeping the concentration of metal ion solutions the same as the solutions used for TC100-M hydrogels.

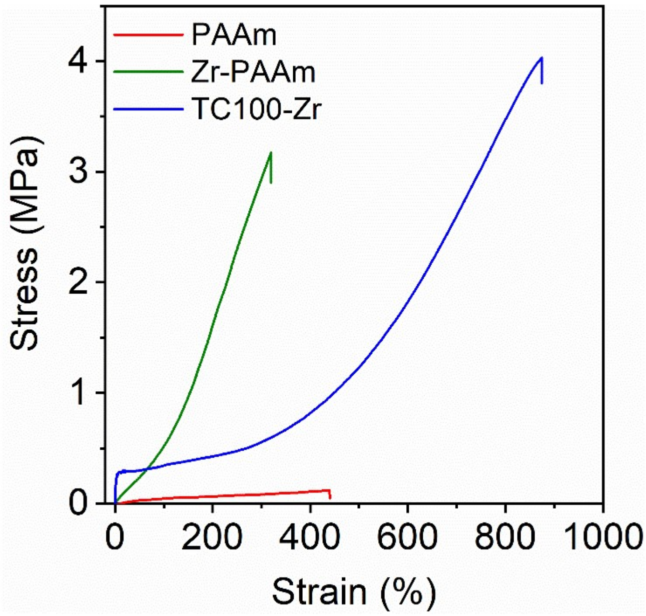


Figure S10. The comparison of tensile stress-strain curves of neat PAAm hydrogels, TC100-Zr hydrogels, and Zr-PAAm hydrogels produced by one-step immersing PAAm aerogels in Zr(IV) solutions.

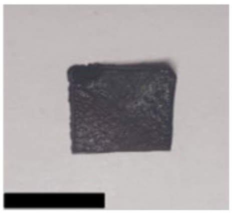
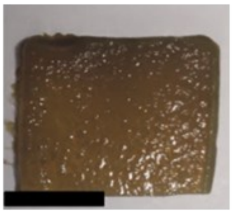
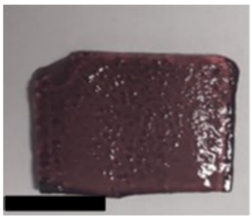
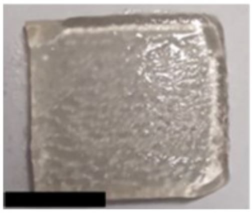
	Before immersed in urea solution	After immersed in urea solution
DC100		
TC100-Cu		
TC100-Fe		
TC100-Al		
TC100-Zr		

Figure S11. The photographs of DC and TC hydrogels before and after immersed in urea solution (5 mol L^{-1}) at RT for 72 hours. The scale bar is 10 mm.

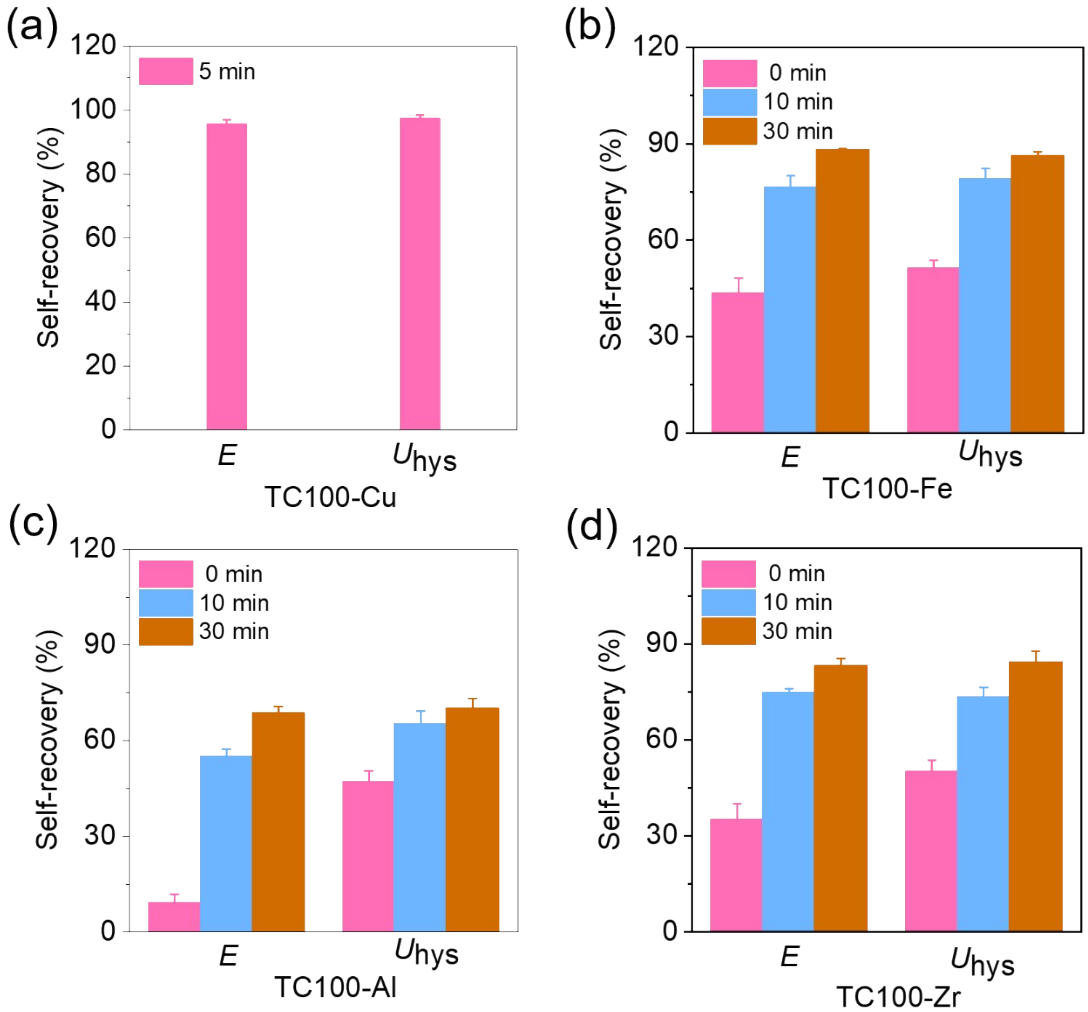


Figure S12. The time-dependent recovery efficiency of TC hydrogels based on elastic modulus (E) and energy dissipation (U_{hys}) at room temperature.

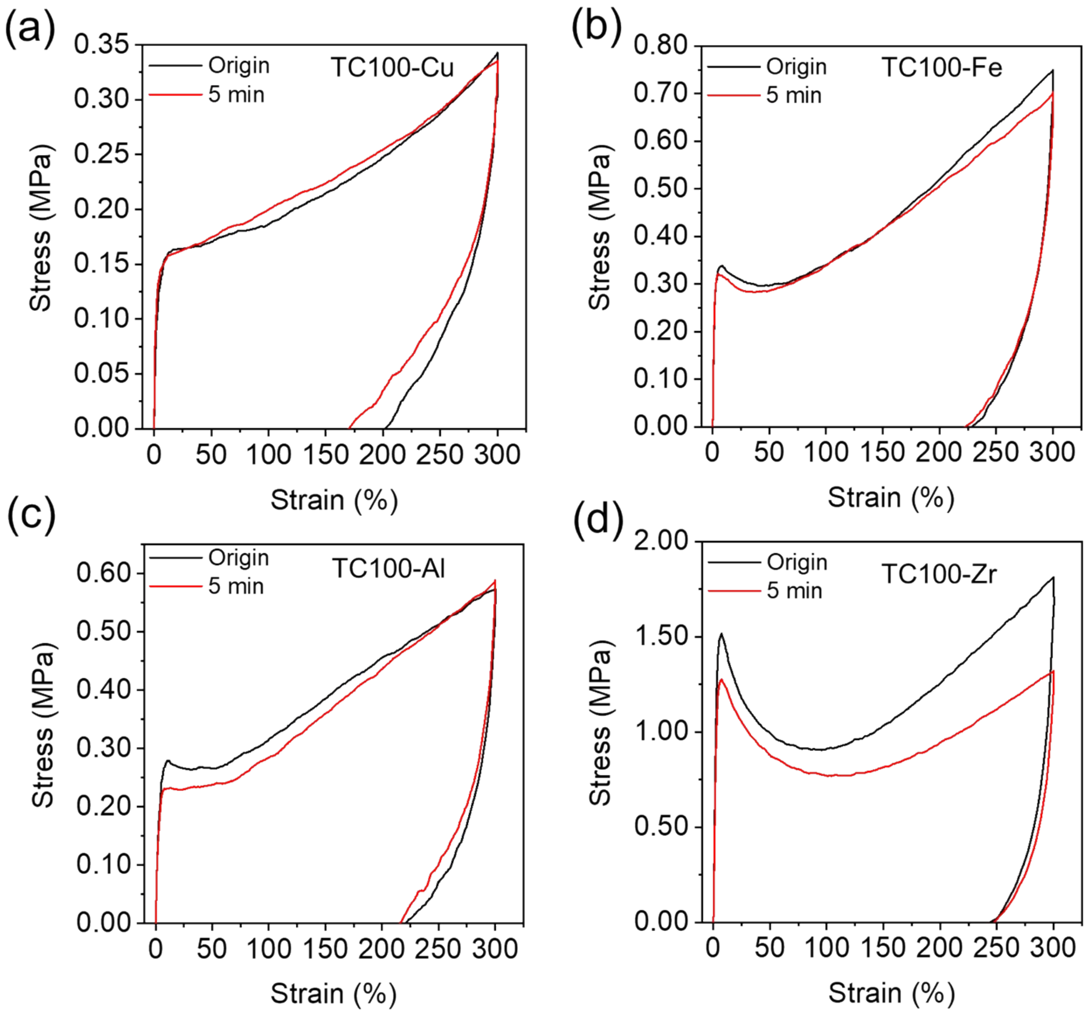


Figure S13. The self-recovery test of TC-M hydrogels at 60 °C for 5 min. (a) TC-Cu hydrogel. (b) TC-Fe hydrogel. (c) TC-Al hydrogel. (d) TC-Zr hydrogel.

For the self-recovery test at 60 °C, these TC hydrogels were first stretched to a maximum strain of 300% for a loading-unloading cycle, and then they were soaked in 60 °C water for 5 min. Then, the self-recovered TC hydrogels were soaked in a large amount of water to cool to room temperature (about 21 °C). Finally, another loading-unloading cycle was conducted for the self-recovered samples, keeping the same maximum strain of 300%.

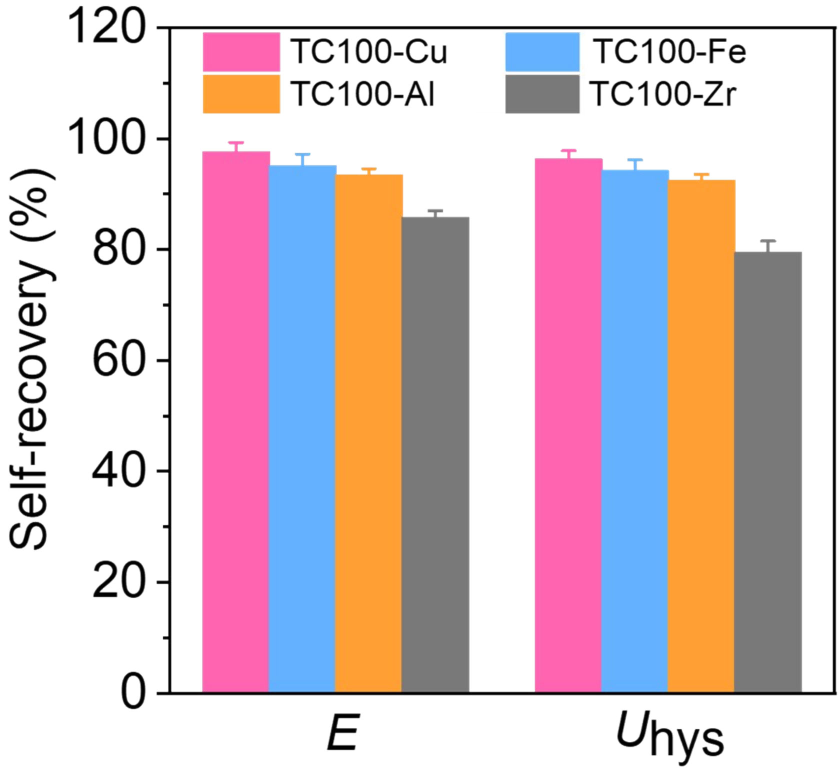


Figure S14. The recovery efficiency of TC hydrogels at 60 °C for 5 min based on elastic modulus (E) and energy dissipation (U_{hys}).

3. References

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