Swelling Enhanced Remanent Magnetization of Hydrogels Crosslinked with Magnetic Nanoparticles

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Experimental Details

Chemicals

 Iron(II) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 97%), acrylic acid (AA, 99% anhydrous), diethyleneglycol diacrylate (DEGDA, 75%), (3-trimethoxysilyl) propyl methacrylate (TPM, 98%), and monosodium phosphate (99%) were obtained from Sigma Aldrich. Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6 H_2O$, >98%) was from Fluka. Hydrochloric acid (HCl, p.a.), potassium nitrate (KNO_3, 99%), acetic acid acid (100% p.a.), sodium chloride (NaCl, p.a.), potassium hydroxide (KOH, p.a.), and sodium hydroxide (NaOH, 99%) were from Merck (Darmstadt, Germany). Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 99%), ammonia solution (NH_4OH, 28-30 wt% in water), sulfuric acid (H_2SO_4, 96%), hydroxylethyl acrylate (HEA, 97% stabilized), phosphoric acid (85 wt%, p.a.), and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50, 98%) were from Acros Organics. All chemicals were used as received. Water purified by a Millipore purification system (Synergy 185) was used in all syntheses and washing steps.

Preparation of thin layers of ferrogel

 As indicated in the main text, thin circular layers of ferrogel were prepared by polymerization of a ferrogel mixture in a mould on a 150 μm thick glass slide, and to ensure fixation of the thin ferrogel layers during swelling experiments, glass slides were coated with (3-trimethoxysilyl) propyl methacrylate (TPM).[22] The glass slides were etched with a 2 M KOH solution overnight and extensively rinsed with water. The slides were placed in a 17 mM aqueous solution of TPM, acidified with a few drops of acetic acid, again overnight. Finally, the glass slides were extensively rinsed with water and dried in an oven at 80°C.

 The monomer mixture composition was 0.33 mL of acrylic acid (AA), 5.00 mL of hydroxylethyl acrylate (HEA), and 0.14 mL of diethyleneglycol diacrylate (DEGDA). A typical ferrogel mixture was prepared as follows: 0.25 mL of 56 mg/mL nanoparticle dispersion was diluted with 0.15 mL of water, 0.05 mL of monomer mixture, and 0.05 mL of initiator solution (V-50, 6 mg/mL). The ferrogel mixture was preheated in an oven at 80°C for five minutes in an Eppendorf vial to start decomposition of the V-50 initiator and to minimize bubble formation in the ferrogel layer. After 5 min, the ferrogel mixture was removed from the oven, and the vial was opened for 2 s before vortex mixing for 1 min. The preheated ferrogel mixture was then gently

added into the mould. The latter was made from multiple layers of Scotch® Crystal Clear Tape into which a circular hole was pierced using pliers (diameters from 2 to 4.5 mm), where a single layer of tape was 45 μm thick. A second glass slide was pushed onto the mould to expel excess ferrogel mixture, and this assembly was put in an oven at 80°C for 30 min to complete the polymerization.

When the ferrogels had cooled down, the glass cover slide and mould were carefully removed. A glass cylinder (10 mm diameter, 10 mm height) was fixed around the ferrogel disk with silicone vacuum grease to serve as a container for aqueous solution. Buffer solutions of different pH but similar ionic strength were added, and a Teflon watch glass was added to prevent evaporation. A pH 3 solution was prepared by dissolving 0.49 g of phosphoric acid in 500 mL of water and adding of 2.79 g of NaCl to obtain an ionic strength of 100 mM. A pH 6 buffer was prepared by dissolving 0.6 g of monosodium phosphate in 500 mL and adding 2.39 g of NaCl, again to obtain an ionic strength of 100 mM. Small amounts of HCl or NaOH were added to adjust the buffer to the desired pH.

Measurements

The thickness of the ferrogel layers exposed to buffer solution was monitored using an inverted optical microscope (Nikon, Eclipse Ti inverted microscope with a Lumenera InfinityX camera, 2× magnification).

The internal magnetic field of the ferrogels was determined in triplicate using a Micromag 2900 alternating gradient magnetometer (AGM) from Princeton Measurement Corporation. A magnetic field of 1.2 MA/m was applied for 20 s, and after a waiting time of 1000 s to allow for the fast Néel relaxation of the smallest nanoparticles,[27] the remanent magnetic dipole moment of the sample was measured; this was divided by the sample volume as determined by weighing to find H_{in}, assuming a gel density of 1 g per cm^3.

During swelling experiments, the field from ferrogel layers was measured using a homebuilt setup. A transverse Hall sensor probe (HMMT-6J04-VR, Lake Shore Cryotronics, Inc.) was placed in a fixed position, and thin hydrogel layers on a glass substrate could be placed on the Hall sensor probe in a reproducible way. Prior to a series of measurements, the gel was magnetized perpendicular to the glass slide using a square neodymium magnet; the gel was removed in the direction perpendicular to the slide to retain the orientation of the magnetic

nanoparticle dipoles. The gels were equilibrated overnight at the initial pH, and fresh buffer solutions were used in each swelling or shrinking step. The background magnetic signal was measured before and after the experiment in a room with an approximately constant temperature of 21°C. The signals were corrected for small temperature changes using the temperature coefficient of the Hall probe, 0.09 Gauss/°C.

For mechanical measurements on the gels, bulk samples in the range of 4-9 mm × 4-9 mm (diameter × height) were prepared from preheated ferrogel mixtures similar to the thin ferrogel layer samples. The ferrogel mixtures were also put in a similar cylindrical mould that was fixed to a glass slide using silicone vacuum grease. During polymerization in the oven, small Teflon watch glasses were used to minimize evaporation of water from the ferrogel mixture. After polymerization, the gels were carefully removed from the moulds and immersed in 10 mL of buffer solution with appropriate pH and ionic strength. The measurements were performed with a DMA 2980 Dynamic Mechanical Analyzer from TA Instruments, Newcastle, England. The diameters of the gels were measured with an electronic caliper. The samples were placed between two parallel plates, and a force ramp was realized from 0.01 N to 1 N at a rate of 0.005 N/min.
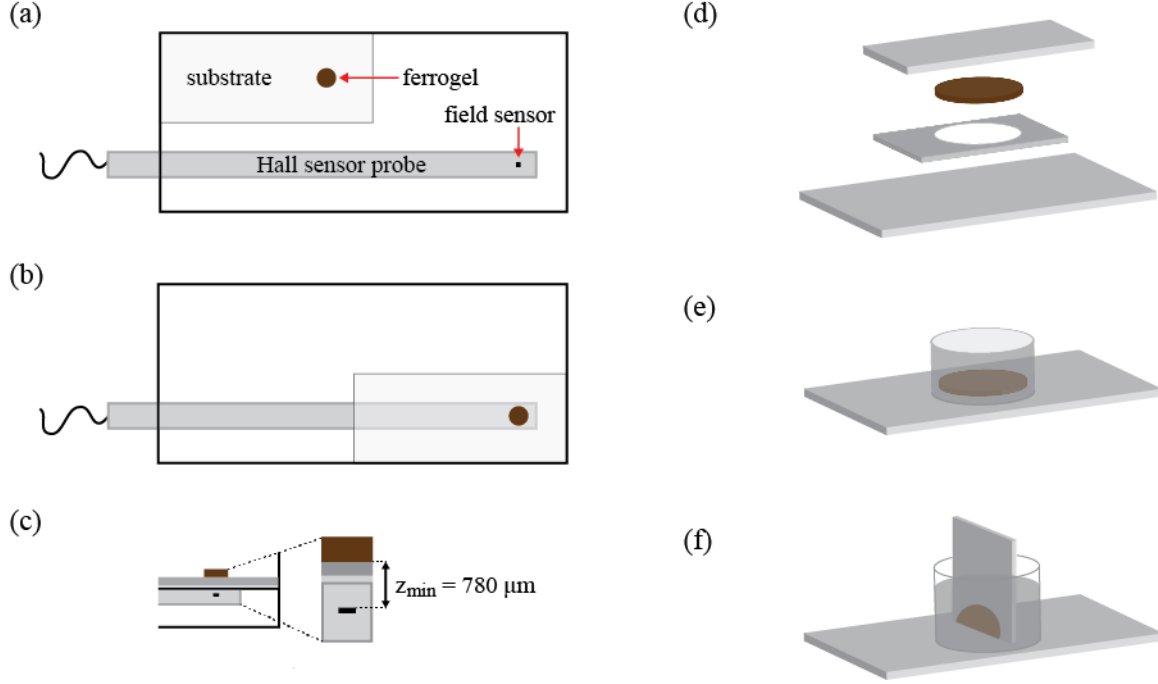
Figure S1. Experimental geometries for the time-dependent measurements of field and thickness of our ferrogels. **(a)** Top view of the setup used to measure the remanent magnetic field of ferromagnetic hydrogel disks: here, to measure the background, the substrate with the ferrogel disk is placed far away from the sensor. The active part of the Hall sensor has an edge of $D = 1$ mm, a value obtained from a specifications sheet provided by the manufacturer. **(b)** Measurement of the external field of the ferrogel; the substrate is now positioned such that the ferrogel is directly on top of the sensor. **(c)** Side view of the setup; the minimal distance from gel to sensor is $z = 780$ μm. **(d)** Schematic representations of the preparation of thin ferrogel layers and **(e)** the sample setup for magnetic remanence measurements, where a glass cylinder is positioned around the thin ferrogel layer into which a buffer solution can be added. **(f)** Schematic representation of the sample holder used during swelling experiments with optical microscopy. The glass slide is broken in half, so that the ferrogel layer is positioned on the edge of the glass slide. In this way, swelling of the thin ferrogel layer can be followed from the side.

Evolution of magnetic remanence during swelling from pH 3 to higher pH values

Figure S2.
Time dependence of the normalized remanent magnetic field during swelling, after equilibration at pH 3 and stepping to pH values of 4, 5, 6, 7, and 8.
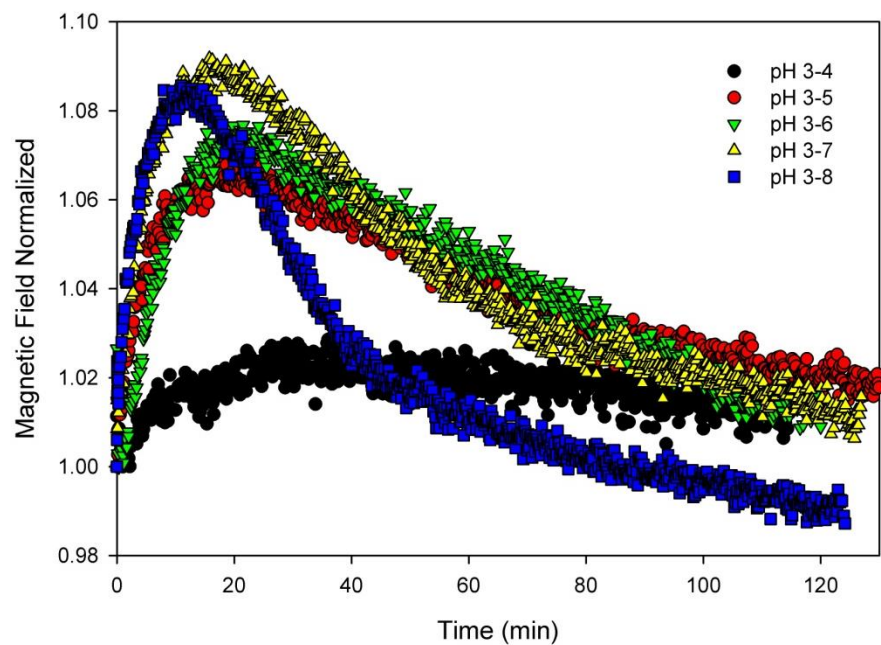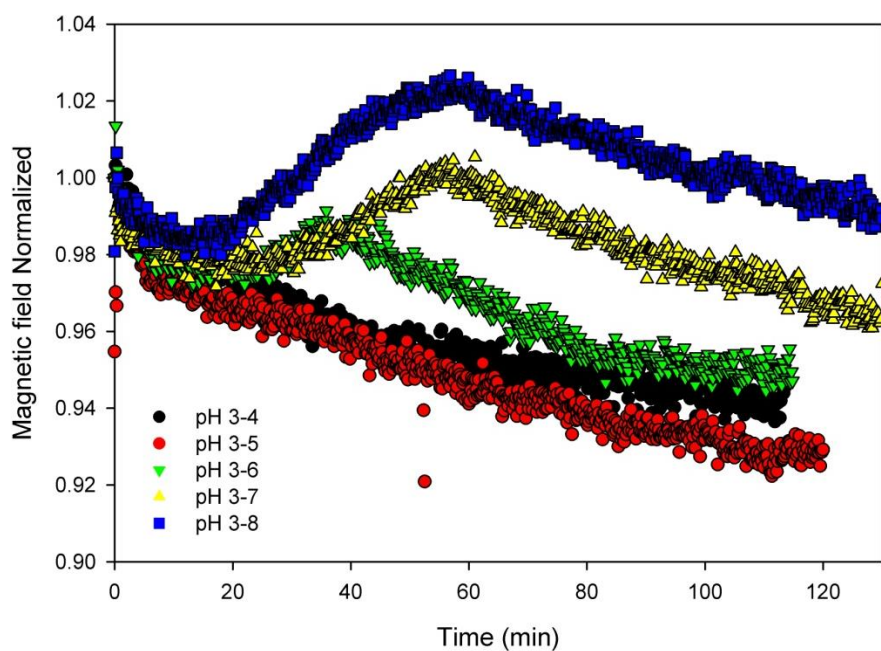

Figure S3.
Shrinking curves following the curves in Figure S2.

Hydrogel swelling theory and numerical simulations approach

Equilibrium volume of hydrogels as a function of pH

Our description of the pH-dependence of hydrogel volume is inspired by De et al.[25] with a few differences. Firstly, in their geometry, the hydrogel is confined between two parallel plates and can only expand laterally. Our own thin hydrogel layers are bound to a substrate and only swell perpendicular to it. Secondly, at low pH, the hydrogels of De et al.[25] are completely collapsed, whereas our hydrogels remain hydrated to a relatively large extent.

The volume of a hydrogel depends on the amount of water that it has absorbed, which is described here by a hydration Hy: the ratio between the thickness d_{gel} of the hydrated hydrogel and the polymer thickness d_{dry} that remains after drying of the gel:

$$Hy = \frac{d_{gel}}{d_{dry}} \tag{S1}$$

At low pH, when the hydrogel is uncharged and has a minimum thickness, the hydrogel has an initial hydration Hy_0, on the order of 10. This depends on the chemical affinity of the polymers in the network for water. At high pH, the ionizable groups are fully dissociated and the volume of the hydrogel increases: counterions of the charged polymer groups create an additional osmotic pressure, attracting water into the gel. To calculate the excess osmotic pressure, we assume a Donnan equilibrium and the presence of Na^+ and Cl^- ions as the main free ions inside and outside the gel. In equilibrium, the cation concentration times the anion concentration should be equal inside and outside the hydrogel:

$$[Na^+]_{in} \times [Cl^-]_{in} = [Na^+]_{out} \times [Cl^-]_{out} \tag{S2}$$

where $[Na^+]$ is the concentration of Na^+ ions, and $[Cl^-]$ is the concentration of Cl^- ions, inside (in) and outside (out) the hydrogel. Assuming Donnan equilibrium during the swelling or shrinking process corresponds to neglecting the effect of electrical fields. Upon swelling of the hydrogel, the concentration of Na^+ ions increases to preserve electroneutrality. The concentration of charged polymer groups can be obtained from

$$[AA^-] = \frac{K\,[AA]_{dry}}{Hy(K + [H^+])} \tag{S3}$$

where K is the dissociation constant of the acidic groups on the polymer, $[AA]_{dry}$ is the concentration of acidic groups in the dry polymer, and $[H^+]$ is the concentration of free H^+ in the hydrogel. This is used to calculate the concentration of the Na^+ ions in the hydrogel,

$$[Na^+]_{in} = \frac{\sqrt{[AA^-]^2 + 4[Na^+]_{out}[Cl^-]_{out}} + [AA^-]}{2} \tag{S4}$$

From the Donnan equilibrium (S2) it follows that

$$[Cl^-]_{in} = \frac{[Na^+]_{out}[Cl^-]_{out}}{[Na^+]_{in}} \tag{S5}$$

The additional osmotic pressure inside the gel compared to outside the gel is then given by

$$\Delta P_{osmotic} = RT([Na^+]_{in} + [Cl^-]_{in} - [Na^+]_{out} - [Cl^-]_{out}) \tag{S6}$$

where R is the gas constant and T is the absolute temperature. In our case of one-dimensional swelling, the pH-dependent additional swelling due to the increased osmotic pressure from Na^+ and Cl^- ions is limited by the spring constant of the hydrogel and can be described as

$$\Delta Hy(pH) = \frac{\Delta P_{osmotic}}{k_{spring}} \tag{S7}$$

where k_{spring} is the spring constant of the hydrogel in units of Pa. The hydration is then given by

$$Hy = Hy_0 + \Delta Hy\,(pH) \tag{S8}$$

where Hy_0 is the hydration of the uncharged hydrogel at low pH. Although the hydration Hy is obtained from equations S3-S8, its value must already be known from the start in equation S3; therefore, the value of Hy is adjusted iteratively until a self-consistent value is obtained.

For simulations, a non-charged hydrogel or ferrogel was assumed at pH 3, with an initial hydration of $Hy_0 = 12.26$, both with and without nanoparticles. The concentration of ionizable monomers was calculated from the initial monomer mixture, $[AA] = 0.81$ M. The concentration of the buffer species was 0.01 M, the ionic strength was 0.1 M, and temperature was 300 K.

Table S1. Values of the pK$_a$ and the spring constant fitted from swelling experiments.

Simulation parameters	Hydrogel	Ferrogel
pK$_a$	4.5	4.7
Spring constant (Pa)	480	320

Dynamic changes in hydrogel volume

Our numerical simulations of the time-dependent thickness of our hydrogels are also inspired by the work of De and coworkers.[25] A main difference is that our gels are so dilute that the slow dynamics that we observe must be accounted for in another way. De et al.[25] are able to describe their results on the basis of effective diffusion coefficients that only take into account the volume fraction of liquid inside their polymer networks, via $D_{eff} = D(Hy/(2+Hy))^2$. We use an empirical diffusion rate reduction factor F_R, so that the effective diffusion coefficient is $D_{eff} = D/F_R$, where D is the literature value of the diffusion coefficient in the limit of high dilution (taken here to be $9.3 \cdot 10^{-9}$ m^2/s for H$^+$ and $1.1 \cdot 10^{-9}$ m^2/s for buffer). Very likely, the factor F_R not only originates from the tortuisity of the porous network but also from the electrical charge at the surfaces of the pores. Romero et al.[31] have demonstrated experimentally that ionic diffusion inside charged nanopores can be much slower than inside uncharged pores, in agreement with theoretical expectation.

In our numerical simulations of the time-dependent thickness of our hydrogels, space is divided into 100 bins that are of equal size only when the entire gel is at equilibrium with the external ionic solution. Once the external pH is changed, the ionic concentration changes inside the gel are calculated along the same lines as De et al.[25] In each time step of the simulation, the pH changes in each bin because of ionic diffusion and dissociation equilibria of the buffer and polyelectrolyte. The ionic concentrations and osmotic pressures are calculated, corresponding to local swelling or shrinking of each individual bin depending on the mechanical spring constant of the gel via equation S7. We use the same continuity equation for hydrogen ions as De et al.[25] to calculate the changes in hydrogen ion concentration:

$$\frac{\partial}{\partial t}\left[Hy[H^+] + \frac{[AA]_{dry}[H^+]}{K + [H^+]} + \frac{Hy[buffer][H^+]}{K_B + [H^+]}\right]$$
$$= \frac{\partial}{\partial X}\left[\left(\frac{H}{1+H}\right)\left(1 + \frac{\overline{D_{HB}}}{\overline{D_H}}\frac{[buffer]}{K_B + [H^+]}\right) \times \left(\overline{D_H}\frac{\partial[H^+]}{\partial x}\right)\right] \tag{S9}$$

where K_B is the dissociation constant of the buffer, [buffer] is the total buffer concentration inside the hydrogel, $\overline{D_{HB}}$ is the diffusion coefficient of the buffer, and $\overline{D_H}$ is the diffusion coefficient of the H$^+$ ions inside the hydrogel. In this way, a different pH profile and hydration profile is calculated at each time step as long as equilibrium has not yet been reached.

The diffusion rate reducing factors F_R and remaining fit parameters are listed in Table S2. An optimal simulation of the time dependent thickness is a balance between the spring constant, the thickness of a dry layer, and the diffusion constant. The remanent magnetic field during swelling is calculated using equations 3 and 9 (main text), where the hydration in each bin determines the thickness t of the bin, its distance z from the field sensor, and the local value of the internal field M.

Table S2. Values used for time-dependent simulations of the remanent magnetic field, including the diffusion rate reduction factors for swelling and shrinking events.

Simulation parameters	Ferrogel
R (mm)	2
z (mm)	0.78
Average M (A/m) at pH 3	365
$F_{R,\text{swelling}}$	32
$F_{R,\text{ shrinking}}$	11
pK_B (swelling)	7.2
pK_B (shrinking)	2.15