

## Article

**A General Strategy to Fabricate Highly Filled Microcomposite Hydrogels with High Mechanical Strength and Stiffness**

Zhandong Gu, Lie Chen, yichao Xu, yusi Liu, Ziguang Zhao, Chuangqi Zhao,  
Wenwei Lei, Qinfeng Rong, Ruochen Fang, Tianyi Zhao, and Mingjie Liu

*ACS Appl. Mater. Interfaces*, **Just Accepted Manuscript** • DOI: 10.1021/acsami.7b17689 • Publication Date (Web): 08 Jan 2018

Downloaded from <http://pubs.acs.org> on January 8, 2018

**Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

**ACS Publications**

ACS Applied Materials & Interfaces is published by the American Chemical Society.  
1155 Sixteenth Street N.W., Washington, DC 20036  
Published by American Chemical Society. Copyright © American Chemical Society.  
However, no copyright claim is made to original U.S. Government works, or works  
produced by employees of any Commonwealth realm Crown government in the course  
of their duties.

# A General Strategy to Fabricate Highly Filled Microcomposite Hydrogels with High Mechanical Strength and Stiffness

Zhandong Gu<sup>†</sup>, Lie Chen<sup>†</sup>, Yichao Xu<sup>†</sup>, Yusi Liu, Ziguang Zhao<sup>†</sup>, Chuangqi Zhao<sup>†</sup>, Wenwei Lei<sup>†</sup>, Qinfeng Rong<sup>†</sup>, Ruochen Fang<sup>†</sup>, Tianyi Zhao<sup>\*, †</sup> and Mingjie Liu<sup>\*, †, ‡</sup>

<sup>†</sup>Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry, Beihang University, Beijing 100191, P. R. China

<sup>‡</sup>International Research Institute for Multidisciplinary Science, Beihang University, Beijing 100191, P. R. China

KEYWORDS: hydrogel, highly filled, microcomposite, strength, stiffness

ABSTRACT: Conventional synthetic hydrogels are intrinsically soft and brittle, which severely limit the scope of their applications. A variety of approaches have been proposed to improve the mechanical strength of hydrogels. However, a facile and ubiquitous strategy to prepare hydrogels with high mechanical strength and stiffness is still a challenge. Here we report a general strategy to prepare highly filled microcomposite hydrogels with high mechanical performance by using the ultrasonic assistant. The microparticles were dispersed in the polymer network evenly,

1  
2  
3 resulting in homogeneous and closely packed structures. The as-prepared hydrogels with  
4 extraordinary mechanical performance, can endure compressive stress up to 20 MPa (at 75%  
5 strain), and exhibit high stiffness (elastic modulus is around 18 MPa). By using our  
6 comprehensive strategy, different hydrogels can enhance their mechanical strength and stiffness  
7 by doping various microparticles, leading to a much wider variety of applications.  
8  
9

## 10 11 12 INTRODUCTION

13  
14  
15  
16 Hydrogel, as one kind of classic polymer materials that contain large amounts of water in their  
17 three-dimensional cross-linked hydrophilic networks, have attracted considerable attention in  
18 varieties of fields, such as tissue engineering<sup>1-4</sup>, water treatment<sup>5-6</sup>, drug delivery<sup>7-10</sup>, and  
19 biosensing<sup>11-12</sup>. However, most of hydrogels usually suffer from low mechanical strength and  
20 limited stiffness due to their intrinsic structural inhomogeneity and lacking of effective energy  
21 dissipation mechanism<sup>13</sup>, which severely limit their applications in many areas, especially in  
22 load-bearing materials, like materials for cartilage replacement<sup>14</sup> and artificial muscles<sup>15</sup>.  
23  
24 Therefore, it is necessary to develop a new kind of hydrogel materials with high mechanical  
25 properties for practical applications.  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39

40 During the past few decades, many efforts have been made to improve the mechanical  
41 strength of hydrogels, and various hydrogel fabricated by different methods have been reported,  
42 such as double-network hydrogels<sup>16-18</sup> (DN gels), nanocomposite hydrogels<sup>19-22</sup> (NC gels), tetra  
43 polyethylene glycol hydrogels (tetra-PEG hydrogels)<sup>23-24</sup>, sliding-ring hydrogels<sup>25-27</sup>,  
44 macromolecular microsphere composite hydrogels<sup>28</sup>, and physical interaction hydrogels<sup>29-41</sup>  
45 (including hydrogen bonding, dipole-dipole interaction, hydrophobic interaction, and  
46 electrostatic interaction).  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

The DN hydrogels, which generally composed of a rigid and brittle heterogeneous polyelectrolyte first network and a soft and ductile second network, exhibit high fracture stress and toughness comparable to rubbers<sup>16</sup>. The NC gels are composed of exfoliated clay uniformly dispersed in an aqueous medium with a number of flexible polymer chains linking them together<sup>36</sup>. They can deform to a large extent without any damage under compression or elongation. This is due to the anisotropic and high aspect ratio morphology of the nanoclay which result in strong interactions between the polymers and nanoclay. Tetra-PEG hydrogels composed of the radiation crosslinking of hydrophilic polymers are soft and highly extensible. These hydrogels typically possess homogeneous networks and avoid the high crosslink density clusters<sup>42</sup>. The well-defined networks of PEG hydrogels have a very high elongation at break (400 ~ 1600 %) with large tensile strength (680 ~ 2390 kPa). Sliding-ring hydrogels were consisted of PEG chains and  $\alpha$ -cyclodextrin ( $\alpha$ -CD), whose crosslinkers are able to slide along the polymer chains, exhibit high extensibility and swelling ratio ( $\approx 400$ )<sup>25</sup>. However, most of the strategies either suffer from the complex fabrication process or limited by the raw materials. Therefore, a facile and ubiquitous strategy to prepare hydrogels combining high mechanical strength with stiffness is desperately needed.

In this study, we synthesized highly filled microcomposite hydrogels (HFM hydrogels) by using ultrasonic-assisted technology and the resultant hydrogels could realize high strength and stiffness simultaneously. The compression strength reaches 20 MPa at 75% strain, and the compressive elastic modulus is increased to 18 MPa. This easy accomplished general strategy could avoid tedious and time-consuming process effectively. Moreover, this strategy can be applied to numerous microparticles and monomers. A variety of microparticles ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaCO}_3$ ) and monomers (N, N-Dimethyl acrylamide, 2-hydroxyethyl methacrylate, acrylic acid,

and acrylamide) were used in this method. We believe that these highly filled microcomposite hydrogels have great potential to be used as load-bearing materials such as structural materials, soft robotics, and artificial tissues.

## RESULTS AND DISCUSSION

The highly filled microcomposite hydrogels (HFM hydrogels) were synthesized through a radical copolymerization process with the monomer, cross-linker, initiator, accelerator and microparticles (Figure 1b). First, the precursor solution with certain concentrate of monomer and cross-linker was prepared. Then a large amount of microparticles were slowly added to the precursor solution in an ultrasonic environment. To make sure the solution was highly filled with microparticles, the ultrasonic was further kept for 10 minutes after the microparticle powders were added. Then the precursor solution became viscous after the ultrasonic stimulation was applied (Figure 1c), demonstrating that the microparticles were closely packed in the precursor solution. Finally, the HFM hydrogels were synthesized via *in situ* free-radical polymerization (Figure 1b). After the reaction, microparticles were trapped in the polymeric network constituted by covalently cross-linked hydrogel chains, forming a white HFM hydrogel (Figure 1c). For comparison, the pure hydrogel without the addition of microparticles was also fabricated following the same procedure

Figure 2 shows the scanning electron microscopy (SEM) images of the microparticles and the corresponding HFM hydrogels with different monomers. The homogeneous and closely packed structures of HFM hydrogels were confirmed by the SEM images. As observed in the SEM images, microparticles were dispersed in hydrogel network evenly regardless of the type

of microparticles and their particle size. This uniformly dispersed structure with rigid inorganic microparticles and soft polymers would contribute to the high mechanical strength. The polymers matrix fill the gaps between the microparticles and connect the neighboring microparticles (Figure S6 Supporting Information). This closely packed structures with rigid microparticles are the key to enhance the stiffness of the hydrogel obviously. Many other particles and monomers were also test to successfully form uniformly dispersed structures. This demonstrate that our method is could be widely used to fabricate high mechanical strength hydrogels.

The resultant hydrogels exhibit excellent mechanical performance with high stiffness and compression strength. For instance, when the HFM hydrogels were prepared with SiO<sub>2</sub> microparticles (particle size,  $\approx 5\ \mu\text{m}$ ) and N, N-Dimethyl acrylamide (DMA) monomer, the hydrogel could sustain loading weight of 2 kg (approximately 800 times its own weight) without any noticeable deformation (Figure. 3a). The stiffness of HFM-DMA hydrogel results from the additional the relatively rigid microparticles and the closely packed of the microparticles in the polymer network. Furthermore, the above mentioned HFM hydrogels could sustain a high compression strain (more than 85%) and will recover most of its original shape after removing the load (Figure. 3c), while the pure hydrogels without microparticles break down easily. We believe that the uniformly dispersed homogeneous structure with inorganic microparticles and soft polymers greatly contribute to the effective energy dissipation, leading to the high mechanical strength property.

The mechanical properties of the HFM hydrogels and the pure hydrogels were measured using compression tests at room temperature. Figure 4a-d show the typical strain-stress curves of HFM hydrogels and the pure hydrogels under compression. Although the pure hydrogels may

not break under deformation during the test, the applied stress with a value as long as 0.54 MPa can easily compress it to 75% strain. However, the HFM-DMA hydrogels filled with SiO<sub>2</sub> is able to sustain the stress of 13.8 MPa (particle size,  $\approx 10\ \mu\text{m}$ ) and 20.5 MPa (particle size,  $\approx 5\ \mu\text{m}$ ) at 75% strain, which is about 25 times and 37 times higher than the pure hydrogels. The stress could achieve higher value when the hydrogels were further compressed. Same to the HFM-DMA hydrogels, 2-hydroxyethyl methacrylate (HEMA) hydrogels filled with SiO<sub>2</sub> (Figure 4c) could also achieve high stress of 9.8 MPa (particles size,  $\approx 10\ \mu\text{m}$ ) and 17.5MPa (particles size,  $\approx 5\ \mu\text{m}$ ) at the strain up to 75%. The HFM hydrogel prepared by HEMA is nonswellable in water, and their mechanical performance will not be affected (Figure S5 supporting information). The mechanical strength of the hydrogels could also be significantly improved by adding different microparticles (Figure S1 – S4 Supporting Information). The microparticles covered by the polymer matrix in the hydrogel network act as physical cross-linking points, can effectively transfer energy across the interface and reduce stress concentration. Figure 4b, d show that the strength of the hydrogels could be easily turned by the changing or the monomer concentration, providing that the mechanical propertied of hydrogels could strongly affected by the concentration of monomers and cross-linkers.

Although numerous approaches to prepare high mechanical strength hydrogels have been proposed, it is still a challenge to synthesize hydrogel with both high toughness and stiffness simultaneously, since these two properties are often inversely related<sup>43</sup>. Most hydrogels are either stiff and brittle with low fracture energy or tough and compliant with low elastic modulus. Here, we demonstrate that the HFM hydrogels could achieve both toughness and stiffness. Figure 3a demonstrates the high stiffness of the hydrogels, the hydrogel could sustain a loading weight of 2 kg (more than 800 times the hydrogels) without any deformation. The elastic modulus of the

HFM hydrogel and the pure hydrogel are shown in Figure 4e-h. Although the pure hydrogel consisting of 40 wt% DMA could reach a high strain, while its elastic modulus is only 0.18 MPa (Figure 4e). The HFM hydrogel filled with SiO<sub>2</sub> particles has a much larger elastic modulus 6.2 MPa (particles size,  $\approx 10\ \mu\text{m}$ ) and 18.2 MPa (particles size,  $\approx 5\ \mu\text{m}$ ), which are nearly 34 times and 100 times larger than that of the pure hydrogels. Same to the DMA hydrogels, the HFM-HEMA hydrogels filled with SiO<sub>2</sub> particles could obtain larger elastic modulus about 10.6 MPa (particles size,  $\approx 10\ \mu\text{m}$ ) and 18.4 MPa (particles size,  $\approx 5\ \mu\text{m}$ ), which are approximately 28 times and 49 times higher than that of the pure hydrogels. This result offer powerful evidence for the validity of our hydrogel fabrication strategy that could obtain the high strength and stiffness simultaneously, owing to the synergistic effect of the rigid microparticles and soft polymer matrix. In the HFM hydrogels, the rigid microparticles increase the stiffness while the polymer matrix dissipates energy to achieve high strength. Other hydrogels filled with various microparticles with different particle size also have much higher elastic modulus than the pure hydrogels (Figure S1 – S4 Supporting Information). The detailed synthesis conditions of hydrogels and mechanical properties are shown in Table 1 and Table 2. From the data of the tables, we could conclude that the mechanical performance is remarkably enhanced by our method, and this microcomposite-reinforced effect can be observed from various microparticles hydrogels with different microparticles.

## CONCLUSION

In this work, highly filled microcomposite hydrogels with excellent mechanical properties were fabricated by a simple and feasible strategy. Microparticles were homogeneously dispersed and closely packed in the polymer network by ultrasonic-assistant. Then the hydrogel was synthesized via *in situ* free-radical polymerization and the microparticles were fixed in the



network. The HFM hydrogels could have a high stiffness due to the closely packed rigid microparticles. Furthermore, the soft polymer matrix covers on the microparticles dissipates energy effectively, resulting the high strength of HFM hydrogels. Thus, the combination of rigid inorganic microparticles and soft polymer matrix in the HFM hydrogel result the synergistic effect on the high mechanical performance. Moreover, this general approach has less limitation in the gelation process and raw materials compared with conventional methods. In summary, our HFM hydrogels fabricated by ultrasonic-assistant exhibit high mechanical performance, could serve as an ideal load-bearing material in a variety of applications. This general strategy for the fabrication of HFM hydrogels study provides new avenues to the universal design and manufacturing of hydrogels, broaden the current research and application scopes of hydrogels with excellent properties.

## EXPERIMENTAL SECTION

**Materials.** N, N-Dimethyl acrylamide (DMA), 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AAc), acrylamide (AAM), ethylene glycol dimethacrylate (EGDMA), ammonium persulfate (APS), N, N, N, N-tetramethylethylenediamine (TEMED), calcium carbonate ( $\text{CaCO}_3$ ) with particle size less than 30  $\mu\text{m}$  were purchased from Sigma-Aldrich. Silicon dioxide ( $\text{SiO}_2$ ) with particle size about 10  $\mu\text{m}$  and 5  $\mu\text{m}$ , aluminum oxide ( $\text{Al}_2\text{O}_3$ ) with particle size about 5  $\mu\text{m}$  were purchased from Shanghai Aladdin Bio-Chem Technology Co. LTD. All the reagents were used without further purification, and Milli-Q water (Millipore, USA) was used in all experiments.

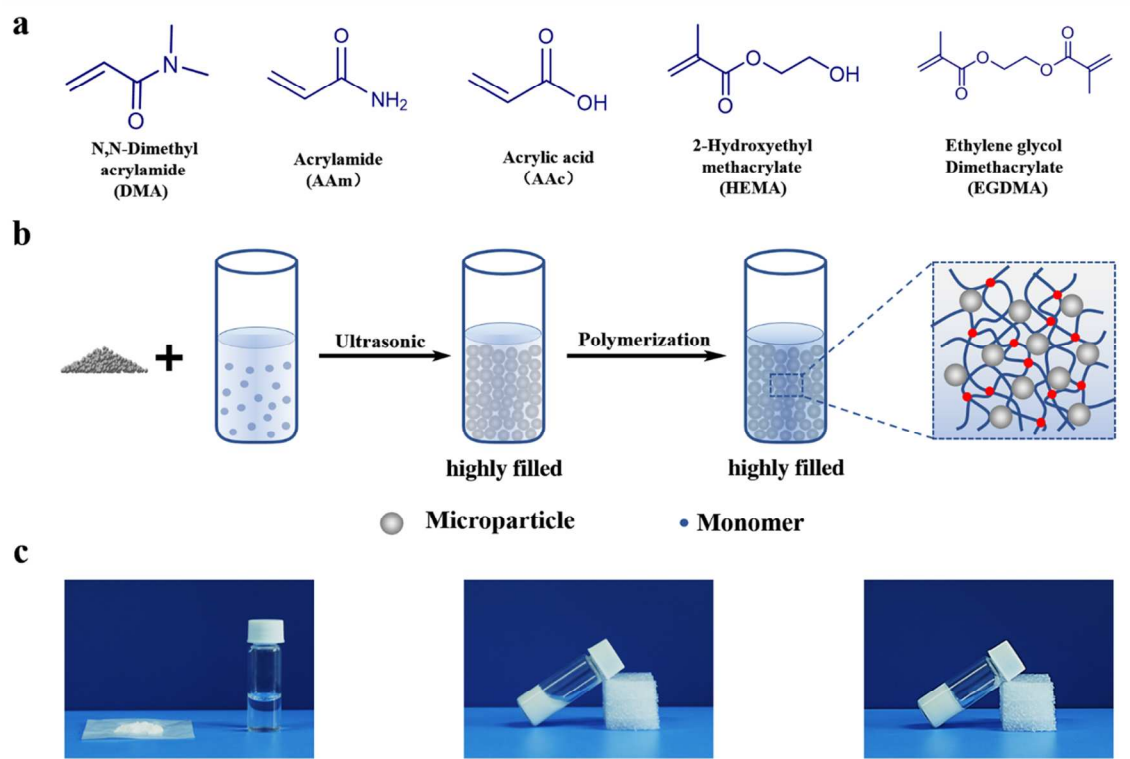
**Preparation of hydrogel.** The highly filled microcomposite hydrogel were fabricated via *in situ* free-radical polymerization with microparticles. Firstly, 20 mL of the precursor solution

containing monomers (DMA, HEMA, AAc, or AAm), chemical cross-linker (EGDMA) and initiator (APS) were prepared. Then, 15  $\mu$ L accelerator TEMED was added to the solution. The monomer concentration was 20 wt% ,30 wt% or 40 wt% of the solution, the concentrations of the chemical cross-linker and initiator were 1 wt% and 0.5 wt% of the monomer respectively. The mixed had been deoxygenated for 20 min with nitrogen gas. Secondly, 5 mL solution was poured into a test tube, then the microparticles were added to the test tube slowly in an ultrasonic environment. (40 KHz, 100W. KQ-2200DV, Kunshan Ultrasonic Instruments Co. LTD) To make sure the solution was highly filled with the microparticle powders, the ultrasonic was further kept for 10 minutes after the microparticle powders were added. Lastly, the test tube was placed in the oven and kept at 40  $^{\circ}$ C for 4 h to complete the polymerization. As control experiment, the pure hydrogels were also prepared by the same procedure without adding microparticle powders.

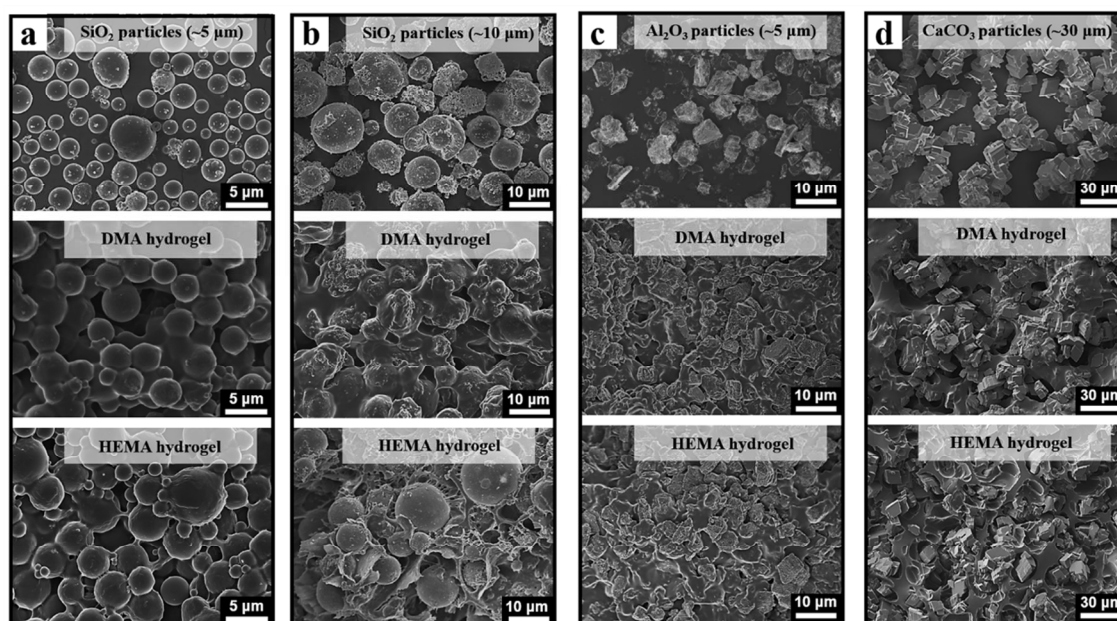
**Characterization.** The morphologies of the HFM hydrogels were performed with a field-emission scanning electron microscope (JSM-7500F, JEOL, Tokyo, Japan) at 5 kV and the samples were coated with a thin layer of gold before examination.

**Mechanical tests.** Hydrogels were prepared in cylindrical shape (12 mm in diameter and 12 mm in height). The dimensions of each sample were measured using a digital caliper before testing. The mechanical tests of the hydrogels were performed at room temperature using a commercial tester equipped with a 1kN load cell (Shen Zhen Suns Technology Stock Co. LTD). The compression tests were conducted at a loading rate of 5 mm/min. The pure hydrogel without microparticles was used as the control. To ensure the accuracy, every test carried out on different types of hydrogels was repeated five times.

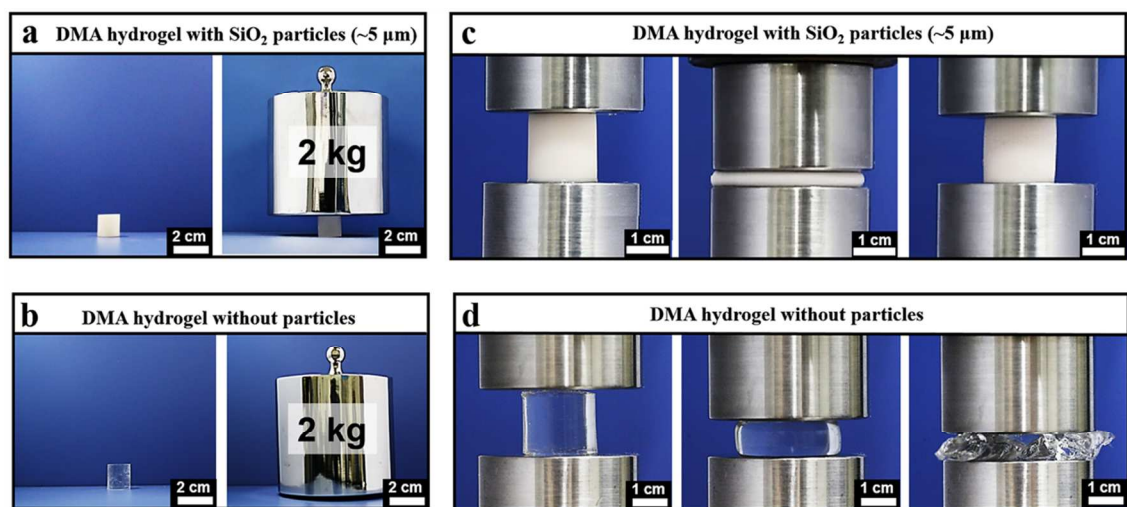
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



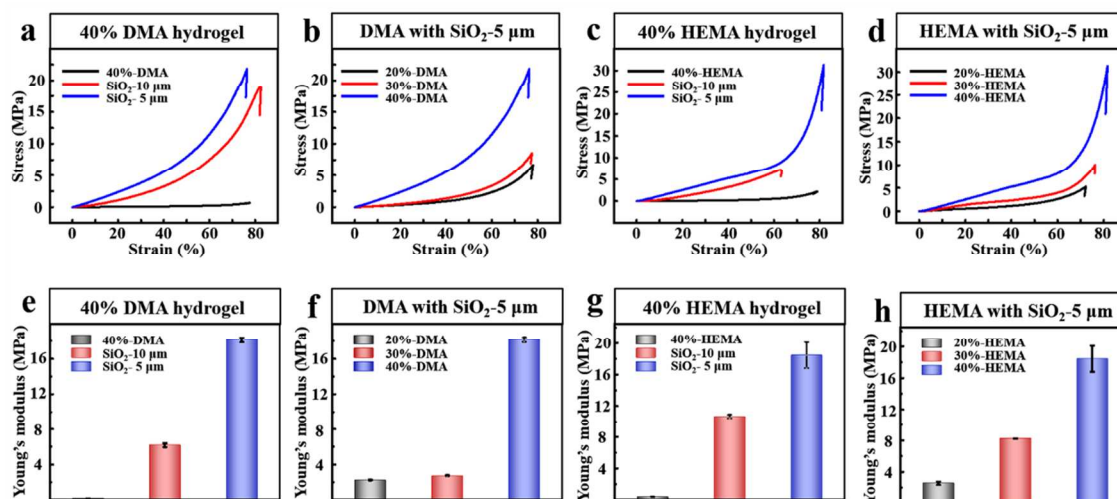
**Figure 1** The schematic illustration of preparation of the highly filled microcomposite hydrogel. (a) The monomers and crosslinker used to prepare the highly filled microcomposite hydrogel (b) Preparation of the highly filled microcomposite hydrogel by using ultrasonic-assistant strategy. (c) Photos of precursor solution before applying ultrasonic (left), after applying ultrasonic (middle) and polymerization (right).



**Figure 2.** SEM images of different particles and the corresponding HFM hydrogels with different monomers. (a) SiO<sub>2</sub> particles ( $\approx 5\mu\text{m}$ ) and corresponding HFM hydrogels (b) SiO<sub>2</sub> particles ( $\approx 10\mu\text{m}$ ) and corresponding HFM hydrogels (c) Al<sub>2</sub>O<sub>3</sub> particles ( $\approx 5\mu\text{m}$ ) and corresponding HFM hydrogels (d) CaCO<sub>3</sub> particles ( $\approx 30\mu\text{m}$ ) and corresponding HFM hydrogels.



**Figure 3.** The optical photographs of the mechanical performance of the HFM hydrogels. (a) HFM hydrogels consisted of 40 wt% DMA and SiO<sub>2</sub> particles ( $\approx 5\ \mu\text{m}$ ) could sustain loading weight of 2 kg without any deformation. (b) Pure hydrogels with 40 wt% DMA could not sustain the loading weight of 2 kg. (c) HFM hydrogels consisted of 40 wt% DMA and SiO<sub>2</sub> particles ( $\approx 5\ \mu\text{m}$ ) could sustain high compression stress and recover most of its original shape (d) Pure hydrogels with 40 wt%. DMA break down easily when compressed.



**Figure 4.** The stress-strain curves and corresponding elastic modulus of various HFM hydrogels. (a), (e) 40 wt% DMA hydrogel with different  $\text{SiO}_2$  particles ( $\approx 10 \mu\text{m}$  and  $\approx 5 \mu\text{m}$ ). (b), (f) DMA hydrogels with  $\text{SiO}_2$  particles ( $\approx 5 \mu\text{m}$ ) and different monomer concentrations. (c), (g) 40 wt% HEMA hydrogel with different  $\text{SiO}_2$  particles ( $\approx 10 \mu\text{m}$  and  $\approx 5 \mu\text{m}$ ). (d), (h) HEMA hydrogels with  $\text{SiO}_2$  particles ( $\approx 5 \mu\text{m}$ ) and different monomer concentrations.

**Table 1** Mechanical properties of the HFM-DMA hydrogels

Monomer DMA (wt %)	Particle	Particle size (μm)	Particle content (wt-%)	compression strength at 75%strain (MPa)	Young's modulus (MPa)	Dissipated energy (MJ/m <sup>3</sup> )
20	-	-	-	0.11 ± 0.01	0.032 ± 0.002	0.015 ± 0.004
20	CaCO <sub>3</sub>	30	43.56 ± 1.34	0.24 ± 0.03	0.232 ± 0.012	0.073 ± 0.06
20	Al <sub>2</sub> O <sub>3</sub>	5	43.72 ± 1.63	0.46 ± 0.05	0.156 ± 0.011	0.065 ± 0.06
20	SiO <sub>2</sub>	10	45.79 ± 1.83	2.22 ± 0.28	0.516 ± 0.015	0.55 ± 0.04
20	SiO <sub>2</sub>	5	65.67 ± 2.33	5.45 ± 0.51	2.22 ± 0.065	1.13 ± 0.16
30	-	-	-	0.37 ± 0.04	0.095 ± 0.002	0.06 ± 0.003
30	CaCO <sub>3</sub>	30	46.06 ± 1.59	0.73 ± 0.06	0.519 ± 0.04	0.019 ± 0.003
30	Al <sub>2</sub> O <sub>3</sub>	5	45.68 ± 1.68	2.17 ± 0.26	0.464 ± 0.064	0.026 ± 0.004
30	SiO <sub>2</sub>	10	49.64 ± 1.88	4.80 ± 0.35	1.15 ± 0.042	0.77 ± 0.08
30	SiO <sub>2</sub>	5	64.21 ± 2.28	7.29 ± 0.66	2.72 ± 0.068	1.57 ± 0.21
40	-	-	-	0.54 ± 0.03	0.18 ± 0.003	0.11 ± 0.02
40	CaCO <sub>3</sub>	30	44.5 ± 1.48	0.88 ± 0.07	0.755 ± 0.022	0.29 ± 0.04
40	Al <sub>2</sub> O <sub>3</sub>	5	42.83 ± 1.36	2.88 ± 0.32	0.677 ± 0.035	0.53 ± 0.04
40	SiO <sub>2</sub>	10	46.77 ± 1.77	13.77 ± 1.14	6.18 ± 0.21	4.21 ± 0.62
40	SiO <sub>2</sub>	5	65.21 ± 2.51	20.52 ± 1.83	18.15 ± 0.29	5.16 ± 0.65

**Table 2** Mechanical properties of the HFM-HEMA hydrogels

Monomer HEMA (wt %)	Particle	Particle size (μm)	Particle content (wt %)	compression strength at 75%strain (MPa)	Young's modulus (MPa)	Dissipated energy (kJ/m <sup>3</sup> )
20	-	-	-	0.0775 ± 0.01	0.0265 ± 0.0014	0.009 ± 0.003
20	CaCO <sub>3</sub>	30	44.57 ± 1.22	0.377 ± 0.04	0.328 ± 0.034	0.057 ± 0.003
20	Al <sub>2</sub> O <sub>3</sub>	5	43.86 ± 1.54	1.259 ± 0.11	0.248 ± 0.008	0.133 ± 0.03
20	SiO <sub>2</sub>	10	50.34 ± 1.78	5.84 ± 0.75	2.19 ± 0.012	0.86 ± 0.004
20	SiO <sub>2</sub>	5	71.49 ± 2.63	7.218 ± 0.77	2.56 ± 0.21	1.02 ± 0.19
30	-	-	-	1.178 ± 0.21	0.202 ± 0.0032	0.15 ± 0.004
30	CaCO <sub>3</sub>	30	42.77 ± 1.55	7.067 ± 0.79	1.04 ± 0.045	0.49 ± 0.06
30	Al <sub>2</sub> O <sub>3</sub>	5	44.36 ± 1.64	3.585 ± 0.43	0.626 ± 0.011	0.40 ± 0.03
30	SiO <sub>2</sub>	10	48.04 ± 1.52	3.89 ± 0.37	9.09 ± 0.074	1.88 ± 0.25
30	SiO <sub>2</sub>	5	64.8 ± 2.18	9.096 ± 1.06	8.22 ± 0.078	2.10 ± 0.16
40	-	-	-	1.559 ± 0.21	0.373 ± 0.0064	0.27 ± 0.03
40	CaCO <sub>3</sub>	30	40.57 ± 1.48	4.463 ± 0.46	1.16 ± 0.012	0.81 ± 0.06
40	Al <sub>2</sub> O <sub>3</sub>	5	44.39 ± 1.29	5.79 ± 0.59	0.706 ± 0.023	1.01 ± 0.26
40	SiO <sub>2</sub>	10	48.54 ± 1.57	9.76 ± 1.03	10.64 ± 0.024	1.66 ± 0.21
40	SiO <sub>2</sub>	5	65.01 ± 2.36	17.50 ± 1.68	18.42 ± 1.62	5.40 ± 0.46



## ASSOCIATED CONTENT

### Supporting Information

The stress-strain curves and corresponding elastic modulus of the HFM hydrogels with different monomers particles.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: zhaoty@buaa.edu.cn

\*E-mail: liumj@buaa.edu.cn

### Notes

The authors declare no competing financial interest

## ACKNOWLEDGMENT

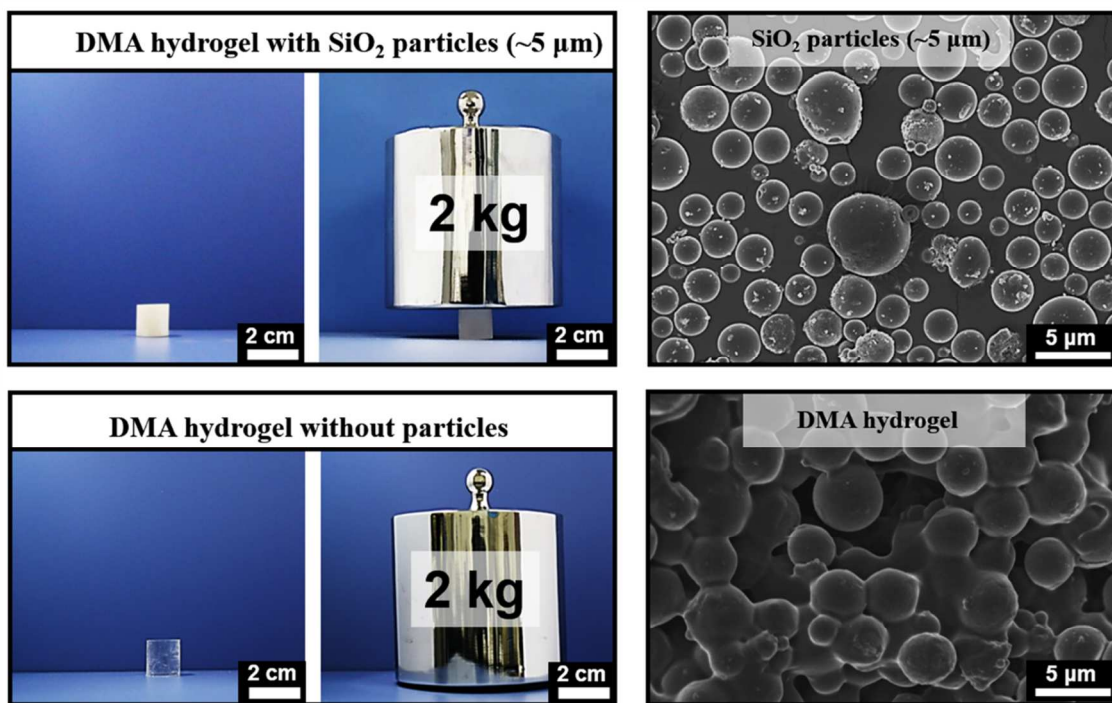
This research was supported by the National Natural Science Foundation (21574004), the National Natural Science Funds for Distinguished Young Scholar (21725401), the National Key R&D Program of China (2017YFA0207800), the 111 project (B14009), the Fundamental Research Funds for the Central Universities, and the National ‘Young Thousand Talents Program’.

## REFERENCES

1. Lee, K. Y.; Mooney, D. J., Hydrogels for tissue engineering. *Chemical Reviews* **2001**, *101*, 1869-1879.
2. Zhang, Y. S.; Khademhosseini, A., Advances in engineering hydrogels. *Science* **2017**, *356*, eaaf3627.
3. Peppas, N. A.; Hilt, J. Z.; Khademhosseini, A.; Langer, R., Hydrogels in biology and medicine: From molecular principles to bionanotechnology. *Advanced Materials* **2006**, *18*, 1345-1360.
4. Zhai, X.; Ma, Y.; Hou, C.; Gao, F.; Zhang, Y.; Ruan, C.; Pan, H.; Lu, W. W.; Liu, W., 3D-Printed High Strength Bioactive Supramolecular Polymer/Clay Nanocomposite Hydrogel Scaffold for Bone Regeneration. *Acs Biomaterials Science & Engineering* **2017**, *3*, 1109-1118.
5. Xue, Z.; Wang, S.; Lin, L.; Chen, L.; Liu, M.; Feng, L.; Jiang, L., A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation. *Advanced Materials* **2011**, *23*, 4270-4273.
6. Cong, H. P.; Qiu, J. H.; Yu, S. H., Thermoresponsive poly(N-isopropylacrylamide)/graphene/Au nanocomposite hydrogel for water treatment by a laser-assisted approach. *Small* **2015**, *11*, 1165-1170.
7. Qiu, Y.; Park, K., Environment-sensitive hydrogels for drug delivery. *Advanced Drug Delivery Reviews* **2001**, *53*, 321-339.
8. Chen, L.; Yao, X.; Gu, Z.; Zheng, K.; Zhao, C.; Lei, W.; Rong, Q.; Lin, L.; Wang, J.; Jiang, L.; Liu, M., Covalent tethering of photo-responsive superficial layers on hydrogel surfaces for photo-controlled release. *Chem Sci* **2017**, *8*, 2010-2016.
9. Yao, X.; Chen, L.; Ju, J.; Li, C.; Tian, Y.; Jiang, L.; Liu, M., Superhydrophobic Diffusion Barriers for Hydrogels via Confined Interfacial Modification. *Adv Mater* **2016**, *28* (34), 7383-9.
10. Chen, L.; Yin, Y.-a.; Liu, Y.-x.; Lin, L.; Liu, M.-j., Design and fabrication of functional hydrogels through interfacial engineering. *Chinese Journal of Polymer Science* **2017**, *35*, 1181-1193.
11. Wang, W.; Zhang, Y.; Liu, W., Bioinspired fabrication of high strength hydrogels from non-covalent interactions. *Progress in Polymer Science* **2017**, *71*, 1-25.
12. Shin, M. K.; Spinks, G. M.; Shin, S. R.; Kim, S. I.; Kim, S. J., Nanocomposite Hydrogel with High Toughness for Bioactuators. *Advanced Materials* **2009**, *21*, 1712-1715.
13. Hu, J.; Kurokawa, T.; Hiwatashi, K.; Nakajima, T.; Wu, Z. L.; Liang, S. M.; Gong, J. P., Structure Optimization and Mechanical Model for Microgel-Reinforced Hydrogels with High Strength and Toughness. *Macromolecules* **2012**, *45*, 5218-5228.
14. Nonoyama, T.; Wada, S.; Kiyama, R.; Kitamura, N.; Mredha, M. T.; Zhang, X.; Kurokawa, T.; Nakajima, T.; Takagi, Y.; Yasuda, K.; Gong, J. P., Double-Network Hydrogels Strongly Bondable to Bones by Spontaneous Osteogenesis Penetration. *Adv Mater* **2016**, *28*, 6740-6745.
15. Ismail, Y. A.; Shin, S. R.; Shin, K. M.; Yoon, S. G.; Shon, K.; Kim, S. I.; Kim, S. J., Electrochemical actuation in chitosan/polyaniline microfibers for artificial muscles fabricated using an in situ polymerization. *Sensors and Actuators B-Chemical* **2008**, *129*, 834-840.
16. Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y., Double-network hydrogels with extremely high mechanical strength. *Advanced Materials* **2003**, *15*, 1155-1158.
17. Haque, M. A.; Kurokawa, T.; Gong, J. P., Super tough double network hydrogels and their application as biomaterials. *Polymer* **2012**, *53*, 1805-1822.

18. Sun, T. L.; Kurokawa, T.; Kuroda, S.; Bin Ihsan, A.; Akasaki, T.; Sato, K.; Haque, M. A.; Nakajima, T.; Gong, J. P., Physical hydrogels composed of polyampholytes demonstrate high toughness and viscoelasticity. *Nature Materials* **2013**, *12*, 932-937.
19. Haraguchi, K.; Takehisa, T., Nanocomposite hydrogels: A unique organic-inorganic network structure with extraordinary mechanical, optical, and swelling/de-swelling properties. *Advanced Materials* **2002**, *14*, 1120-1124.
20. Wang, Q.; Mynar, J. L.; Yoshida, M.; Lee, E.; Lee, M.; Okuro, K.; Kinbara, K.; Aida, T., High-water-content mouldable hydrogels by mixing clay and a dendritic molecular binder. *Nature* **2010**, *463*, 339-343.
21. Wu, D.; Yi, M.; Duan, H.; Xu, J.; Wang, Q., Tough TiO<sub>2</sub>-rGO-PDMAA nanocomposite hydrogel via one-pot UV polymerization and reduction for photodegradation of methylene blue. *Carbon* **2016**, *108*, 394-403.
22. Zhao, N.; Yang, M.; Zhao, Q.; Gao, W.; Xie, T.; Bai, H., Superstretchable Nacre-Mimetic Graphene/Poly(vinyl alcohol) Composite Film Based on Interfacial Architectural Engineering. *ACS Nano* **2017**, *11*, 4777-4784.
23. Kamata, H.; Akagi, Y.; Kayasuga-Kariya, Y.; Chung, U. I.; Sakai, T., "Nonswellable" hydrogel without mechanical hysteresis. *Science* **2014**, *343*, 873-875.
24. Bu, Y.; Shen, H.; Yang, F.; Yang, Y.; Wang, X.; Wu, D., Construction of Tough, in Situ Forming Double-Network Hydrogels with Good Biocompatibility. *ACS Appl Mater Interfaces* **2017**, *9*, 2205-2212.
25. Okumura, Y.; Ito, K., The polyrotaxane gel: A topological gel by figure-of-eight cross-links. *Advanced Materials* **2001**, *13*, 485-487.
26. Ito, K., Novel Cross-Linking Concept of Polymer Network: Synthesis, Structure, and Properties of Slide-Ring Gels with Freely Movable Junctions. *Polym. J* **2007**, *39*, 489-499.
27. Nepogodiev, S. A.; Stoddart, J. F., Cyclodextrin-Based Catenanes and Rotaxanes. *Chemical Reviews* **1998**, *98*, 1959-1976.
28. Huang, T.; Xu, H. G.; Jiao, K. X.; Zhu, L. P.; Brown, H. R.; Wang, H. L., A Novel Hydrogel with High Mechanical Strength: A Macromolecular Microsphere Composite Hydrogel. *Advanced Materials* **2007**, *19*, 1622-1626.
29. Jeon, I.; Cui, J.; Illeperuma, W. R.; Aizenberg, J.; Vlassak, J. J., Extremely Stretchable and Fast Self-Healing Hydrogels. *Adv Mater* **2016**, *28*, 4678-4683.
30. Sun, J. Y.; Zhao, X.; Illeperuma, W. R.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z., Highly stretchable and tough hydrogels. *Nature* **2012**, *489*, 133-136.
31. Tuncaboylu, D. C.; Sari, M.; Oppermann, W.; Okay, O., Tough and Self-Healing Hydrogels Formed via Hydrophobic Interactions. *Macromolecules* **2011**, *44*, 4997-5005.
32. Chen, Q.; Zhu, L.; Chen, H.; Yan, H.; Huang, L.; Yang, J.; Zheng, J., A Novel Design Strategy for Fully Physically Linked Double Network Hydrogels with Tough, Fatigue Resistant, and Self-Healing Properties. *Advanced Functional Materials* **2015**, *25*, 1598-1607.
33. Lin, P.; Ma, S.; Wang, X.; Zhou, F., Molecularly engineered dual-crosslinked hydrogel with ultrahigh mechanical strength, toughness, and good self-recovery. *Adv Mater* **2015**, *27*, 2054-2059.
34. Yang, Y.; Wang, X.; Yang, F.; Shen, H.; Wu, D., A Universal Soaking Strategy to Convert Composite Hydrogels into Extremely Tough and Rapidly Recoverable Double-Network Hydrogels. *Adv Mater* **2016**, *28*, 7178-7184.

35. Zhang, Y.; Li, Y.; Liu, W., Dipole-Dipole and H-Bonding Interactions Significantly Enhance the Multifaceted Mechanical Properties of Thermoresponsive Shape Memory Hydrogels. *Advanced Functional Materials* **2015**, *25*, 471-480.
36. Haraguchi, K.; Li, H. J.; Matsuda, K.; Takehisa, T.; Elliott, E., Mechanism of forming organic/inorganic network structures during in-situ free-radical polymerization in PNIPA-clay nanocomposite hydrogels. *Macromolecules* **2005**, *38*, 3482-3490.
37. Zhao, Z.; Zhang, K.; Liu, Y.; Zhou, J.; Liu, M., Highly Stretchable, Shape Memory Organohydrogels Using Phase-Transition Microinclusions. *Adv Mater* **2017**, *29*, 1701695.
38. Lin, P.; Zhang, T.; Wang, X.; Yu, B.; Zhou, F., Freezing Molecular Orientation under Stretch for High Mechanical Strength but Anisotropic Hydrogels. *Small* **2016**, *12*, 4386-4392.
39. Zhao, Z.; Liu, Y.; Zhang, K.; Zhuo, S.; Fang, R.; Zhang, J.; Jiang, L.; Liu, M., Biphasic synergistic gel materials with switchable mechanics and self-healing capacity. *Angewandte Chemie International Edition* **2017**, *56*, 13464-13469.
40. Xu, B.; Li, Y. M.; Gao, F.; Zhai, X. Y.; Sun, M. G.; Lu, W.; Cao, Z. Q.; Liu, W. G., High Strength Multifunctional Multiwalled Hydrogel Tubes: Ion-Triggered Shape Memory, Antibacterial, and Anti-inflammatory Efficacies. *Acs Applied Materials & Interfaces* **2015**, *7*, 16865-16872.
41. Dai, X. Y.; Zhang, Y. Y.; Gao, L. N.; Bai, T.; Wang, W.; Cui, Y. L.; Liu, W. G., A Mechanically Strong, Highly Stable, Thermoplastic, and Self-Healable Supramolecular Polymer Hydrogel. *Advanced Materials* **2015**, *27*, 3566-3571.
42. Sakai, T.; Matsunaga, T.; Yamamoto, Y.; Ito, C.; Yoshida, R.; Suzuki, S.; Sasaki, N.; Shibayama, M.; Chung, U.-i., Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers. *Macromolecules* **2008**, *41*, 5379-5384.
43. Lake, G. J.; Thomas, A. G., STRENGTH OF HIGHLY ELASTIC MATERIALS. *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **1967**, *300*, 108-119.



## Table of Contents