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¹ Super Stretchable and Compressible Hydrogels Inspired by Hook-² and-Loop Fasteners

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ABSTRACT: Insp	pired by hook-and-loop fas	steners, we designed a ZrP	

6 hydrogel network containing α -zirconium phosphate (ZrP) two-dimen-7 sional nanosheets with a high density of surface hydroxyl groups serving 8 as nanopatches with numerous "hooks," while polymer chains with 9 plentiful amine functional groups serve as "loops." Our multiscale 10 molecular simulations confirm that both the high density of hydroxyl 11 groups on nanosheets and the large number of amine functional groups 12 on polymer chains are essential to achieve reversible interactions at the 13 molecular scale, functioning as nano hook-and-loop fasteners to dissipate 14 energy. As a result, the synthesized hydrogel possesses superior 15 stretchability (>2100% strain), resilience to compression (>90% strain), 16 and durability. Remarkably, the hydrogel can sustain >5000 cycles of 17 compression with torsion in a solution mimicking synovial fluid, thus 18 promising for potential biomedical applications such as artificial articular



19 cartilage. This hook-and-loop model can be adopted and generalized to design a wide range of multifunctional materials with 20 exceptional mechanical properties.

21 INTRODUCTION

22 Hydrogels have attracted great attention and found widespread 23 application.¹⁻⁶ However, conventional hydrogels are usually 24 mechanically weak, which significantly limits their potential 25 applications in artificial articular cartilages,⁷ contact lenses,⁸ gel ²⁶ actuators,^{9,10} etc. Especially in the engineering of cartilage 27 tissue, favorable biocompatibility and biodegradability make 28 hydrogels an excellent candidate to replace the damaged 29 cartilage tissue and serve as the scaffold for cells, but the 30 limited strength of hydrogels causes failures under inevitable 31 repetitive loads at the cartilage tissues.¹¹ Strengthening and/or 32 toughening hydrogels thus have been a major research focus. 33 The first milestone was laid by Gong and co-workers, ^{12–19} who 34 invented double-network hydrogels showing superior mechan-35 ical performance. Suo and co-workers²⁰⁻²⁵ developed a series 36 of alginate/polyacrylamide hydrogels that make full use of 37 reversible cross-links, which exhibited outstanding mechanical 38 properties because the strong covalent bonds serve to maintain 39 the entire structure and the weak ionic bonds help dissipate 40 energy under deformation. Haraguchi²⁶⁻³⁰ and Aida³¹⁻³⁴ 41 chose clays as effective reinforcers in the hydrogel structure, 42 leading to highly stretchable tough hydrogels or moldable 43 hydrogels. Meanwhile, many others³⁵⁻⁴⁹ made significant 44 contributions and enriched this field of research. 45 Zhao^{10,50-54} outlined two key guidelines to design tough 46 hydrogels: energy dissipation under deformation and configuration recovery after strain,⁵⁵ which can typically be achieved 47 via weak reversible interactions.^{20,55} However, in conventional 48 hydrogels, weak interacting points are usually scattered 49 throughout the system, leading to a slow and incomplete 50 recovery in response to deformation. To overcome this 51 challenge, inspired by hook-and-loop fasteners, an analog to 52 weak interactions between chemicals,^{56,57} we designed a 53 hydrogel network containing similar nano "hook-and-loop 54 fastener" structures using α -zirconium phosphate (ZrP) 2- 55 dimensional nanosheets to facilitate rapid, effective, and highly 56 reversible energy dissipation. The resultant hydrogel possesses 57 superior stretchability (>2100% strain), resilience to compres- 58 sion (>90% strain), and durability, promising for various 59 applications.

EXPERIMENTAL SESSION

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Materials. Acrylamide (AM, >98%, TCI) was purified by 62 recrystallization from water/ethanol and then dried in a vacuum. All 63 the other chemicals, including zirconyl chloride octahydrate (ZrOCl2 \cdot 64

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Figure 1. (a) Digital picture of a *Xanthium* bur. (b) Images of a physical hook-and-loop fastener and the corresponding illustration of a nano hookand-loop fastener (geometry not related to real bonds), where the partially charged hydroxyl groups on the ZrP-NS surface serve as hooks, while the partially charged amine groups on polymer chains act as loops. Their ionic interactions result in a hook-and-loop effect at a nanoscale. (c) Procedures to synthesize the ZrP-containing hydrogel and its microstructure (not drawn to scale).

65 8H2O, 98%, Aldrich), phosphoric acid (85%, Aldrich), allylamine 66 (98%, Aldrich), *N*,*N*'-methylenebisacrylamide (MBAA, 97%, Alfa 67 Aesar), potassium persulfate (KPS, 99%, ACROS), sodium bisulfite 68 (SBS, Fisher), and propylamine (PA, 99%, ACROS), were used as 69 received without further purification.

Synthesis and Exfoliation of α -Zirconium Phosphate (ZrP). 70 71 ZrP microcrystals were synthesized according to the procedures 72 described in an earlier report.⁵⁸ In brief, 6.0 g of ZrOCl₂ 8H₂O was 73 mixed with 60.0 mL of 6.0 M H₃PO₄ and sealed in a Teflon-lined 74 pressure vessel. The reaction was carried out at 200 °C for 24 h to 75 synthesize ZrP microcrystals with a diameter of ca. 600-800 nm. The prepared ZrP microcrystals were exfoliated by allylamine (or 76 propylamine as a control) in an aqueous dispersion, with a molar 77 ratio of ZrP to amine of 1:1.59 The allylamine-exfoliated ZrP (ZrP-78 79 allylamine) was used as one of the monomers to synthesize hydrogels 80 PAM-10ZrP-C and PAM-10ZrP, while the propylamine-exfoliated 81 ZrP [ZrP(PA)] was used to synthesize PAM-10ZrP(PA)-C. The 82 concentrations of ZrP-allylamine and ZrP-PA were determined using 83 the ZrP content. All hydrogels contained ca. 78 wt % of water. The 84 detailed composition of the samples is listed in Table S1.

A series of aqueous solutions were prepared by dissolving 0.020 g 66 of MBAA, 0.300 g of KPS, and 0.100 g of SBS in 8.00, 10.00, and 87 10.00 g of water, respectively.

Synthesis of Hydrogel PAM-C. A mixture of 2.000 g of AM
(monomer), 0.1000 g of MBAA (chemical cross-linker), and 0.006 g
of KPS (initiator, 0.20 g of the solution) was added to 7.50 g of water.
The mixture was magnetically stirred for 10 min and ultrasonicated

for another 30 min in an ice bath. The hydrogels were synthesized in 92 two types of perfluoroalkoxy tubes (Fluorostore), one with an internal 93 diameter of 6.0 mm and the other 23.0 mm. The oxygen in the tubes 94 was removed through three cycles of the freeze-vacuum-thaw method 95 by N_2 gas before the reaction. All of the following experiments were 96 carried out in such an oxygen-free system. A sample of 0.002 g of SBS 97 (0.20 g of the solution) was injected into the solution to initiate the 98 free radical polymerization at 25 °C for 20 h. PAM-C is the control 99 sample without ZrP-NSs and thus no ionic cross-linking.

Synthesis of Hydrogel PAM-10ZrP(PA)-C. A mixture of 2.000 g 101 of AM (monomer), 0.0005 g of MBAA (chemical cross-linker, 0.20 g 102 of the solution), 0.006 g of KPS (initiator, 0.20 g of the solution), and 103 2.40 g of H_2O (solvent) was added to 5.00 mL of ZrP(PA) aqueous 104 dispersion (4 wt %). All of the following steps are the same as 105 described in the synthesis of hydrogel PAM-C. PAM-10ZrP(PA)-C is 106 the control sample without ionic bonding between the polymers and 107 the nanosheets.

Synthesis of Hydrogel PAM-10ZrP. A mixture of 2.000 g of AM 109 (monomer), 0.006 g of KPS (initiator, 0.20 g of the solution), and 110 2.60 g of H_2O (solvent) was added to 5.00 mL of allylamine- 111 exfoliated ZrP aqueous dispersion (4.0 wt %). All of the following 112 steps are exactly the same as described in the synthesis of hydrogel 113 PAM-C. PAM-10ZrP is the control sample without chemical cross- 114 linking.

Synthesis of Hydrogel PAM-10ZrP-C. A mixture of 2.000 g of 116 AM (monomer), 0.0005 g of MBAA (chemical cross-linker, 0.20 g of 117 the solution), 0.006 g of KPS (initiator, 0.20 g of the solution), and 118



Figure 2. (a) Pictures of a cylindrical PAM-10ZrP-C hydrogel sample (6 mm in diameter and 40 mm in length) being aggressively pressed by a brand-new razor blade, remaining intact, and exhibiting no visible cracking after being stretched immediately; (b) pictures of a cylindrical PAM-10ZrP-C sample (23 mm in diameter and 5 mm in height) before, during, and immediately after being compressed by 90.0%; (c) pictures of a cylindrical PAM-C sample (23 mm in diameter and 5 mm in height) before and after being gently compressed; (d) representative tensile stress-strain curves of the hydrogel samples; (e) representative compressive stress-strain curves of the hydrogel samples; (f) cyclic compression test result of PAM-10ZrP-C.

119 2.40 g of H₂O (solvent) was added to 5.00 mL of allylamine-120 exfoliated ZrP aqueous dispersion (4.0 wt %). All of the following 121 steps are the same as described in the synthesis of hydrogel PAM-C. Materials Characterization. Thermogravimetric analyses (TGA) 122 were carried out with a TGA Q500 analyzer (TA Instruments). The 123 124 hydrogel samples were heated from room temperature to 120 °C at a 125 rate of 10 °C/min and isothermed for 3 h in a nitrogen flow. The water content was determined by the weight loss of the samples. 126 Small-angle X-ray scattering (SAXS) characterization was carried out 127 128 by using a Bruker NANOSTAR instrument. X-ray diffraction (XRD) 129 patterns were obtained using a Bruker D5005 powder diffractometer 130 with Cu K α beam at 40 kV and 40 mA.

Before all of the following characterizations, the hydrogel samples were dried in a specific way to maintain the original morphology. The samples were first freeze-dried under -55 °C with a pressure lower than 10^{-3} Pa for 72 h and then further vacuum dried at 80 °C for 24 h. Transmission electron microscopy (TEM) was performed using a BEOL microscope (JEM 1200EXII). Ultrathin films (ca. 80–100 nm thick) were prepared for TEM imaging by thin-sectioning dried gels embedded in epoxy resin using an ultramicrotome (Reichert-Jung Ultracut E). Fourier transform infrared (FTIR) spectra of the dried 139 hydrogels were obtained using an FTIR spectrophotometer 140 (PerkinElmer Spectrum 100) with milled dried hydrogels by the 141 conventional KBr pellet method. The FTIR spectra of ZrP powders 142 and allylamine exfoliated ZrP were also obtained by the same method. 143

Mechanical Tests. The tensile stress—strain measurements were 144 performed using a MTS CMT4104 at 25 °C. The specimens were 145 cylindrical samples with a diameter of 6 mm and a length of 60 mm. 146 The crosshead speed was set to be 50 mm/min. The stress was 147 calculated on the basis of the initial cross-section. 148

The compression tests were carried out using a Lloyd LRSKPlus at 149 25 °C. The cylindrical samples with a diameter of 23 mm and a length 150 of 5 mm were placed on the lower platen, and the strain rate was set 151 to be 50 mm/min. The stress was calculated on the basis of the initial 152 cross-section. 153

The preliminary compression cyclic loading test was performed 154 using a universal tester (Lloyd LR5KPlus) at 25 °C. The cylindrical 155 samples with a diameter of 23 mm and a length of 5 mm were placed 156 on the lower platen, and the strain rate was set to be 50 mm/min. The 157 repetitive strain between 80 and 60% was applied 500 times.

Sample	Types of Interaction			Tensile Results				Compressive Results				
	Nanosheet Interaction	Covalent Cross- linking	Ionic Bonding	Hydrogen Bonding	Young's Modulus (MPa)	Stress at 500% (MPa)	Stress at 1000% (MPa)	Tensile Strength at Break (MPa)	Tensile Strain at Break (%)	Modulus of Toughness (MJ/m ³) ^{a)}	Compressive Strength (MPa)	Strain (%)
PAM-10ZrP-C	~	~	\checkmark	\checkmark	$0.200 \\ \pm \\ 0.050$	$0.280 \\ \pm \\ 0.030$	$0.360 \\ \pm \\ 0.040$	$0.680 \\ \pm \\ 0.040$	2160 ± 90	$\begin{array}{c} 8.80 \\ \pm \\ 0.70 \end{array}$	1.210± 0.040	90.0 ^{b)}
PAM-10ZrP	~		\checkmark	\checkmark	$0.049 \\ \pm \\ 0.006$	0.090 ± 0.012	$0.190 \\ \pm \\ 0.030$	$0.430 \\ \pm \\ 0.030$	2110 ± 110	$4.60 \\ \pm \\ 0.70$	0.652± 0.009	90.0 ^{b)}
PAM- 10ZrP(PA)-C	~	\checkmark		\checkmark	0.020 ± 0.008	$0.035 \\ \pm \\ 0.005$	$0.067 \\ \pm \\ 0.012$	$0.240 \\ \pm \\ 0.050$	2200 ± 300	2.00 ± 0.50	0.237± 0.012	90.0 ^{b)}
PAM-C		\checkmark		\checkmark	-	-	-	-	-	-	0.288 ± 0.018	59.7 ±0.6

Table 1. Mechanical Properties of the Hydrogels

^aThe modulus of toughness data were calculated from the areas under the tensile stress-strain curves. ^bThe samples can sustain an even higher compressive strain, but the test stopped at this value because at 90.0% strain, the deformation already became so significant that the sample was squeezed out of the compression platen.

The cyclic tensile tests were performed using a universal tester 160 (MTS CMT4104) at 25 °C. The specimens were in a cylindrical 161 shape with a diameter of 6 mm and a length of 60 mm. The crosshead 162 speed was set to be 50 mm/min for both loading and unloading. After 163 each loading/unloading cycle, the sample was left to recover for 10 164 min before the next cycle was tested. The stress was calculated on the 165 basis of the initial cross-section.

Articular Cartilage Application (Hip Simulation). The axial compression tests were carried out on the samples using a Bose 3220 kg dynamic mechanical tester (US) at room temperature before and after the cyclic loading tests (compression or compression with torsion). The cylindrical specimens were placed on the lower platen, and they were compressed to 50% strain at a strain rate of 0.1 mm/s.

The compression cyclic loading tests were carried out using a Bose 173 3220 dynamic mechanical tester (US) either at room temperature in 174 air or at 37 $^{\circ}$ C in a protein buffer solution (15 g/L of bovine serum 175 albumin and phosphate-buffered saline), mimicking synovial fluid. 176 The repetitive strain between 100 and 50% was applied 5000 times at 177 1 Hz.

The compression with torsion cyclic loading tests were carried out 179 using a Bose 3220 dynamic mechanical tester (US) either at room 180 temperature in air or at 37 °C in the same aforementioned protein 181 buffer solution. The 5000-time biaxial loading includes the repetitive 182 compression with the strain between 100 and 50% at 1 Hz and the 183 repetitive torsion with an angular displacement of 45° at 1 Hz (please 184 see more details in Section S3).

185 RESULTS AND DISCUSSION

Hydrogels Inspired by Hook-and-Loop Fasteners. 186 187 Burs in nature are able to stick onto clothes upon contact, owing to the high density of tiny hooks on their surface 188 (Figure 1a).⁶⁰ An even better-known example, the hook-and-189 190 loop fastener, with dense tiny hooks on one piece and coils of 191 loops on the other, can perform similarly. Once the two parts 192 are attached, the high density of hooks and loops create 193 abundant weak physical interactions to form desirable 194 fastening. Moreover, one can peel them apart and stick them 195 together repeatedly and instantly. Inspired by this, we 196 rationally design to incorporate ZrP nanosheets (ZrP-NSs, 197 Figure 1b) with a high density of acidic hydroxyl groups (~4 198 groups/nm²) on both sides (Figure S1, other details of ZrP-

NSs are shown in Figures S2-S5)^{61,62} serving as "hooks," 199 while copious basic amine groups on polymer chains in a 200 polyacrylamide-co-allylamine (PAM-co-AA) hydrogel act as 201 "loops" (Figure 1b). The hooks and loops interact through 202 reversible ionic bonds to form numerous nano hook-and-loop 203 fasteners within the hydrogel. Thanks to the high density of 204 acidic hydroxyl groups on ZrP-NSs (Figure 1b,c), the nano 205 hook-and-loop patches ensure rapid and effective ionic 206 bonding upon contact, endowing the resultant hydrogel with 207 exceptional stretchability (>2100% tensile strain), remarkable 208 compression resilience (>90% compressive strain), and fast 209 recovery. Such nanopatches can also serve as excellent 210 nanoreinforcers.^{63,64}

The hydrogel was synthesized through an in situ 212 copolymerization of acrylamide (AM), MBAA, and allyl- 213 amine-exfoliated ZrP (ZrP-allylamine) (Figure 1c), denoted as 214 PAM-10ZrP-C (mass ratio of ZrP/PAM is 10%), and is 215 chemically cross-linked (C) by MBAA. To thoroughly 216 understand each component's role, three controls, PAM- 217 10ZrP, PAM-10ZrP(PA)-C, and PAM-C, were prepared (see 218 Table S1 for details). All hydrogels contained 78 wt % of water. 219

Superior Stretchability and Compressibility of Hydro- 220 gels. The PAM-10ZrP-C hydrogel is highly stretchable and 221 compression resilient (Figure 2). Impressively, even with a 222 f2 brand-new razor blade, the hydrogel can be barely cut and 223 exhibits no visible cracking even after being stretched 224 immediately (Figure 2a; Movie S1). Overall, the PAM- 225 10ZrP-C hydrogel remarkably outperformed all controls in 226 terms of tensile and compressive moduli of toughness (Figure 227 2b-e, Table 1), which is defined as the total area under the 228 ti stress-strain curve. PAM-C could not withstand clamp 229 compression due to extreme fragility, and thus no tensile 230 data could be obtained. By comparing PAM-C and PAM- 231 10ZrP(PA)-C, clearly the ZrP-NSs, even without ionic 232 interactions with the PAM network, demonstrated a reinforce- 233 ment effect.⁶⁵ Surprisingly, PAM-10ZrP(PA)-C was over- 234 shadowed by PAM-10ZrP, suggesting that even without 235 chemical cross-linking, because of the effective ionic bonding 236

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Figure 3. (a) Models of the interactions between a short polymer chain and a ZrP-NS, a long polymer chain and a ZrP-NS, and a long polymer chain and a bunch of its counterparts. (b-c) Comparisons of (b) spring force and (c) cumulative work ΔW done during the pulling process. (d) Interactions between a long polymer and a ZrP-NS. The polymer chain only contains the $-NH_3^+$ group. The ZrP-NS has the $-O^-$ group with various area densities. (e) Snapshots of a polymer chain on a ZrP-NS during the pulling process. On the ZrP-NS, the oxygen atoms are color coded in yellow in the $-O^-$ groups along the pulling pathway and red in other $-O^-$ groups. (f) Comparison of ΔW during the pulling process as a function of area density of $-O^-$ groups on nanosheets. (g) ΔW at a distance of 8.0 nm as a function of area density of $-O^-$ groups.

237 by the ZrP nanopatches, PAM-10ZrP still exhibits impressive 238 performance.

The significant strength difference between PAM-10ZrP-C 2.39 and PAM-10ZrP indicates a leap in mechanical performance 240 brought by chemical cross-linking. The relatively low degree of 241 cross-linking (2.5 wt % of chemical cross-linker added, Table 242 S1) ensures that the stretchability of PAM-10ZrP-C is barely 243 ompromised, while both the modulus and tensile strength 244 were remarkably improved. The different tensile strengths of 245 these four hydrogels suggest that both strong (i.e., covalent 246 coss-linking) and weak (i.e., ionic bonding) bonds are 247 essential for a high-performance hydrogel.²⁰ However, the 248 nanopatches are key to achieve extraordinary properties. As 249 250 discussed, the covalent cross-linking itself makes the hydrogel fragile, but the addition of hook-and-loop nanopatches helps 251 dissipate energy much more effectively during deformation, 252 validated by the analysis of cyclic tensile tests (Table S2 and 253 Figure S6). Also note that strain-hardening was observed in all 254 the samples containing ZrP-NSs, which is owing to the gradual 255 256 alignment of nanosheets,⁶⁴ as observed by both SAXS characterization (Figure S7) and molecular modeling below. 257 As designed, PAM-10ZrP-C exhibits exceptional compres-258 259 sion resilience (Figure 2b; Movie S2). After compression to 260 10.0% of the original thickness, it promptly recovered within 1 s (Movie S2), while PAM-C shattered after gentle compression 261 (Figure 2c). PAM-10ZrP-C exhibited the highest fracture 262 strength under compression among the hydrogels (Figure 2e; 263 Table 1). The stress of PAM-10ZrP-C reached 1.210 MPa at 264 90.0% compressive strain. Both PAM-10ZrP and PAM-265 10ZrP(PA)-C can sustain fracture strain up to 90.0%, but 266 their strengths were much lower than those of PAM-10ZrP-C. 267 The reversible ionic bonding between the polymer loops and 268 269 the nanopatch hooks undergoes formation and destruction 270 throughout the compression of the hydrogel. PAM-C, despite 271 its decent compressive modulus because of chemical crosslinking, is very fragile for its limited fracture strain and 272 strength. 273

PAM-10ZrP-C also demonstrates extraordinary resistance to 274 cyclic compression. Even after 500 cycles of compressing the 275 sample to 80% of its original height and releasing to 60%, it 276 stayed intact (Figure 2f). The slight decrease of the maximum 277 force with increasing cycles could be the result of unavoidable 278 displacement of the hydrogel on the compression platens 279 during testing. Nonetheless, the barely changed properties at 280 different cycles indicate the high reversibility of the weak 281 bonding within the hydrogel, again thanks to the nano hook- 282 and-loop effect.

A comparison of the mechanical properties of PAM 284 nanocomposite hydrogels using different nanofillers is 285 summarized in Table S3. PAM-10ZrP-C, among all the PAM 286 hydrogels, exhibits an excellent balance in high tensile strength, 287 superior stretchability, and top modulus of toughness. It 288 should be noted that each design of the hydrogel contains 289 different concentrations of water, different nanofillers, and 290 different concentrations of nanofillers. Thus, this table is to 291 simply give a brief overview, while the high modulus of 292 toughness of our design (PAM-10ZrP-C) highlights the 293 advantage of the nano hook-and-loop effect in energy 294 dissipation during the deformation process, which also leads 295 to excellent stretchability and compressibility of resultant 296 hydrogels. 297

Nano Hook-and-Loop Effect Revealed by all-Atom ²⁹⁸ Molecular Simulations. To better understand the mecha- ²⁹⁹ nism, multiscale molecular dynamics (MD) simulations were ³⁰⁰ conducted to thoroughly investigate the interactions between ³⁰¹ the ZrP-NSs and the polymer chains and to assess the nano ³⁰² hook-and-loop effect. As shown in Figure 1a, two main ³⁰³ interactions between the ZrP nanopatches and the polymer ³⁰⁴ chains generate the nano hook-and-loop effect: (1) ionic ³⁰⁵ interactions between the deprotonated hydroxyl groups ($-O^-$, ³⁰⁶ acting as hooks) and the protonated amine groups ($-NH_3^+$, ³⁰⁷ 308 behaving as loops; note that the $-NH_2$ group in the amide is 309 much less basic and thus is ignored in terms of potential ionic 310 interactions), and (2) hydrogen bonding between hydroxyl 311 groups and amine/amide groups, which generates a similar but 312 weaker hook-and-loop effect compared to ionic interactions. 313 The loops on polymer chains will interact with those hooks on 314 ZrP-NSs upon contact. As a hook-and-loop fastener in our 315 daily life, the all-atom MD simulations prove that a sufficiently 316 high density of hooks and a sufficient number of loops on 317 nanosheets and polymers, respectively, are the two most 318 important factors to form strong reversible interactions.

First, as expected, our modeling shows that sufficiently long 319 320 polymer chains in the hydrogel guarantee a sufficiently high 321 density of loops at the nanoscale. As given in Figure 3a, three 322 different systems are established in simulations: (1) short 323 PAM-co-AA chain (with a ratio of x/y = 10:1 as given in 324 Figure 1b) adhering on a ZrP-NS; (2) long polymer chain 325 (with five repeats of the short chain) adhering on a ZrP-NS; 326 (3) long polymer chain interacts with other surrounding 327 counterparts. On the surface of ZrP-NSs, 50% of the hydroxyl 328 groups are deprotonated by allylamine during exfoliation and 329 distributed randomly on the surface. To directly investigate the 330 interactive forces and energy barrier experienced by the 331 polymer chains, we utilize the steered molecular dynamics 332 (SMD) simulation to pull a terminal of the polymer by a 333 moving force in the x direction.^{66,67} Specifically, the terminal 334 carbon atom is pulled by a moving spring force in the x335 direction as shown in Figure 3a. During the pulling process, the 336 applied force (Figure 3b) and the cumulative work (ΔW , 337 Figure 3c) done by the spring are calculated.

For the short polymer chain, the force value has an obvious 338 339 periodic increment and decrement, which is the evidence of 340 repeatedly creating and breaking the weak ionic bonds. 341 However, due to the small number of functional groups in 342 the short chain, weak bonding interactions cannot maintain 343 during the entire process. After a distance of $D\approx7$ nm, the 344 short polymer chain was detached from the nanosheet due to 345 the breakage of all the weak bonds (see the decrease of the 346 force in the green region of Figure 3b and snapshots in Figure 347 S8). For the long polymer chain, it is initially stretched by the 348 spring force, as indicated by the increasing force before $D\approx 5$ 349 nm (blue region as noted in Figure 3b). After this, a portion of 350 the polymer chain is further extended. Additionally, the spring 351 force maintains a larger averaged force value with periodic 352 fluctuation. Furthermore, its ΔW value dramatically increases 353 with an increasing portion of the long polymer chain extended. 354 After $D\approx7$ nm, the long chain has a larger ΔW value than the 355 short chain (the green region in the figure). Moreover, because 356 of its large number of functional groups in the long chain, the 357 polymer chain can adhere onto the nanosheet surface during 358 the entire process. Combining the results for both short and 359 long polymer chains on the ZrP-NS, we can find two key 360 points for the effective interactions between the polymer and 361 nanosheet: (1) the functional groups along with the polymer 362 chain can form reversible weak ionic bonds with the 363 nanosheet; (2) a large number of functional groups on a 364 polymer chain in the hydrogel are necessary to maintain a 365 repeatable and strong interactive force with the ZrP-NSs. 366 Compared with the results of polymer-ZrP interactions, both 367 the force and ΔW for the case of polymer-polymer 368 interactions are much lower. Considering that real polymer 369 chains are usually much longer than the model chains 370 discussed above, the functional group number requirement

on polymer chains can be easily met. Most importantly, the 371 above results clearly show that the incorporation of ZrP-NSs 372 significantly strengthen the interactions with the polymers and 373 thus can store much more energy during deformation. 374

For the polymer-ZrP interactions above, both hydrogen 375 bonding and ionic interactions exist. Before evaluating the 376 effect of hydroxyl density on ZrP-NSs, we need to clarify and 377 differentiate the contributions of the hydrogen bonding and 378 ionic interactions. To this end, two different systems are 379 established in our all-atom simulations: (1) a polymer chain 380 with only $-\text{CONH}_2$ groups (with a ratio of x/y = 11:0 as given 381 in Figure 1b) adhering on the ZrP-NS whose surface has only 382 protonated hydroxyl groups; (2) a polymer chain with only 383 $-NH_3^+$ groups (with a ratio of x/y = 0.11) adhering on the 384 ZrP-NS whose surface has only deprotonated hydroxyl groups. 385 The polymer length in both systems is the same as the long 386 chain in Figure 3a. In this way, -CONH₂ groups on the 387 polymer of the first system can only form hydrogen bond 388 interactions with the -OH groups on the ZrP-NS, while the 389 $-NH_3^+$ groups on the polymer of the second system can only 390 form the ionic-bond interaction with the $-O^-$ groups on the 391 nanosheet. We also utilized the SMD simulations to compare 392 the cumulative work ΔW between the two systems. At the 393 same loop and hook densities on both the polymer and 394 nanosheet, it is shown in Figure S9 that the ΔW values of ionic 395 binding are overall larger than those of hydrogen bonding. The 396 difference in the cumulative work between them increases with 397 the pulling distance. Therefore, we can infer that the ionic 398 bonds between $-NH_3^+$ and $-O^-$ make the main contribution 399 to the mechanical performance of the hydrogel. 400

Importance of the "Hook" Density Revealed by 401 Coarse-Grained MS. Next, we aim to evaluate how the 402 density of hydroxyl groups (hooks) on ZrP NSs affects the 403 nano hook-and-loop interactions. As we have proved, ionic 404 bonds make the major contribution to the interactive strength 405 between the polymer and ZrP in comparison to hydrogen. 406 Therefore, we focus on the ionic interactions in this part. The 407 polymer chains in this set of simulation only contain -NH3⁺ 408 groups (with a ratio of x/y = 0.11). In addition, we replaced a 409 portion of deprotonated hydroxyl groups on the ZrP-NS 410 surface by $-CH_3$ groups, which have no ionic interactions with 411 amine groups, mimicking the formation of α -zirconium 412 phosphonate, a derivative of ZrP.⁶⁸ Changing the ratio 413 between $-CH_3$ and $-O^-$ groups on ZrP allows us to 414 arbitrarily alter the $-O^-$ group area density on the ZrP 415 surface (both functional groups are evenly distributed on the 416 surface). Moreover, we systematically assess how the 417 deprotonated hydroxyl group density affects the nano hook- 418 and-loop effect by pulling a long polymer chain on a ZrP-NS 419 (Figure 3d-g). As given in Figure 3d, with a small $-O^-$ area 420 density on ZrP, the polymer cannot firmly attach. The ΔW_{421} increases dramatically after the $-O^-$ area density of 0.98 /nm² 422 (Figure 3f). This is particularly apparent at a larger pulling 423 distance (Figure 3g). The above results clearly show that in 424 order to achieve an effective hook-and-loop effect, a sufficiently 425 high density of functional groups on the ZrP-NS surface, i.e., 426 1.97 groups/nm², is necessary. Moreover, it is interesting to 427 find that the polymer terminal "smartly" choses the pathway of 428 $-O^{-}$ groups during the pulling process (Figure 3e), which is 429 believed to be owing to the ionic interactions. 430

We further utilized the coarse-grained (CG) MD simu- 431 lations to evaluate how the nano hook-and-loop effect would 432 contribute to the macroscopic mechanical properties of the 433



Figure 4. (a) CGMD model of the hydrogel. The pink points on the nanosheet are active hooks. The beads on the polymer chains are the loops. The dynamic bond interaction between a hook and a loop is controlled by the binding and unbinding energy barriers. (b) Comparison of stress and strain curves for the hydrogels with different hook densities, with shades representing the error range. (c, d) (c) Stress and (d) strain energy of the hydrogels at strain = 4 as a function of hook density on a nanosheet. (e) Snapshots of the nanosheets in a hydrogel during the tension process and its corresponding P_2 values (the shade representing the error bar).

434 resultant hydrogels. In the CGMD simulations, a polymer 435 chain is represented by the well-known finitely extensible 436 nonlinear elastic model.⁶⁹ Each polymer chain in our 437 simulation is composed of 200 repeating units. Each repeating 438 unit in a polymer chain acts like a "loop." Each ZrP-NS is 439 represented by a rigid circular disc with active "hooks" (Figure 440 4a). The interaction between a hook and a loop is represented 441 by a dynamic bond interaction. The formation and dissociation ⁴⁴² of the hook–loop interaction are captured by the Bell model,⁷⁰ ⁴⁴³ which is controlled by binding and unbinding energy barriers ⁴⁴⁴ $E_{\rm B}$ =1 $k_{\rm B}T$ and $E_{\rm UB}$ = 12 $k_{\rm B}T$.^{71,72} The $E_{\rm UB}$ value is chosen to ⁴⁴⁵ mimic the weak ionic interactions.⁷³ In our simulations, we 446 systematically change the area density of hooks on a nanosheet. 447 The mechanical properties of the hydrogel are simulated by a 448 uniaxial tension. As given in Figure 4b, the stress of the 449 hydrogel dramatically increases with the hook density. $_{450}$ Specifically, the stress at strain = 4 increases from ca. 0.1 (at $_{451}$ 0.05/ σ^2) to ca. 0.4 ε/σ^3 (at 0.5/ σ^2), after which it saturates 452 (Figure 4c, ε and σ are the energy and length units, 453 respectively). Furthermore, the strain energy of the hydrogel 454 follows a similar trend to its stress (Figure 4d). In addition, we 455 would like to emphasize that these CGMD simulations are

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based on the reduced Lennard-Jones units, which makes the 456 numbers of stress and strain energy in Figure 4c,d small. 457 Nevertheless, we still can observe that the simulated stress and 458 strain energy can be tripled at strain = 4 when the hook density 459 increases, which is statistically significant. All of these results 460 show that the nano hook-and-loop interactions can help 461 significantly enhance the mechanical performance of the 462 hydrogels. Moreover, during the tension process, the 463 simulation confirms the alignment of ZrP-NSs as shown in 464 the SAXS characterization (Figure S7). The nanosheets 465 reorient themselves to align with the tensile direction (Figure 466 4e). The orientation of the nanosheets is further quantified by 467 the P_2 value, ^{74,75} with $P_2 = -0.5$ and 1.0 representing all 468 nanosheets parallel and vertical to the tensile direction, 469 respectively. For our system, the P_2 value decreases from 0.1 470 to a value of ca. -0.3 at strain = 4, signaling the alignment of 471nanosheets along the tensile direction. 472

On the basis of all the experimental and modeling results, we 473 illustrate the whole process of stretching/compressing hydro- 474 gel PAM-10ZrP-C (Figure 4e). For the as-prepared hydrogel, 475 ZrP-NSs are randomly dispersed in a crosslinked polymer 476 network. ZrP-NSs are attached to polymer chains with ionic 477 pubs.acs.org/Langmuir



Figure 5. (a) Illustration of a joint (redrawn from the literature);⁷⁶ (b, c) digital pictures showing the setup of hip simulation in (b) air and in a (c) protein buffer solution; (d) load on PAM-10ZrP-C before and after the hip simulation under compression only (C) or simultaneous compression and torsion (C + T).

478 bonds (and hydrogen bonds). When deformation occurs, the 479 system will respond to the change instantly. At first, the flexible 480 polymer chains unfold and detangle under tension, heading to 481 an ordered structure. As a result, the ordered polymer chains 482 render the attached nanosheets to be aligned with each other 483 along the stretching direction. Meanwhile, the displacement of 484 polymer chains leads to the breakage and recombination of the 485 weak ionic bonding. Compared with the polymer coils, the 486 stretched/unfolded chains interact with the ZrP-NSs much 487 more effectively, particularly when the functional group density 488 is sufficiently high. Under a greater extent of deformation, the 489 inner force drives nanosheets to align along the stretch 490 direction and pack more tightly. Consequently, the polymer 491 chains have a higher possibility to interact with the ZrP-NSs, going through the recurring binding/breaking process, 492 493 dissipating the energy.⁵

Articular Cartilage Application of Hydrogels. PAM-494 495 10ZrP-C was further evaluated for articular cartilage 496 application (Figure 5a) considering its exceptional compres-497 sion resilience in both room temperature air and a 37 $^\circ C$ 498 protein buffer solution (mimicking synovial fluid). For the 499 sample in air (Figure 5b), after 5000 cycles of compression to 500 50% of initial dimension, or compression to 50% of initial 501 dimension with a torsion of 45° (Figure S10), the stiffness of 502 the sample increased slightly, which should be due to the water 503 loss during testing. In contrast, the sample in the buffer 504 solution (Figure 5c) gave a modest drop in the load after the 505 cyclic loading tests, probably because of the softening 506 stemming from water absorption and the affected ionic 507 interaction by the buffer solution; however, the sample ⁵⁰⁸ remained stable during testing (Figure 5d). Either case proved 509 the extraordinary stability and durability of PAM-10ZrP-C, 510 thanks to the nano hook-and-loop effect.

511 CONCLUSIONS

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512 In summary, inspired by hook-and-loop fasteners, we designed 513 a unique hydrogel network containing numerous ZrP nano-514 patches to achieve the nano hook-and-loop effect. This leads to 515 ultra-stretchability, superior compression resilience, and high 516 durability of the resultant hydrogels, promising for demanding 517 applications such as artificial articular cartilage. Both the 518 experimental and modeling results demonstrate the signifi-519 cance of the nano hook-and-loop effect, which is expected to 520 inspire the design of the next-generation multifunctional soft 521 materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at 524 https://pubs.acs.org/doi/10.1021/acs.langmuir.1c00924. 525

Article

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Composition of the hydrogels, crystal structure, SEM 526 images, TEM images, and AFM images of ZrP, FT-IR 527 spectra and XRD patterns of ZrP and hydrogels, 528 hysteresis and cyclic tensile test results of the hydrogel, 529 SAXS 2D patterns and the scattering curves of the 530 hydrogel, all-atom model and method, the steered 531 molecular dynamics simulation process at different 532 distances, comparison of hydrogen bonds with ionic 533 bonds, 5000 cycles of concurrent compression and 534 torsion, and comparison table of the mechanical 535 properties of the PAM nanocomposite hydrogels 536 (PDF) 537

Cut-and-stretch demonstration of hydrogel PAM-10ZrP- 538 C (Movie S1) (AVI) 539

Compression test of hydrogel PAM-10ZrP-C (Movie 540 S2) (AVI) 541

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609 Author Contributions

L.S. conceived the idea and supervised the research. F.D., J.L., 610 611 and G.W. synthesized samples and conducted character-612 izations. H.D. conducted characterizations, analyzed the data, and optimized the system. Z.S. and Y.L. developed and 613 analyzed the simulations. L.Q. and J.O. conducted the hip 614 simulation. S.E.C. conducted SAXS characterization. S.Z., 615 T.A.P.S., A.T.S., and L.L. contributed to the design of the 616 617 project and data analysis. F.D., H.D., Z.S., and L.S. wrote the first draft of the manuscript, and all authors contributed to 618 619 revising the manuscript. F.D., H.D., and Z.S. made equal 620 contribution.

621 Notes

622 The authors declare no competing financial interest.

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