

Supporting Information

Programmable Responsive Shaping Behavior Induced by Visible Multi-dimensional Gradient of Magnetic Nanoparticles

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Materials:

FeCl₂·4H₂O (98 %, Sigma-Aldrich Co., U.S.), FeCl₃·6H₂O (98 %, Sigma-Aldrich Co., U.S.), ammonia (28 %, Wako Chemical Co., Japan), N-isopropylacrylamide (NIPAAm) (99 %, Acros Co., Belgium), Laponite XLS (92.32 wt% Mg_{5.34}Li_{0.66}Si₈O₂₀(OH)₄Na_{0.66}, 7.68 wt% Na₄P₂O₇, Rockwood Co., U.S.), N,N,N',N'-tetramethylethylenediamine (TEMED) (98 %, TCI Co., Japan), and ammonium persulfate (APS) (99%, TCI Co., Japan). All reagents were used as received. All solutions used in experiments were prepared in deionized water.

Magnet (commercial magnetic rubber: 800 Gausse, Daiso Co., Japan) was used to apply magnetic field. The commercial magnetic rubber was a roll: 1000mm long, 30 mm wide, 3 mm thick. The certain size and shape of the magnetic rubber was cut by knife as we needed.

Preparation of MNP:

Preparation of Fe₃O₄ nanoparticles was carried out according to the well-established co-precipitative reaction protocol. Typically, FeCl₂·4H₂O (1.68 g) and FeCl₃·6H₂O (4.1 g) were dissolved in water (100 mL), and co-precipitated by adding concentrated ammonia (28%, 25

mL) under N₂ atmosphere at 80 °C. The dispersion was kept at 80 °C for 1 h. Then, it was cooled to room temperature. MNPs were collected with help of a magnet and washed with deionized water for several time until pH was 7. The MNP slurry was obtained with help of a magnet. The MNP slurry contains 15 wt% MNP (Figure S1), and the size of MNP is about 11~14 nm (Figure S2).

Preparation of BL gel strip, HBL gel strip, gel plate I (inserted with a 3D symmetric gradient of MNP), and gel plate II (inserted with a 3D asymmetric gradient of MNP):

All hydrogels were prepared in a self-made container consisting of two glass plates and one rubber spacer (**Scheme S3**). The glass plates are common slides, whose size is 76mm×26mm×1.2mm. The rubber spacer was made by cutting a regular window from a soft rubber plate, whose size is the same as that of the glass plate. The thickness of the rubber space is 1.5 mm, the window of the rubber space is 66mm×16mm. So the as-prepared gel plate is 66mm×16mm×1.5mm.

BL gel strip: First, a solution consisting of monomer (NIPAAm, 0.6 g), crosslinker (Laponite XLS, 0.09 g), and water (5 g) was obtained. Secondly, the MNP slurry (1 g) was slowly dropped into the solution under vigorous shaking. Then, 60 µL of initiator solution (APS, 10 wt%) and 5 µL of accelerator (TEMED) were added into the solution under ice-bath. The obtained prepolymerization solutions containing MNP was poured into the self-made container consisting of two glass plates and one rubber spacer. Finally, after the container was sealed by clamps, a magnet with 800 Gauss magnetic induction (30 mm wide, 80 mm long) was attached right under the bottom of the container. The magnetic rubber is longer and wider than the glass plate. Polymerization carried out under this magnetic field at 20 °C for 24 h, and a BL gel was obtained (**Scheme S4**).

HBL gel strip: The preparation of HBL gel is almost the same as that of BL gels, except that two magnets were used. The details of the arrangement is shown in **Scheme S5**, including the sequence, the magnetic induction, the exact size and positions of the two magnets. The two magnets were directly attached the glass plates.

Gel plate I and gel plate II: The preparation of gel plate I and gel plate II is similar to the preparation of HBL gel. But, the width of magnet I is smaller than both magnet II and the container. The details of the arrangement is illustrated in **Scheme S6** and **Scheme S7**, including the sequence, the magnetic induction, the exact size and positions of the two magnets. The relative positions of the two magnets were different in Scheme S6 and Scheme S7, to obtain different 3D gradient of MNP.

Measurement methods:

Thermogravimetric analysis was performed on a Seiko Exstar 6000 TG/DTA 6200 thermal analyzer (Seiko Instruments, Chiba, Japan) in static air from 30 to 200 °C with a heating rate of 10 °C min⁻¹. The MNP slurry was diluted by deionized water and dropped onto grids for transmission electronic microscopy (JEOL JEM2100).

The obtained gels were rinsed in deionized water at room temperature for one week to attain equilibrium swelling ratio and remove remain monomer with change water for several times. The equilibrium swollen gels were put into deionized water in a beaker with a water-bath at 40 °C or 20 °C, and their shapes were recorded by a digital camera (Canon PowerShot SX110IS, Japan) at intervals. The dispersion of MNP aggregations in BL gel strip were observed using a microscopy (Olympus CX31-P, Japan) connected to a camera (Olympus DP20, Japan), where BL gel strip was cut in cross section for measurement.

Preparation of uniform MNP-loaded gels and pure PNIPAAm NC gels:

A uniform MNP-loaded hydrogel was prepared by the same method used for the BL gel, except that magnetic field was not applied during the polymerization. The recipe of the uniform MNP-loaded hydrogel is the same as that of the BL gel. In addition, a pure PNIPAAm NC gel was also prepared, whose recipe is the same as the uniform MNP-loaded hydrogel except that the MNP slurry (1g) was replaced by the same amount of water. The uniform MNP-loaded hydrogel and the pure PNIPAAm NC gel were prepared in glass tubes (interior size = 5 mm diameter × 60 mm length). For measurements of tensile properties and deswelling behavior, the hydrogels were used as-prepared in order to retain the same size for all gel samples. The solid contents of the uniform MNP-loaded hydrogel and the pure PNIPAAm hydrogel are 12.5wt% and 10.3wt%, respectively.

Measurements of Tensile Properties for uniform MNP-loaded gels and pure PNIPAAm NC gels

Tensile strength measurements were performed on as-prepared hydrogels of the same size (5mm diameter × 60mm length) using an EZ-L universal material tester (Shimadzu Co.). The conditions were as follows: temperature 25 °C, a sample size of 5 mm in diameter and 60 mm length, gauge length of 30 mm, crosshead speed of 100 mm/min. The strain under stress is defined as the change in length relative to the initial length of the specimen. The strength was calculated on the basis of the initial cross section.

Measurements of deswelling kinetics for uniform MNP-loaded gels and pure PNIPAAm NC gels

Hydrogels were put into water at 40 °C. For each measurement, the hydrogels were removed from the water and weighted after excess water removed from the surface by wet

filter papers. All starting gels were as-prepared hydrogels with the same sample size (5 mm diameter \times 30 mm length). Deswelling ratios are represented by the ratio of weights of the deswollen gel (W_t) to the corresponding as-prepared gel (W_0).

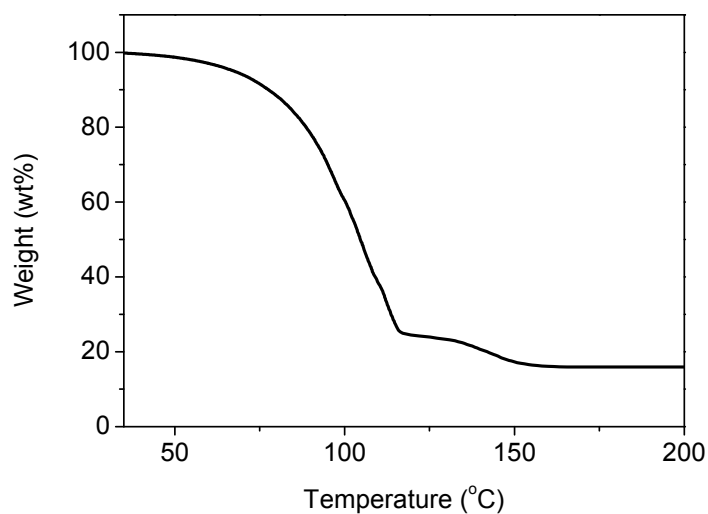


Figure S1. Thermogravimetry graph of MNP slurry. (i.e. MNP content: 15 wt%).

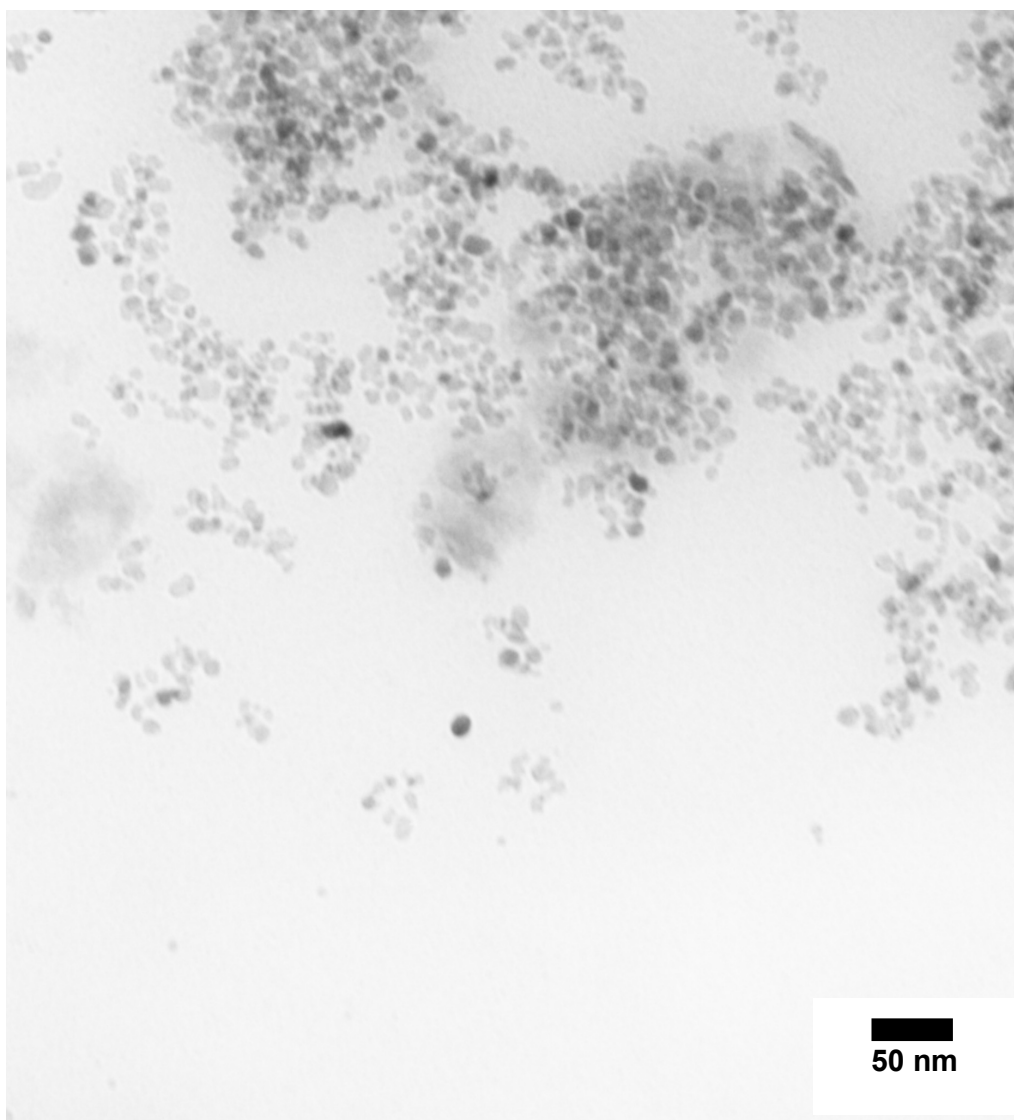


Figure S2. TEM image of MNP.

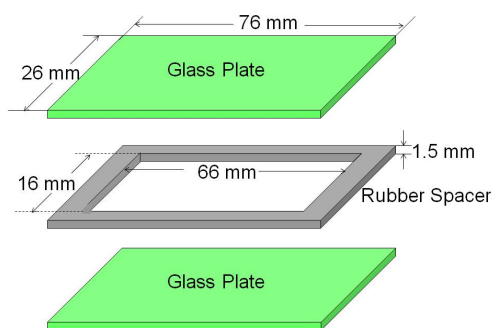
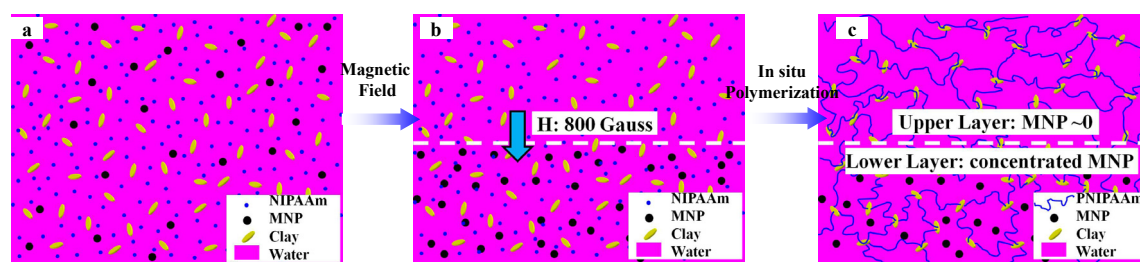
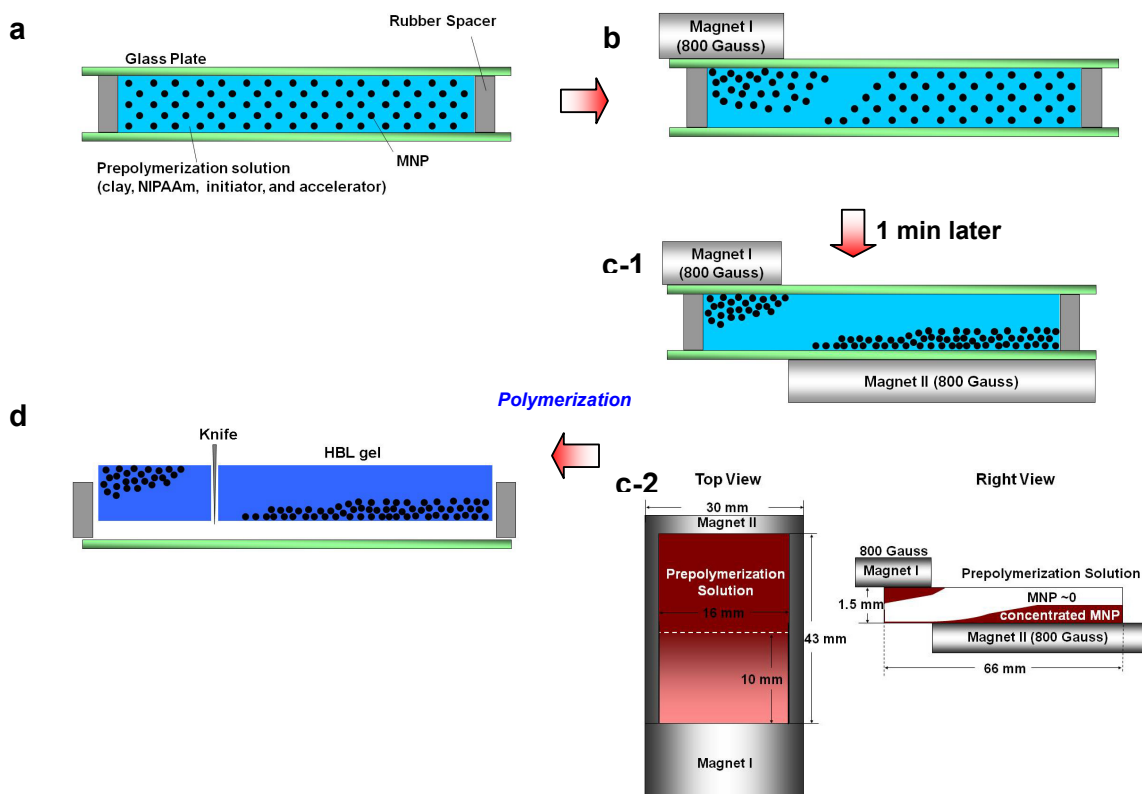


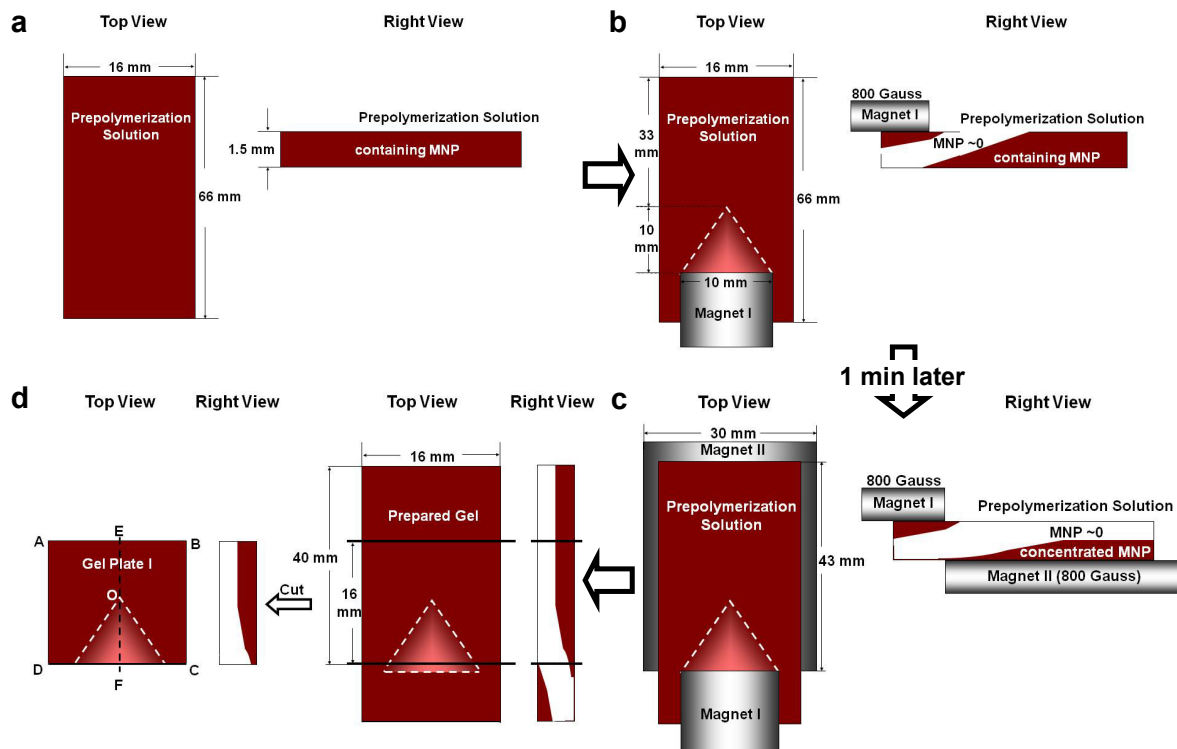
Figure S3. The size and structure of the self-made container.



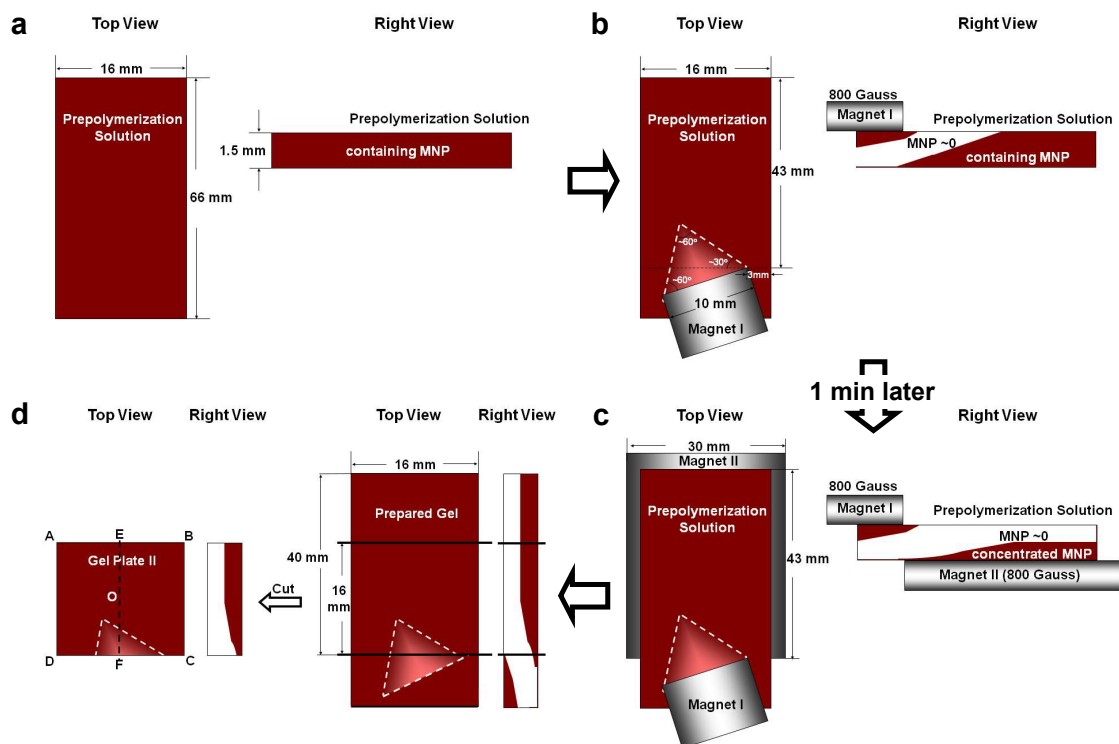
Scheme S4. 'Programming process' and preparation of BL gel strip: a) Prepolymerization solution of clay, MNP, and monomer; b) Formation of bilayer structure in prepolymerization solution under an external magnetic field; c) Formation of BL gels.



Scheme S5. ‘Programming process’ and preparation of HBL gel strip: a) Prepolymerization solution of clay, MNP, and monomer in a thin container; b) Concentrating MNP near one end of the upper plate by magnet I; c) Horizontal gradient of MNP on the bottom plate built by magnet II; d) Formation of HBL gel after polymerization.



Scheme S6. ‘Programming process’ and preparation of gel plate I inserted with a 3D symmetric gradient of MNP: a) Prepolymerization solution of clay, MNP, and monomer in a thin container; b) Concentrating MNP near one end of the upper plate by magnet I; c) a 3D symmetric gradient of MNP on the bottom plate built by magnet II; d) Formation of gel plate I after polymerization.



Scheme S7. ‘Programming process’ and preparation of gel plate II inserted with a 3D asymmetric gradient of MNP: a) Prepolymerization solution of clay, MNP, and monomer in a thin container; b) Concentrating MNP near one end of the upper plate by magnet I; c) a 3D asymmetric gradient of MNP on the bottom plate built by magnet II; d) Formation of gel plate II after polymerization.

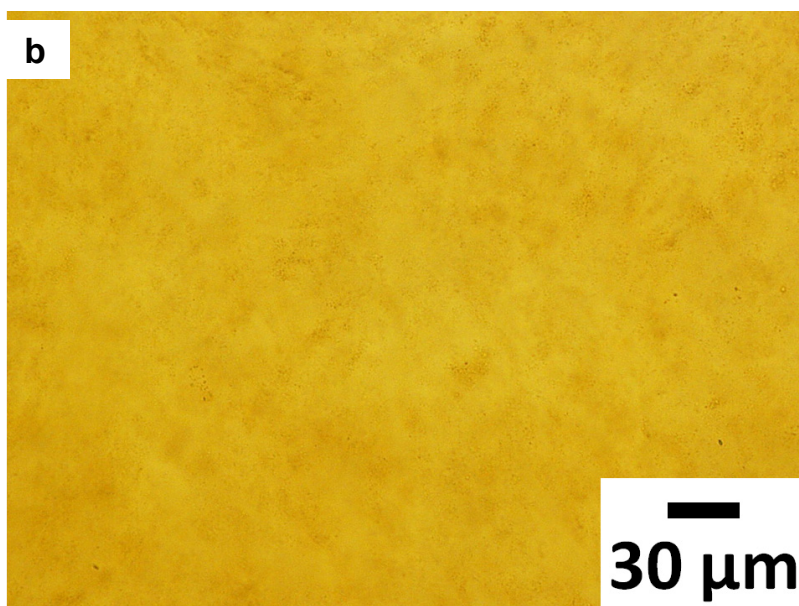
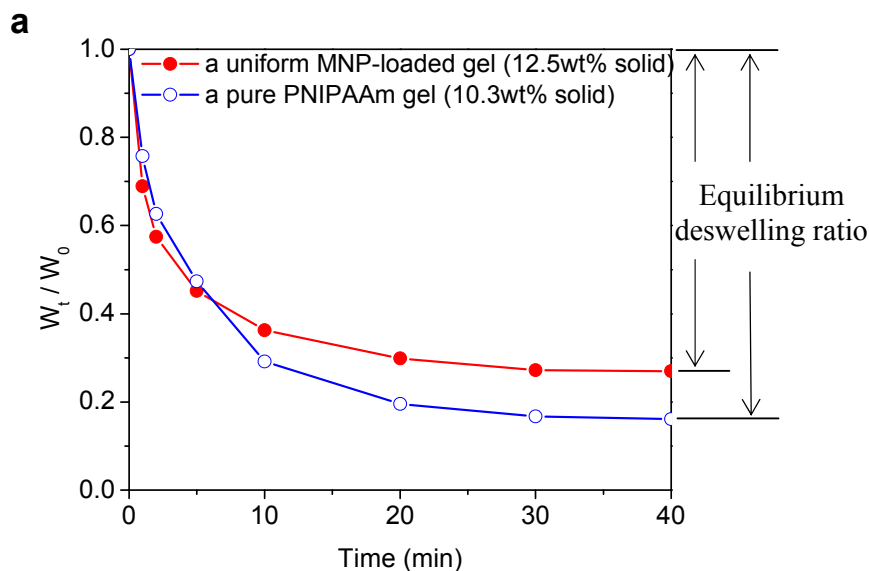


Figure S8. a) Deswelling kinetics of a pure PNIPAAm gel (solid content: 10.3 wt%) without MNP and a uniform MNP-loaded PNIPAAm gel (solid content: 12.5 wt%) at 40 °C. b) Microscopy image of a uniform MNP-loaded PNIPAAm gel.

Because of the absence of magnetic field during polymerization, the number of MNP aggregations is low, and their size is small, shown in Figure S8-b. So, the initial deswelling rate of the uniform MNP-loaded gel is little faster than that of the pure PNIPAAm gel, shown in Figure S8-a. In addition, because the solid content of the MNP-loaded gel is higher than that of the pure PNIPAAm gel, the equilibrium deswelling ratio of the former is lower than that of the latter.

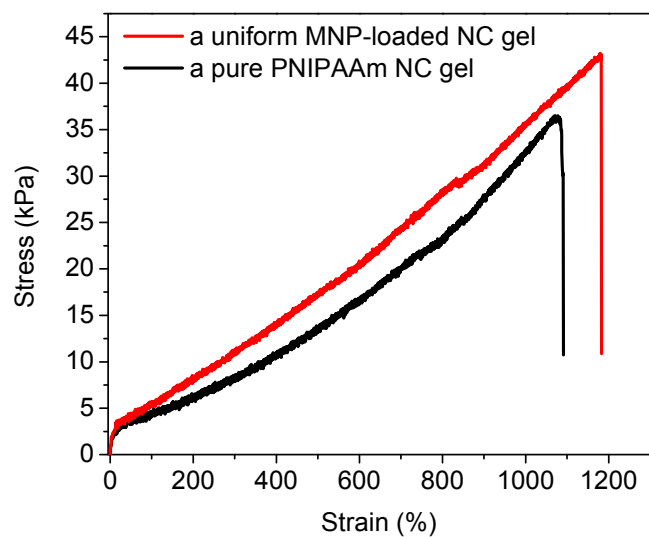


Figure S9. Tensile properties of a uniform MNP-loaded PNIPAAm NC gel and a pure PNIPAAm NC gel.