Supporting Information

Metal-Organic Frameworks: A Universal Strategy towards Super-elastic Hydrogels

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Materials and Methods

1. Materials

Acrylamide (AM), N,N,N',N'-tetramethylethylenediamine (TEMED), 2-hydroxyethyl (HEA), and 5-fluorouracil (5-Fu) were purchased from Aladdin Industrial Corporation. Ammonium persulfate (APS), N,N-dimethylformamide (DMF), acetic acid, zinc nitrate hexahydrate ($Zn(NO_3)_2$), silica (SiO_2, 500 nm), cobaltous nitrate hexahydrate ($Co(NO_3)_2$), methanol (CH_3OH), zirconium tetrachloride ($ZrCl_4$), 1,4-benzenedicarboxylic acid (BDC), N,N'-methylenebisacrylamide (MBAA), acetic acid (HAc), sodium phosphate dibasic (Na_2HPO_4), and sodium dihydrogen phosphate (NaH_2PO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-methylimidazole (2-IMI) was supplied by Heowns Industrial Corporation. Rhodamine b (RhB) was purchased from Shanghai D&B Biological Science and Technology Co., Ltd. Distilled water was purchased from Nanjing Wanqing chemical glassware instrument Co., Ltd. All chemicals and solvents were used without further purification.

2. Methods

2.1. Preparation of MOF nanoparticles: ZIF-8 and ZIF-67 powders were synthesized by mixing 2-IMI with metal salts in methanol and stirring at room temperature. Briefly, ZIF-8 was synthesized by dissolving 6.6 g (80 mmol) 2-IMI and 2.97 g (10 mmol) $Zn(NO_3)_2$ in 300 mL methanol and vigorously stirring for 24 h at ambient condition. After stirring, the ZIF-8 powders was separated by centrifugation at 8000 rpm for 5 min, washed with CH_3OH several times to remove unreacted

materials and vacuum dried at room temperature for 12 h. The synthesis process of ZIF-67 was similar to ZIF-8, just replace $Zn(NO_3)_2$ with $Co(NO_3)_2$. UiO-66 was synthesized by dissolving 1.2 g $ZrCl_4$, 0.855 g BDC, and 9 mL HAc in flask which contain 300 mL DMF, then placed in 120 ^oC oil bath and reacted for 24 h. After cooling to room temperature, the precipitates were obtained by centrifugation at 8000 rpm for 5 min, and washed with DMF and ethanol for three times, respectively. Finally, the product was dried under vacuum at 120 ^oC for 12 h.

2.2. Preparation of gel solution: 2.8 g AM and 1.2 g HEA were mixed with 12 g distilled water in a 20 mL vial under magnetic stirring for 10 min, then added 40 mg APS and a certain amount MBAA (1, 5, 10, and 40 mg) into the mixture, the gel solution was obtained after 5 min stirring.

2.3 Preparation of MOF hydrogels: The MOF hydrogels were prepared by simple mixing the 0.6 g MOF powders with 5.4 g gel solution under stirring for 20 min, then 10 μL catalysts TEMED was added into the mixture, the MOF hydrogels can be formed within 1 min. MOF hydrogels with different mass fractions of MOF can be prepared by adjusting the mass of MOF powders (the as-prepared hydrogels have been denoted as MOF-*X*%-M_y, where *X* is the weight percentage of the MOF in hydrogels, and *M* represents the cross-linker, and *y* is the weight (mg) of cross-linker, MBAA).

2.4 Rhodamine b adsorption tests: At first, 2 g ZIF-8-10%-M_{10} hydrogels was added to 1000 mL beaker which contained 500 mL 0.1 mg mL^{-1} RhB solution. Then, 1.8 g pure-M_{10} hydrogels and 0.2 g ZIF-8 powders (loading in semi-permeable dialysis bag, molecular weight 3500) were dispersed in two other beakers for a comparison test. We took 1 mL RhB solution from each beaker at different intervals, the mass of adsorption RhB was evaluated by UV-Vis spectra, it was noted that all samples were diluted 3 times for UV-Vis measurements.

2.5 Drug sustains release test: The 5-Fu loading was performed at room temperature, under stirring for 2 days, 200 mg ZIF-8 powders(loading in semi-permeable dialysis bag, molecular weight 3500) was (dried at 120 ^{o}C in vacuum oven for 12 h) added to 50 mL methanol solution containing 0.3 g 5-Fu. After centrifugation, ZIF-8 powders loaded with 5-Fu was dried at 50 ^{o}C in vacuum oven overnight, these ZIF-8 powders were divided into two parts, one was used to prepare ZIF-8-10%-M_{10} hydrogels, and the other was reserved. Meanwhile, 200 mg pure-M_{10} hydrogels was immersed in 50 mL methanol solution contained 0.3 g 5-Fu for 2 days. Finally, 50 mg ZIF-8 powders, 50 mg pure-M_{10} hydrogels which have already adsorbed 5-Fu, 50 mg ZIF-8-10%-M_{10} hydrogels which were prepared from ZIF-8 powders containing 5-Fu were added to three paralleled 200 mL beakers which contained 100 mL phosphate buffer saline (PBS, pH = 7.4, 0.1 M). The released percentage of 5-Fu was estimated by UV-Vis adsorption spectroscopy. Briefly, 1 mL PBS solution from each beaker at different intervals, and then 1 mL fresh PBS was added into the beaker. The concentration of

released 5-Fu was measured by UV-Vis (it was noted that all samples were diluted 3 times for UV-Vis measurements), so that the release percentage was obtained.

Characterization

3.1 Field Emission Scanning Electron Microscope (FE-SEM): The Pure hydrogels and ZIF-8 hydrogels were first frozen in liquid nitrogen and then placed in a freeze dryer (LC-10N-50A) for 12 h of freeze drying to remove all the moisture. The cross section of hydrogels samples were observed in SEM (FEI 3D).

3.2 X-ray diffraction (XRD): The XRD of MOF powders, pure hydrogels, and MOF hydrogels were performed in Ultimal IV. The scanning speed is 10° min^{-1} from 5° to 40°.

3.3 Fourier transforms infrared spectroscopy (FT-IR) measurement: The FT-IR of ZIF-8 powders, pure hydrogels, and ZIF-8 hydrogels were performed in Nicolet 5700. ZIF-8 powders can be directly measured, while pure hydrogels and ZIF-8 hydrogels need to be compressed into thin films.

3.4 Nitrogen adsorption: To explore the samples surface area, nitrogen adsorption-desorption isotherm was measured. The pure hydrogels and ZIF-8 hydrogels were firstly frozen in liquid nitrogen and then placed in a freeze dryer. After freeze dried for 12 h, the hydrogels were measured in ASAP 2020 V3.01 H.

3.5 Mechanical measurement: Specimens for tension and compression were prepared with diameter of 2.8 mm and 24 mm, respectively. The tensile and compressive tests were performed on a tensile tester (MTS E42) at ambient condition with a speed of 30 mm min^{-1} (It should be noticed that the fixture on MTS E42 are removable and fixture-choosing depends on test type, tension or compression). All the reported values of mechanical properties were the average based on at least three independent measurements for each sample.

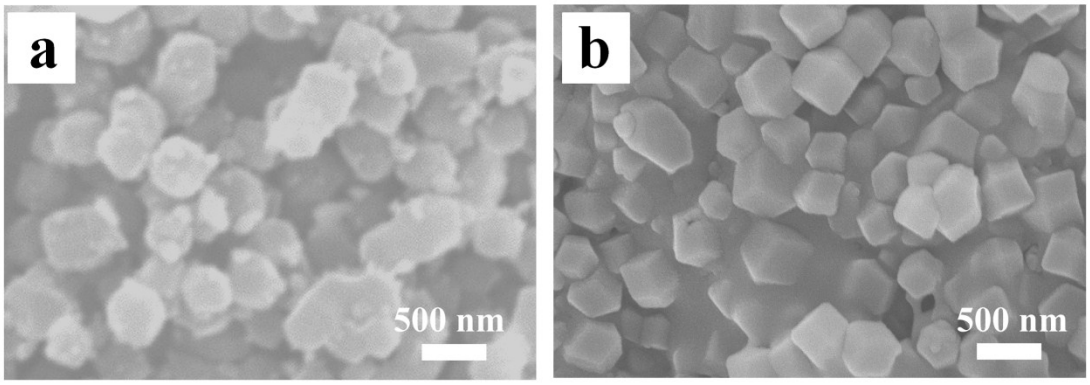

Figure S1. The SEM images of (a) ZIF-67 powders and (b) UiO-66 powder.

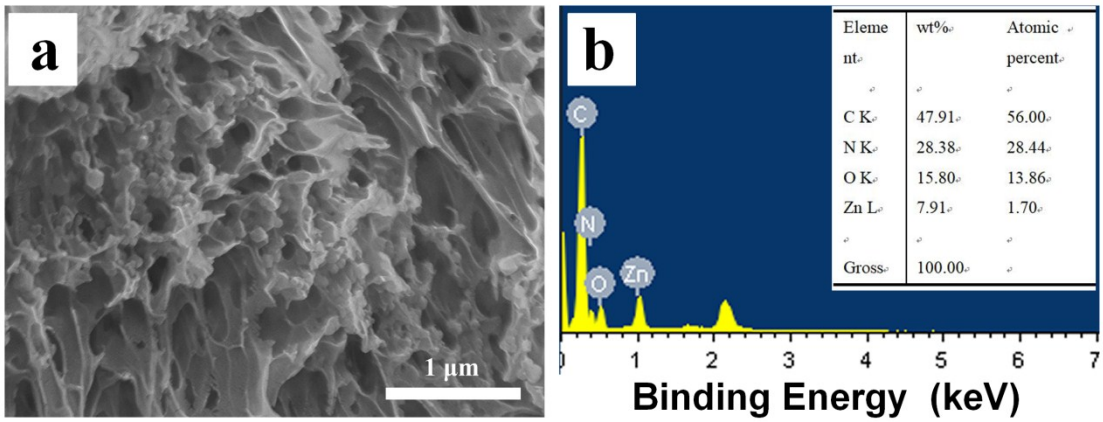

Figure S2. (a) The SEM image and (b) SEM-EDX image of ZIF-8-10%-M_{10} hydrogels.

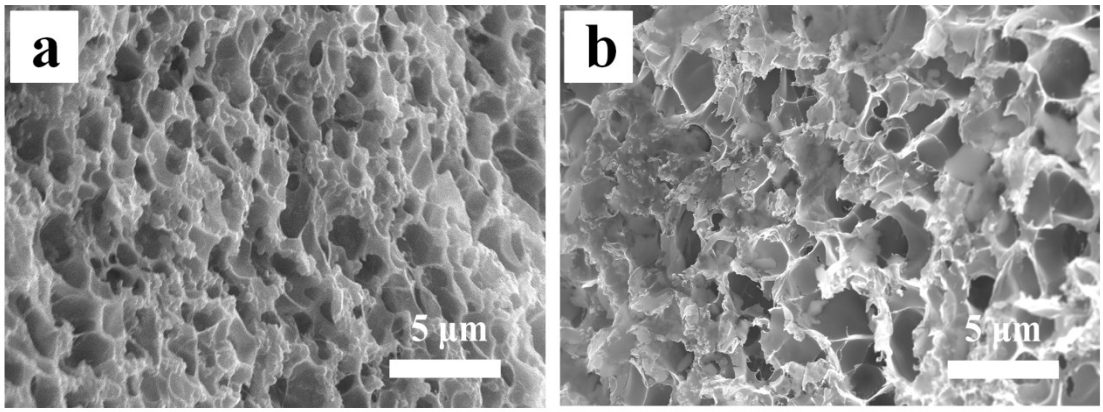

Figure S3. The SEM images of (a) ZIF-67-10%-M_{10} hydrogels and (b) UiO-66-10%-M_{10} hydrogels.

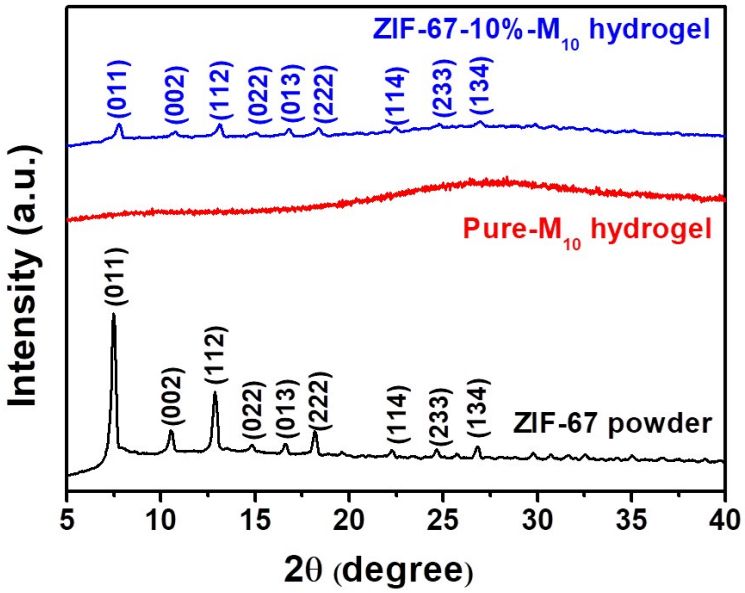

Figure S4. XRD patterns of ZIF-67 powders, pure-M_{10} hydrogels, and ZIF-67-10%-M_{10} hydrogels.

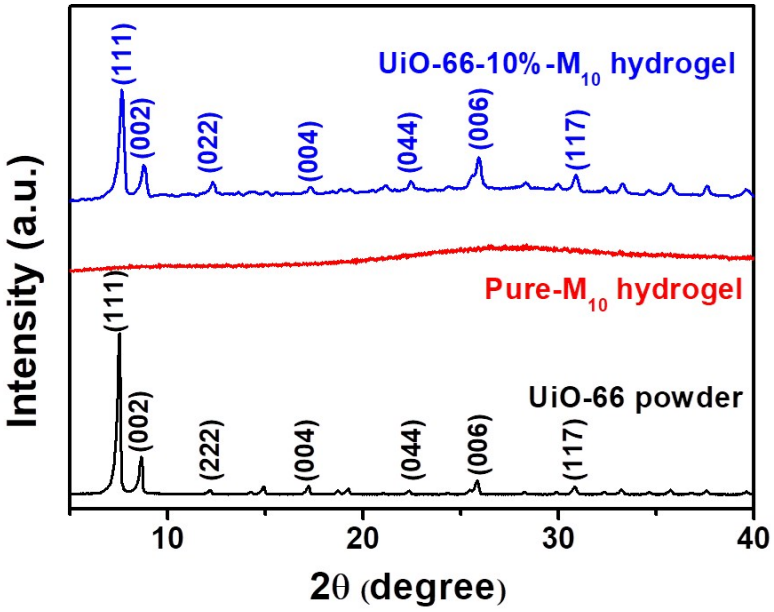

Figure S5. XRD patterns of UiO-66 powders, pure-M_{10} hydrogels, and UiO-66-10%-M_{10} hydrogels.

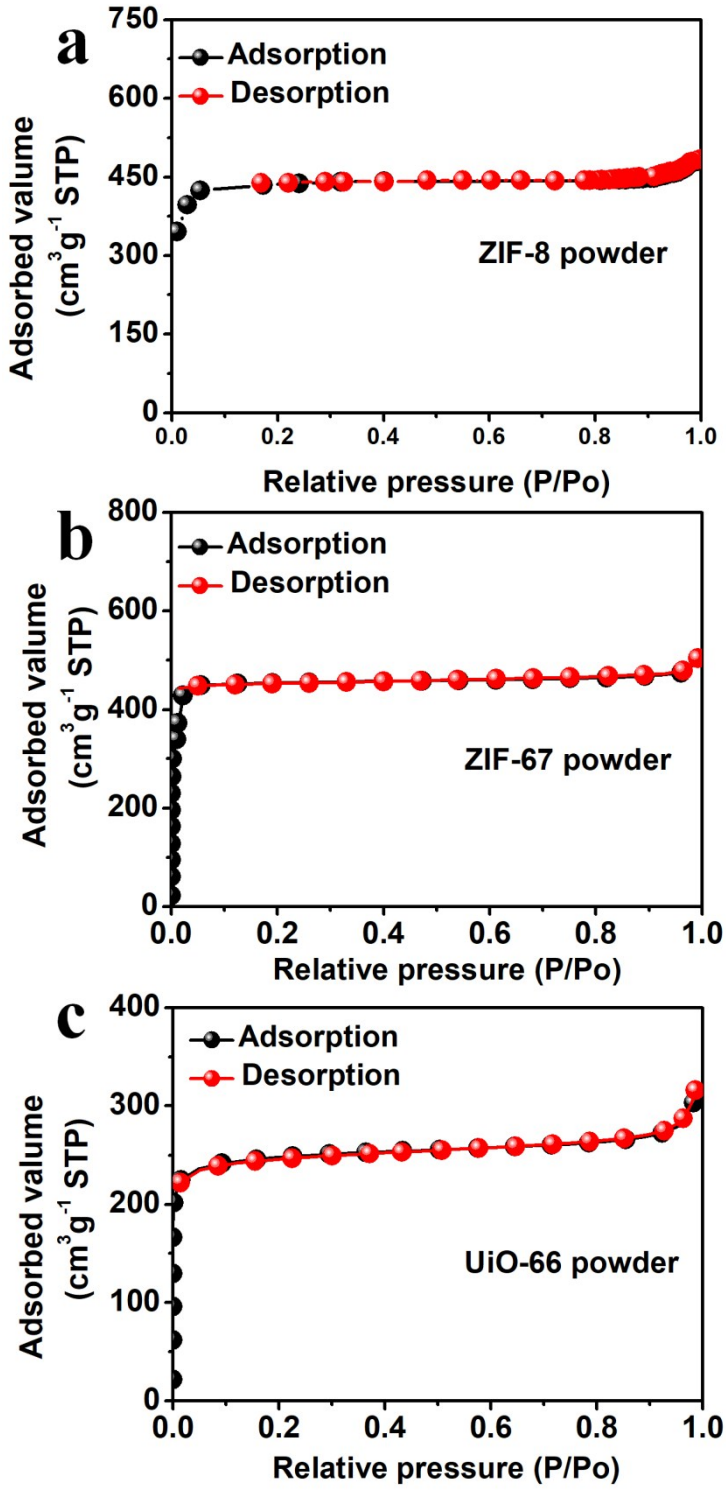

Figure S6. Nitrogen adsorption and desorption of (a) ZIF-8 powders. (b) ZIF-67 powder. (c) UiO-66 powder.

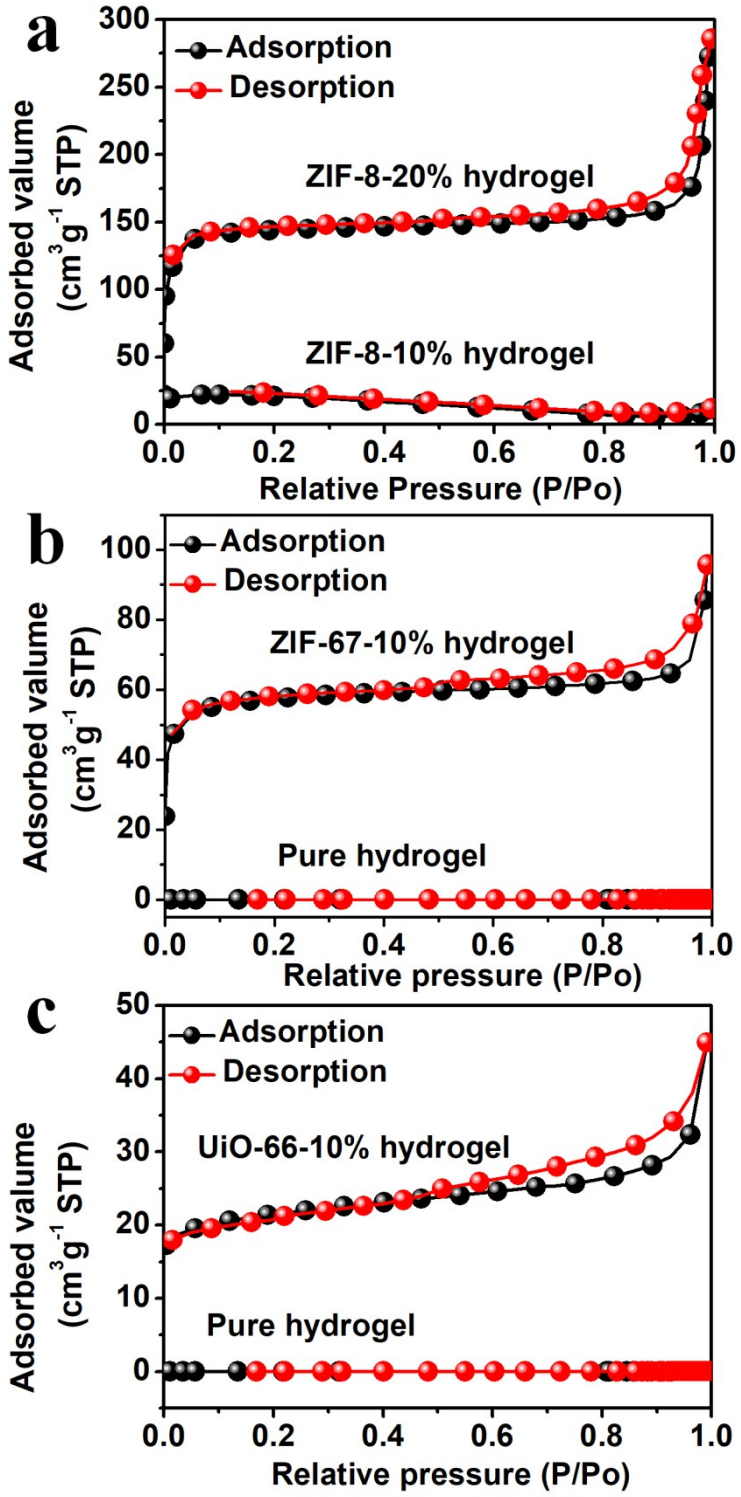

Figure S7. Nitrogen adsorption and desorption of (a) ZIF-8-10% and ZIF-8-20% hydrogels, (b) pure hydrogels and ZIF-67-10% hydrogels, (c) pure hydrogels and UiO-66-10% hydrogels.

Table S1. The composition of precursor solution before adding MOFs.

Precursor solution [a]	H_2O (g)	AM (g)	HEA (g)	APS (mg)	MBAA (mg)
A	12	2.8	1.2	40	1
B	12	2.8	1.2	40	5
C	12	2.8	1.2	40	10
D	12	2.8	1.2	40	40

[a] The gel solution with different cross-linker, MBAA.

Table S2. The composition of control gels and MOF hydrogels

Hydrogels	MOF Content (g)	SiO_2 (g)	Precursor solution (g) [a]	TEMED (μL) [b]	Content of water (%) [c]
Pure-M_1	/	/	A-3	5	75
ZIF-8-5%-M_1	0.15	/	A-2.85	5	72.2
ZIF-8-10%-M_1	0.3	/	A-2.7	5	67.5
ZIF-8-20%-M_1	0.6	/	A-2.4	5	60
ZIF-67-10%-M_1	0.3	/	A-2.7	5	67.5
UiO-66-10%-M_1	0.3	/	A-2.7	5	67.5
ZIF-8-10%-M_5	0.3	/	B-2.7	5	67.5
ZIF-8-10%-M_{10}	0.3	/	C-2.7	5	67.5
ZIF-8-10%-M_{40}	0.3	/	D-2.7	5	67.5
Pure-M_5	/	/	B-3	5	75
Pure-M_{10}	/	/	C-3	5	75
Pure-M_{40}	/	/	D-3	5	75
SiO_2-10%-M_1	/	0.3	A-2.7	5	67.5
SiO_2-10%-M_5	/	0.3	B-2.7	5	67.5
SiO_2-10%-M_{10}	/	0.3	C-2.7	5	67.5
SiO_2-10%-M_{40}	/	0.3	D-2.7	5	67.5

[a] Precursor solution prepared from Table S1. [b] The catalyst of N,N,N',N'-tetramethylethylenediamine (TEMED). [c] The content of water in different hydrogels.

Table S3. The tensile properties of different hydrogels

Hydrogels	ε (%) [a]	σ (kPa) [b]	E (kPa)[c]	T (kJ m^{-3})[d]
Pure-M_1	417±60	18±3	85.1±8	47.9
ZIF-8-5%-M_1	2033±242	63±7	98±7	635.2
ZIF-8-10%-M_1	2060±235	52±7	194±12	544.8
ZIF-8-20%-M_1	758±99	101±9	2310±196	500.2
ZIF-67-10%-M_1	2000±331	56±6	161±13	627.8
UiO-66-10%-M_1	1640±198	97.9±9	110±11	783.7
ZIF-8-10%-M_5	1525±153	38.7±3	358±47	361.8
ZIF-8-10%-M_{10}	838±137	130±11	625±84	674.8
ZIF-8-10%-M_{40}	80±9	73±5	2205±236	38.6
Pure-M_5	141±34	24.8±2	262±28	22.3
Pure-M_{10}	112±28	30.6±4	366±52	21
Pure-M_{40}	75±12	40.3±3	857±115	19
SiO_2-10%-M_1	697±119	176±33	36.9±7	743.7
SiO_2-10%-M_5	267±42	144±19	95.7±19	228.2
SiO_2-10%-M_{10}	166±37	127±15	114.2±25	122.9
SiO_2-10%-M_{40}	43.7±9	102±14	323.6±77	25.5

[a] The tensile strain (ε) at the break of during the mechanical test; [b] The tensile stress (σ) at the break of during the mechanical test; [c] The Young's modulus (E) estimated from the slope of the fitting line to the liner region of tensile strain-stress curves; [d] The tensile toughness (T) estimated by integrating the area under strain-stress curves up to the tension breaking point.

Table S4. Comparison of the tensile mechanical properties of previous nanocomposite hydrogels

Nanocomposite Hydrogels	ε (%) [a]	σ (kPa) [b]	E (kPa)[c]	Ref
PAAm/CNT-PAA	508	82.3	420.2	[1]
PNIPAAm/CNT-PAA	465	97.4	-	[2]
PAAm/SDBS/GO	2869	155.4	36.6	[3]
PAA/Fe^{+3}/GO	2980	776.8	50.7	[4]
PAAm/GPO	3500	650.2	52.3	[5]
PNIPAAm/Laponite	1112	68.8	4.0	[6]
ZIF-8 hydrogels	2060	52	194	This work

[a] The tensile strain (ε) at the break of during the mechanical test; [b] The tensile stress (σ) at the break of during the mechanical test; [c] The Young's modulus (E) estimated from the slope of the fitting line to the liner region of tensile strain-stress curves;

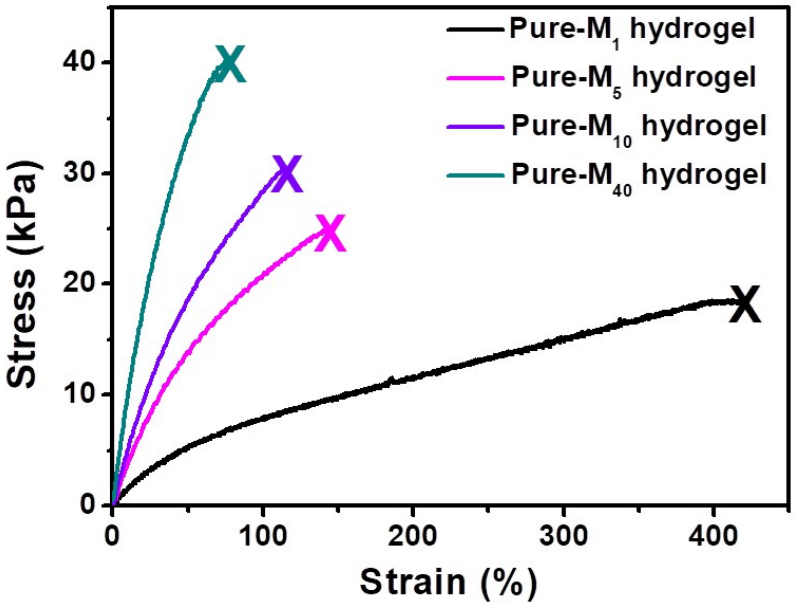

Figure S8. Tensile curves of pure hydrogels with different amount of MBAA.

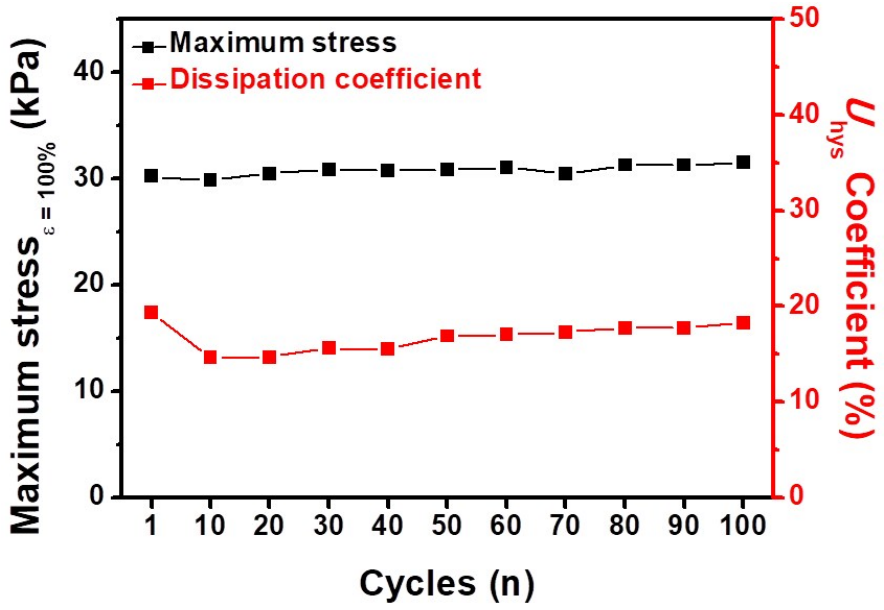

Figure S9. The maximum stress and dissipation coefficient of ZIF-8-10%-M_{10} hydrogels every 10 cycles during the 100 cycles tensile tests at a strain of 100% (ε at 100%)

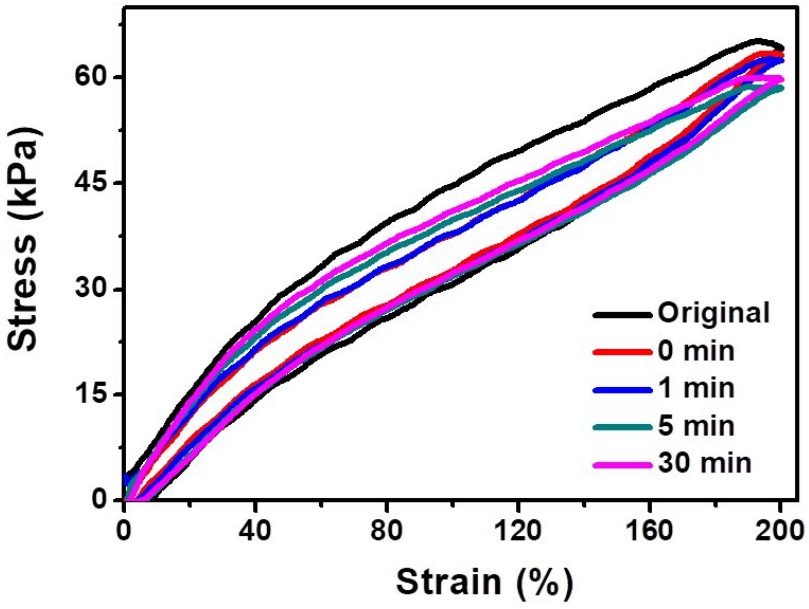

Figure S10. Self-recovery behavior of stretched of ZIF-8-10%-M_{10} hydrogels.

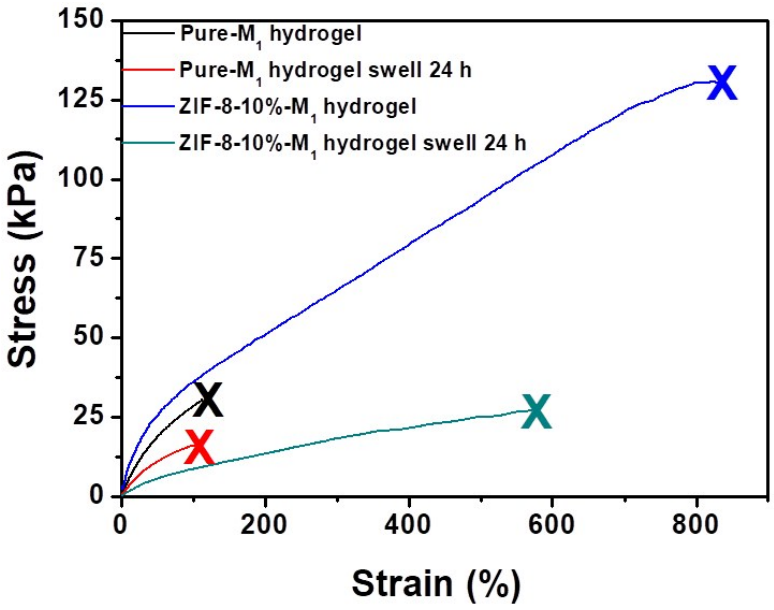

Figure S11. Tensile curves of pure-M_{10} and ZIF-8-10%-M_{10} hydrogels before and after swelling 24 h.

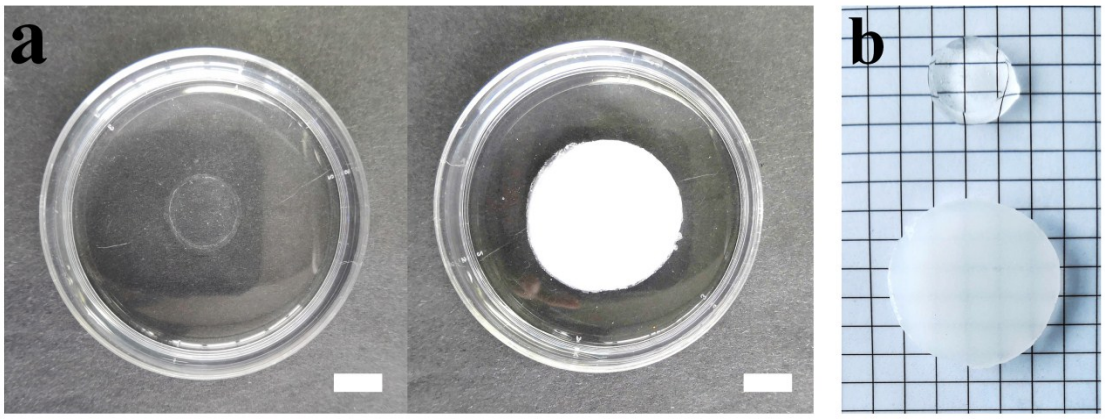

Figure S12. (a) Images of pure-M_{10} (Left) and ZIF-8-10%-M_{10} hydrogels (Right) immersion in water after four months of swelling and (scale bar 1 cm) (b) Images of pure-M_{10} (Top) and ZIF-8-10%-M_{10} hydrogels (Bottom) after four months of swelling. A small square in the images indicates 0.5 cm.

Table S5. The compressive properties of different hydrogels.

Hydrogels	σ (kPa) [a]	Uhys coefficient (%) [b]
ZIF-8-10%-M_1	129±7	122.3
ZIF-8-10%-M_5	307±4	90.2
ZIF-8-10%-M_{10}	465±5	48.6
ZIF-8-10%-M_{40}	1005±7	20.7
Pure-M_1	205±3	80.4
Pure-M_5	300±4	48.7
Pure-M_{10}	427±5	20.1
Pure-M_{40}	117±2	6.4

[a] The compressive stress (σ) at the break of during the mechanical test; [b] The energy dissipation coefficient (U_{hys} coefficient) was determined by the percentage which is the ratio of enclosed part area (circled by one mechanical test cycle) to compression curve part.

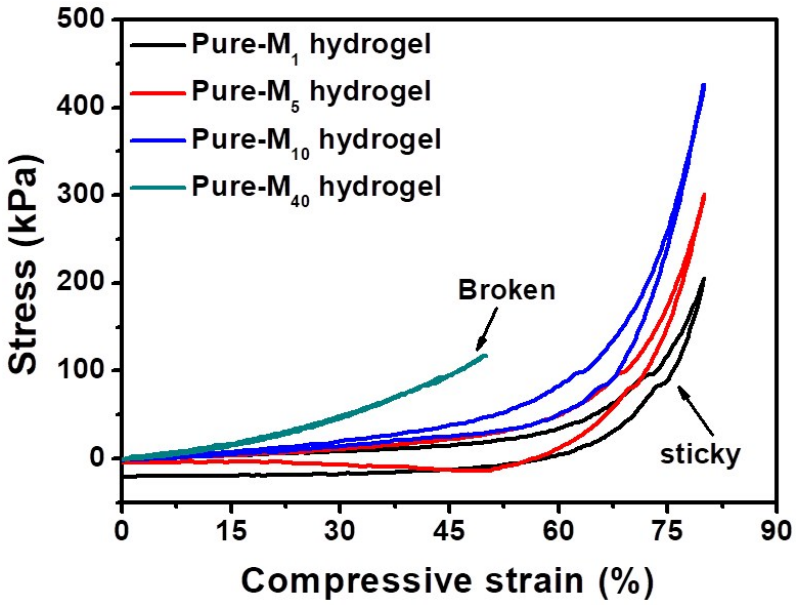

Figure S13. The compressive curves of pure hydrogels with different content of MBAA.

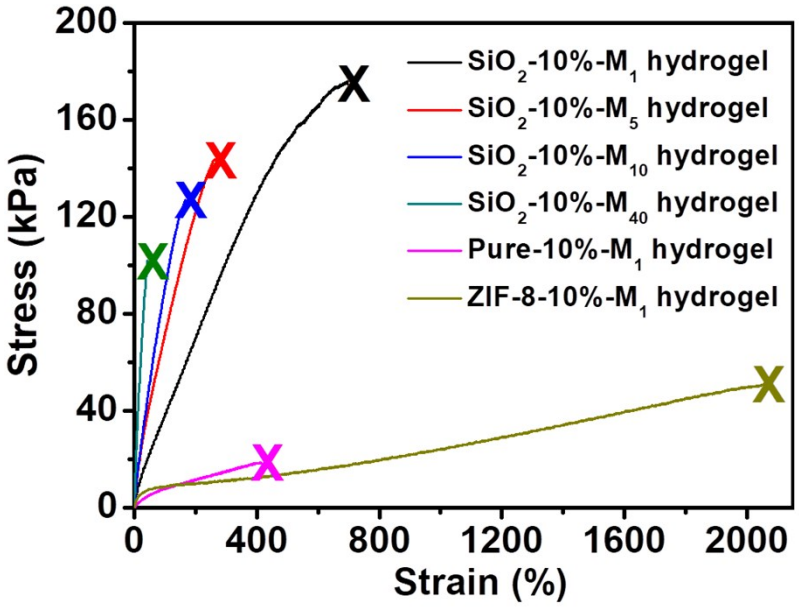

Figure S14. Tensile curves of pure-M_1, ZIF-8-10%-M_1 hydrogels, and SiO_2 hydrogels with different dosage of cross-linker, MBAA.

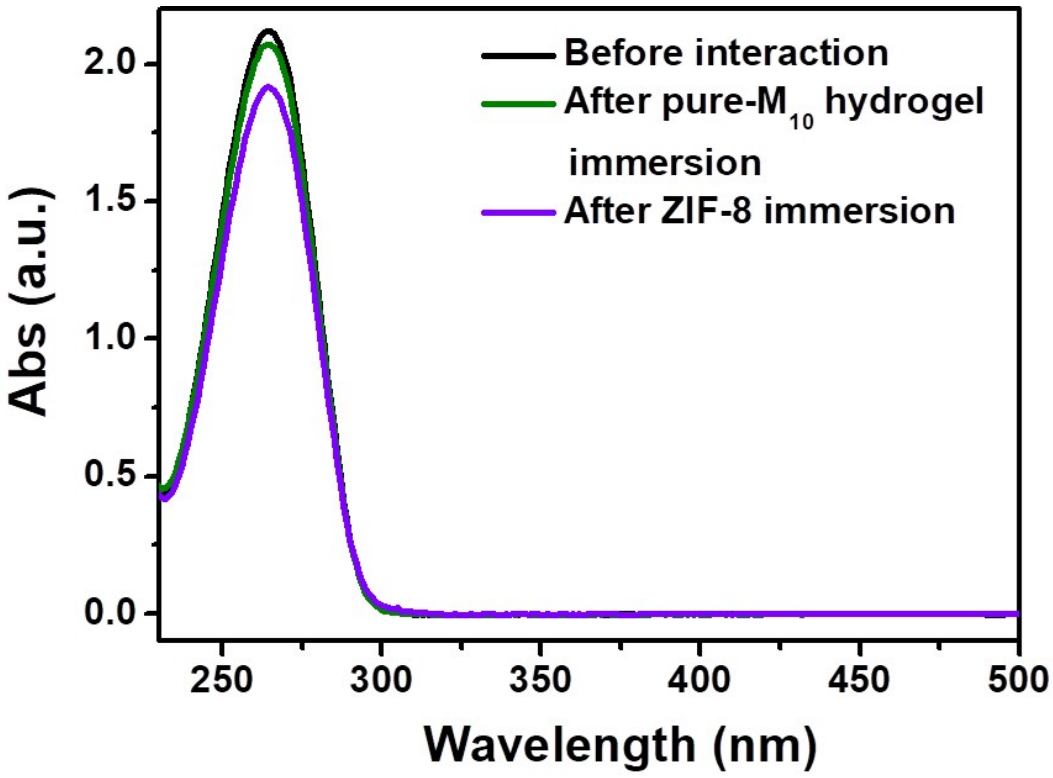

Figure S15. The UV-Vis adsorption spectra of 5-Fu methanol solution before and after the pure-M_{10} hydrogels and ZIF-8 powders immersion. It was observed that the intensity of 5-Fu methanol solution which contains ZIF-8 powders was lower than that contains pure hydrogels, indicating that ZIF-8 powders have a larger 5-Fu adsorption capacity than pure-M_{10} hydrogels.

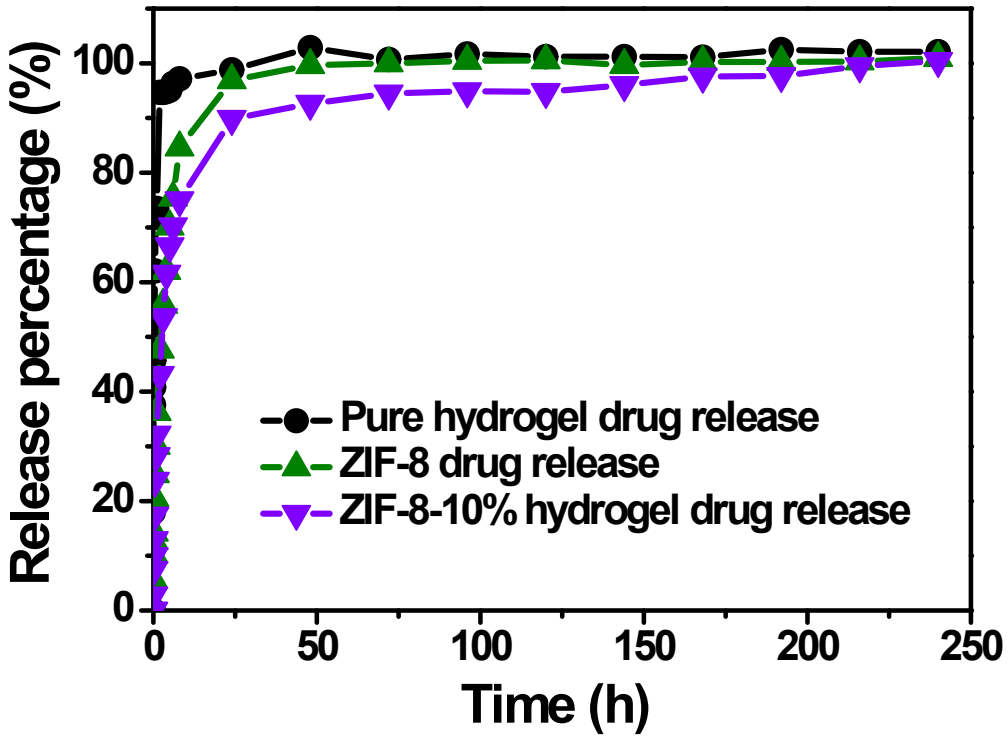

Figure S16. 5-Fu releasing profiles from ZIF-8 powders, pure-M_{10} hydrogels, and ZIF-8-10%-M_{10} hydrogels.

Video S1. The Video S1 was the car crushing test of ZIF-8-10%-M_{40} hydrogels. At first, 3 g ZIF-8 powders was added to a 50 mL beaker that contains 27 g gel solution under magnetic stirring. After 20 min ZIF-8-10%-M_{40} hydrogels solution were obtained, then the catalysts TEMED was added into the mixture continually stirring for several seconds and poured into the petri dish immediately. Finally, a pancake-like hydrogels was obtained (diameter = 72 mm, thickness = 8 mm). The car crushing test was performed on street using a family car (weight 1.4×10^3 kg). In the Video S1, it can be seen that no damage was found for the hydrogels after crushed back and forth for a car, indicating that ZIF-8 hydrogels has superior mechanical properties.

Video S2. The Video S2 was the bouncing performance of ZIF-8-10%-M_{40} hydrogels. Similar to Video S1, ZIF-8-10%-M_{40} hydrogels solution were prepared firstly, then adding the catalyst TEMED to the hydrogels solution, after stirring for several seconds, the hydrogels solution was injected into the ping pang ball immediately. A hydrogels ball (diameter = 38 mm) was obtained when removing the ZIF-8-10%-M_{40} hydrogels ball from the ping pang mold. The bouncing test was performed at room temperature, in the Video S2, the hydrogels ball could be repeated bounced without any damage, showing excellent mechanical recovery and elasticity.

Reference

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