Supporting Information

Super tough magnetic hydrogels for remotely triggered shape morphing

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Movie S1

This movie shows a flower-like soft bilayer self-folds in alternating magnetic field. The bilayer consists of magnetic PNIPAm hydrogel (at 1M NaOH) and a commercial elastomer VHB 4905 (3M company). The alternating magnetic field is generated by a solenoid (red circles). The bilayer is placed on an acrylic sheet to be in the middle of the alternating magnetic field. The magnetic field strength is 10.33 kA/m with a frequency of 187 kHz. Upon the application of alternating magnetic field, only the magnetic hydrogel is heated. Once the temperature is higher than LCST, the PNIPAm hydrogel layer will shrink and make the bilayer bend. Thus, this structure will self-fold like a flower.

Movie S2

This movie demonstrates the temperature increase of the soft bilayer during the self-folding process. The experimental set-up is the same as Supplementary Movie 1. Upon the application of alternating magnetic field, the bilayer is heated, while the acrylic supporting sheet is never heated. The bilayer is heated from ~20°C to ~50°C in 3.5 min. Along with the temperature increase, the bilayer gradually self-folds like a flower.

Movie S3

This movie shows that the heated bilayer can recover to its initial shape when immersed in cold water. After heated, the PNIPAm magnetic hydrogels is dehydrated. The heated bilayer is

transferred into cold water ~20°C. Due to the swelling of the PNIPAm magnetic hydrogel in cold water, the folded bilayer expands like a blossoming flower. The process demonstrates that we can program the shape of the bilayer reversibly, which is promising for shape morphing of soft structures.

Mechanical test

Tensile and compressive tests of tough magnetic hydrogels were performed using a tensile tester (Instron model 5966) with a 1000 N load cell. To characterize the fracture properties of magnetic hydrogels, we used a set up known as the pure shear test (see Fig. S4). The samples for pure shear test had a height of 5mm, a width of 25mm and a thickness of ~1mm, with a crack length of 10mm.

Swelling test

Swelling tests were performed by immersing as-prepared gels in a large amount of water at room temperature. We measured the mass of the samples at intervals. Swelling ratio Q is denoted as the ratio of weights of the swollen hydrogel to that of the initial hydrogels.

Calculation of polymer volume fraction

To calculate polymer volume fraction of hydrogels, the hydrogels were cut into a disk shape. The diameter d_0 of the disk is 10mm and the thickness is 1mm. The gels were immersed into NaOH solutions of different concentrations. After reaching equilibrium, the current diameter d of the hydrogels was measured with caliper. The volume ratio of the immersed gels was equal to $(d/d_0)^3$. Thus the polymer volume fraction of the immersed gels is given by¹:

$$\phi = \phi_0 / (d/d_0)^3$$

where ϕ_0 is the initial polymer volume fraction of NC5 hydrogels. We derived $\phi_0=9.09\%$, since the initial input of DMA solution is 3ml, and the water volume is 30ml.

The content of magnetic nanoparticles

The content of magnetic nanoparticles was estimated by the TGA experiments as shown in Fig. S1. We measured the TGA curves of both the NC5 nanocomposite hydrogel and the magnetic NC5 hydrogel. The sharp degradation for both samples at T \approx 100°C corresponds to the water evaporation of water. A second degradation for both samples at T \approx 350°C may correspond to the main chain breakdown of PDMA ². The residual weight of the NC5 hydrogel at 900°C is 11wt%, while for magnetic NC5 hydrogel the value is 25wt%. The difference of residual weight between these two samples is due to the presence of magnetic nanoparticles. Thus the content of magnetic nanoparticles in the magnetic NC5 hydrogels was estimated to be 14wt%. The number is closed to the value of a reported magnetic hydrogel prepared by the in-situ precipitation method ³.



Fig. S1 Weight loss as a function of temperature for the pristine NC5 nanocomposite hydrogel and the magnetic NC5 hydrogel.

Compressive test of magnetic hydrogels

For compressive test, the as-prepared nanocomposite hydrogels were cylinder-shaped with a height of \sim 17.5 mm and a diameter of \sim 19 mm, and after swelling in NaOH solutions of different

concentrations, the tough magnetic hydrogels had different dimensions. We controlled the maximum compressive strain to be 80% for all the samples.



Fig. S2 The photos for the compressive tests of the pristine hydrogel, 5M-magnetic hydrogels and 1M-magnetic hydrogels.

FTIR spectra of PDMA hydrogels immersed in deionized water and processed by a NaOH solution

We conducted FTIR analysis to characterize the functional groups of PDMA hydrogels immersed in deionized water and highly concentrated NaOH solutions (5M). Two disks (diameter=10mm) of nanocomposite hydrogels (NC5) were prepared. One was immersed in deionized water till equilibrium. The other one was first immersed in NaOH solutions with a concentration of 5M for 24h, where the gel turned white and shrunk much. Then the phase-separated gel was immersed in deionized water till equilibrium. To eliminate water molecules from the samples, the two gel disks were frozen at -79 °C and dried in vacuum chamber for 36h. FTIR spectra were recorded on a Thermo Scientific Nicolet iS10 FTIR spectrometer.

The FTIR spectra of the two gels are shown in Fig.S3. The two gels show almost the same spectrum as each other. The sharp peak at 1608.97cm⁻¹ for PDMA hydrogel immersed in deionized water and that at 1614.71 cm⁻¹ for PDMA hydrogel immersed in NaOH @ 5M correspond to the bonds for amide. The expected hydrolysis of PDMA hydrogel in NaOH aqueous solution did not occur. If hydrolysis happens, a peak for carbonyl stretching bonds should be observed around 1716 cm⁻¹.⁴



Fig.S3 (a) FTIR spectra of PDMA hydrogels immersed in deionized water and processed by a NaOH solution of 5M (b) The swollen gel and the frozen-dried gel for the samples immersed in deionized water. (c) Volume ratio of the PDMA hydrogels, which were firstly immersed in NaOH solutions with concentration C and then immersed in deionized water.

Fig.S3b shows the swollen gel and the frozen-dried gel for the gels immersed in deionized water. Fig.S3c shows the volume ratio of the PDMA hydrogels, which were firstly immersed in NaOH solutions with concentration C and then immersed in deionized water. Their equilibrium volume ratio is almost the same as the one in pure water, which also means that no hydrolysis happens. From the evidence of FTIR analysis and swelling test, it can be concluded that no hydrolysis occurs to PDMA gel even in highly concentrated NaOH solutions.

Determination of toughness using pure shear test

We determined the toughness of the magnetic hydrogels using the pure shear test introduced by Rivlin and Thomas⁵. As shown in Fig. S4, two identical samples with the same dimensions were synthesized, one sample was unnotched and the other sample was notched. The unnotched sample was used to measure the stress-stretch curve of the magnetic hydrogels in pure shear state; while the notched sample was used to measure the critical stretch where crack starts to propagate.

In the pure shear configuration, regions far away from the crack tip are either fully relaxed or uniformly deformed since the width is much larger than the height. Therefore, in the steady state the propagation of the crack can be regarded as lateral translation of a uniformly deformed region into a fully relaxed region with the same width ⁶. The energy stored in the uniformly region can be determined by the stress-stretch curve of the unnotched sample, i.e., AHW(λ), where W(λ) is the strain energy density (the integral area under the stress-stretch curve), A is the sectional area and H is the height. When the stretch of the notched sample reaches the critical stretch $\lambda = \lambda_c$, the crack starts to run. The energy required to advance the crack by a unit area at the reference state (i.e., toughness) is equal to AHW(λ_c) /A. Therefore, the toughness of the magnetic hydrogels can be expressed as Γ =HW(λ_c).



Fig. S4 Experimental determination of fracture energy using pure shear test. Two samples of the same gel were tested in tension. One sample was unnotched, and the other sample was notched. The schematics and stress-stretch curves of (a) the unnotched sample and (b) the notched sample. The characteristic swelling/deswelling of magnetic nanocomposite hydrogels during the synthesizing process

We prepared blank nanocomposite hydrogels with different clay contents and immersed these hydrogels into Fe^{2+}/Fe^{3+} solutions. It is seen from Fig. S5 that all the samples swell in the iron-ion solutions and the equilibrium swelling ratio decreases with the clay content because of the decrease of polymer chain length. Once the iron-ion loaded hydrogels were immersed in the 5M NaOH solutions, all the hydrogels deswelled immediately. We measured three samples for each case to calculate the mean value.



Fig. S5 The mass change of the magnetic nanocomposite hydrogels during the synthesizing process. All the samples swelled in the $Fe^{2+/}Fe^{3+}$ solutions and deswelled after immersion in NaOH solutions. Values represent the mean and standard deviation (n = 3).

Fracture simulation of magnetic NC hydrogels

We used finite-element software ABAQUS to simulate the fracture of the magnetic NC hydrogels. We separately stretch two identical samples: one is unnotched, the other one is notched. The two dimensional (2D) finite-element model consists of a strip with the same dimension as the experimental sample. The fracture process is simulated by placing a layer of cohesive element on the center crack plane. The height is 5mm, the width is 25mm and the crack length is 10mm. The stress-stretch relation of the magnetic hydrogels is fitted by the 3-term Ogden model. We directly input the experimental data from the pure test and uniaxial test of magnetic hydrogels into the software to get the parameters for the Ogden model. The finite-element calculations are performed with ABAQUS/Explicit to prevent the convergence problem of cohesive element. The Poisson's

ratio of the soft materials is set to be 0.499. The magnetic hydrogel is modeled by the plane-stress 4-node linear elements with reduced integration (CPS4R). The crack plane is modeled by the cohesive element implemented in ABAQUS (COH2D). The crack initialization is governed by the quadratic nominal stress criterion:

$$\left(\frac{\langle t_n \rangle}{t_n^0}\right)^2 + \left(\frac{t_s}{t_s^0}\right)^2 + \left(\frac{t_t}{t_t^0}\right)^2 = 1$$
(S1)

where $t_{(\cdot)}$ represent the nominal surface tractions on the crack surface, and the subscripts *n* and *s* represent the normal direction and two tangential directions. We used the linear damage evolution relation. The critical nominal stress is set to be $t_n^0 = t_s^0 = t_t^0 = 4.8MPa$; the stiffness of the cohesive zone is K=3.84×10⁴ MPa and the intrinsic fracture energy is Γ_0 =600Jm⁻². We fix the bottom surface of the hydrogel strip and pulled the upper surface upwards with a constant velocity, during which the upper surface is constrained in the horizontal direction. The nominal stress is extracted by the retraction force of the upper surface divided by the width. More details on the simulation can be found in Ref[9]⁷.

The simulation can capture the stress-stretch curves for both the unnotched and notched samples (Fig.S6a-b). In Fig S6c-f, we gave the snapshots of the fracture simulation of magnetic NC5 hydrogels at different stretches.



Fig. S6 Comparison between experiments and simulations on fracture of magnetic NC5 hydrogels. Stress-stretch curves of (a) unnotched sample and (b) notched sample. (c-f) The Mises stress fields for the fracture process of the hydrogel at different stretches.

Phase separation of PNIPAm hydrogels in NaOH solutions

The PNIPAm nanocomposite hydrogels also suffer from phase separation in high-concentration NaOH solutions.



Fig. S7 The NC5 PNIPAm hydrogels and the magnetic NC5 PNIPAm hydrogels prepared in 0.5M, 1M, 2M, 3M and 5M NaOH solutions.

Magnetic hysteresis loops of PNIPAm and PDMA magnetic hydrogels

It is clear from these hysteresis loops that these magnetic hydrogels demonstrate ferromagnetic behavior at room temperature. The saturation magnetization, remanent magnetization and coercivity of magnetic PNIPAm hydrogels (1M) are 10.34 emg g⁻¹, 1.33 emg g⁻¹ and 32.67 Oe, respectively (Fig. S8a). While for magnetic PDMA hydrogels (5M), the saturation magnetization, remanent magnetization and coercivity are 23.68 emg g⁻¹, 0.56 emg g⁻¹ and 8.32 Oe, respectively (Fig. S8b).



Fig. S8 Magnetic hysteresis loops of (a) PNIPAm and (b) PDMA magnetic hydrogels.

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