Supporting Information

Self-strengthening stimuli-responsive nanocomposite hydrogels

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Experimental Section

Materials: N-isopropylacrylamide (NIPAM, stabilized with 4-methoxyphenol) was purchased from Tokyo Chemical Industry (TCI) America. N,N'-methylenebisacrylamide (BIS), and 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) were obtained from Sigma-Aldrich (St Louis, MO, USA). Potassium Chloride (KCl) was obtained from Fisher Chemical (Hampton, NH, USA). Laponite-RD (nanoclay) was purchased from BYK-Chemie (Wesel, Germany). All chemicals were used as received without further purification.

Preparation of Nanocomposite Hydrogels: 5 mL batch solutions for NC-3, NC-10, and NC-17 were prepared by mixing 0.4965 g NIPAM (monomer), 0.0038 g BIS (chemical crosslinker), 0.02 g Irgacure 2959 (photoinitiator), and deionized (DI) water together via a vortex mixer (Dlab Mx-S) until the solution is clear. Next, 0.1707 g (3 wt%), 0.6314 g (10 wt%), and 1.1306 g (17 wt%) of nanoclay (NC) were added to each of the batch solutions. The solutions were then manually mixed with a spatula to break up any clumps of NC and placed into a Thinky Mixer (AR-100, Thinky) for 2 minutes. These two steps were repeated until the NC was homogeneously dispersed throughout. The resulting solutions were then placed into their 1 mm deep glass molds and irradiated with 365 nm UV light (Omnicure S2000, Excelitas Technologies) for 1 minute at 180 mW/cm^2 (total UV dose of 10.8 J/cm^2) to crosslink. Once crosslinked NC-PNIPAM was formed, the samples were transferred to 23 °C DI water for at least 24 hours. The DI water was refreshed every hour for the first three hours to remove any unreacted chemical species.

Swelling Profile vs Time: To observe the initial swelling behavior of NC-PNIPAM, biopsy samples made with 3 wt%, 10 wt%, and 17 wt% NC were immersed in water for at least 24 hours (Fig. S2). Their diameters were measured every 20 minutes for the first three hours, then every hour for the following four hours. After five hours, measurements resumed revealing the equilibrium swelling ratio for each NC-PNIPAM sample. The average swelling ratio was taken among the three biopsy samples per NC-PNIPAM sample.

Cyclic Swelling/Deswelling: Three discs for each NC-3, NC-10 and NC-17 of 5 mm diameter were cut from the original NC-PNIPAM by biopsy. Then, they were imaged and measured with a digital microscope (Keyence VHX). The swelling ratio of the samples was defined by D_T/D_0; where D_T represents the measured diameter at temperature T, and D_0 represents the diameter in the as-prepared state. The biopsy samples were then transferred into 23 °C DI water for at least 24 hours, then 50 °C DI water for 24 hours, and then again into 23 °C DI water for 24 hours. The samples were cycled between 50 and 23 °C DI water 5 times with their diameters measured after each step. The ratios from the three samples per NC-*X* were averaged together to get the final value.

Nanoindentation: To evaluate the evolution of Young's moduli of the NC-PNIPAM, nanoindentation was performed on the NC-3, NC-10 and NC-17 samples underwater in the swelled or reswelled condition. After crosslinking, a biopsy was used to cut three thin discs with diameters of 5 mm and a thickness of 1 mm from each NC-PNIPAM sample. The thin discs were immersed in 23 °C DI water for at least 24 hours and then probed with the Nanoindenter (Piuma, Optics11).

Nine nanoindentations in a 3 × 3 matrix with 100 μm spacing were performed at random on each thin disc for a total of 27 nanoindentations per type of NC-PNIPAM. After the initial swell (S), the samples were transferred to a hot water bath at 50°C for 24 hours to deswell (DS) and then transferred to a 23 °C water bath to reswell (RS) for 24 hours. Following the subsequent reswelling, nanoindentation was performed again to measure the change in Young's modulus. This nanoindentation procedure was done for samples up to the fifth cycle.

X-ray Diffraction: X-ray diffraction (XRD) measurements were carried out using freeze-dried NC-PNIPAM with different concentrations of NC. XRD profiles of milled dried samples were measured by using an X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation (λ = 0.154 nm), employing a parallel beam measurement package and running at 40 kV and 40 mA.

Swelling/Deswelling in 0.01 M KCl: To observe the effect of 0.01 M KCl on the swelling ratio, the cyclic swelling/deswelling experiment was repeated in different swelling media. The experimental procedure is the same except that after an initial 24-hour swelling period in DI water, the samples were switched to a 0.01 M KCl solution and allowed to reach their new equilibrium swelling ratio for at least 24 hours. A fresh 0.01 KCl solution was used for each step and the average value of the three discs was used to represent each NC-PNIPAM sample.

Scanning Electron Microscopy: The microstructures of NC-PNIPAM samples were characterized by scanning electron microscopy (SEM) (FEI Quanta FEG 250). To prepare freeze-dried NC-*X*-S and NC-*X*-RS samples, the NC-PNIPAM samples were first swelled or reswelled in DI water at 23 °C for at least 24 hours to allow them to reach the fully swelled state. Next, NC-*X*-S and NC-*X*-RS samples were rapidly frozen in liquid nitrogen for 10 minutes. The water in the porous hydrogel network became ice crystals. The frozen samples were dried by a freeze dryer (Labconco FreeZone) at - 80 °C for 72 hours. The microstructures were then preserved for later characterization. Subsequently, the freeze-dried samples were coated with iridium for 8 seconds in order to prevent the charging of specimens during SEM imaging.The internal pore sizes of the NC-PNIPAM samples were obtained by SEM imaging and calculated by ImageJ. The energy-dispersive X-ray spectroscopy (EDX) mapping of Mg and Si was conducted by FEI Quanta FEG 250 as well.

Tensile Testing: For all three conditions (S, RS3 and 0.01 M KCl), three samples of NC-10 and NC-17 each were prepared and cut into certain dimensions in the as-prepared state (1 cm in width, 6.35 cm in length, and 1 mm in thickness) according to the ASTM standard D638 – 14 type V. A strain rate of 2 mm s^{-1} was used for all experiments. Representative curves were plotted and the average elongation at break and ultimate tensile strength were used for comparison.

UV-VIS Characterization: The UV/vis spectra of NC-*X*-S and NC-*X*-RS3 sheets (1 mm thickness in the as-prepared state) were characterized by a UV/vis spectrophotometer (Agilent Cary 60, Santa Clara, USA). The NC-PNIPAM sheets were held between two glass substrates to prevent sliding and deformation.

SAXS characterization: NC-PNIPAM samples for SAXS characterization were prepared by freeze-drying NC-X-RS1 and NC-X-RS5 samples. The SAXS experiments were performed using an X-Ray Diffractometer (XRDynamic 500, Anton Paar, Austria) X-ray beam with CuKa radiation (1.541 Å) was used for the experiments. The X-ray exposure time was 8 minutes for each sample.

Weight swelling ratio of the NC-PNIPAM hydrogel: NC-PNIPAM hydrogels were swollen in DI water at 23 °C for over 24 hours to reach the equilibrium swelled state. Five samples for each composition were then carefully biopsy-punched into thin disks with 10 mm diameter and 1 mm thickness. Then NC-PNIPAM thin disks were transferred into a water bath at 50 °C abruptly and deswelled for 24 hours. The weight of the swelled and deswelled samples was measured after carefully absorbing excessive water on the sample surface by filter papers. Dried hydrogels were weighed after air drying of swelled hydrogels in an oven at 50 °C for 12 hours. The weight swelling ratio of NC-PNIPAM hydrogels is defined by the weight of water absorbed by $\eta = (W_{23}-W_{dry})/(W_{50}-W_{dry})$, where W_{23} and W_{50} is the weight of hydrogel equilibrated at 23 or 50 °C, respectively, W_{dry} is the weight of the dried hydrogel. The weight swelling ratio indicates the water absorption ability per unit hydrogel weight.

SUPPLEMENTARY FIGURE

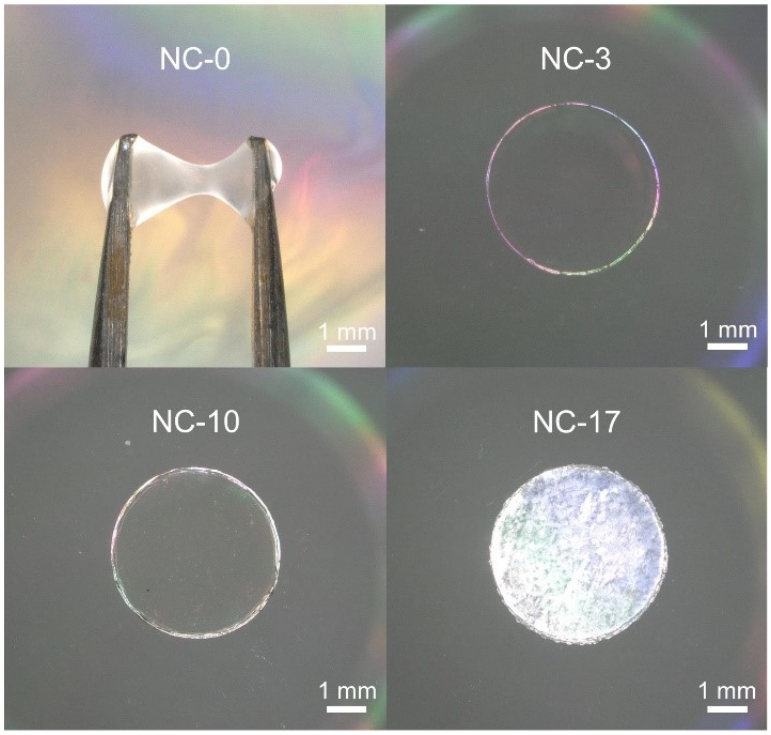

Figure S1. Microscopic images of as-prepared NC-*X* hydrogels. NC-0 was unable to be handled due to the minimal amount of chemical crosslinker present. The transparency of the cured NC-PNIPAM decreases with increasing NC concentration.

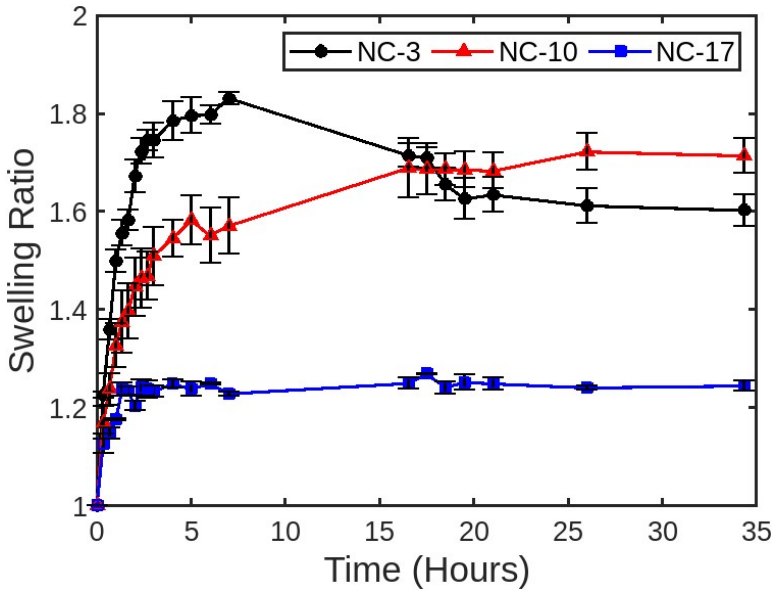

Figure S2. Swelling ratios of NC-3, NC-10, and NC-17 hydrogels over time. Equilibrium swelling is reached after 24 hours.

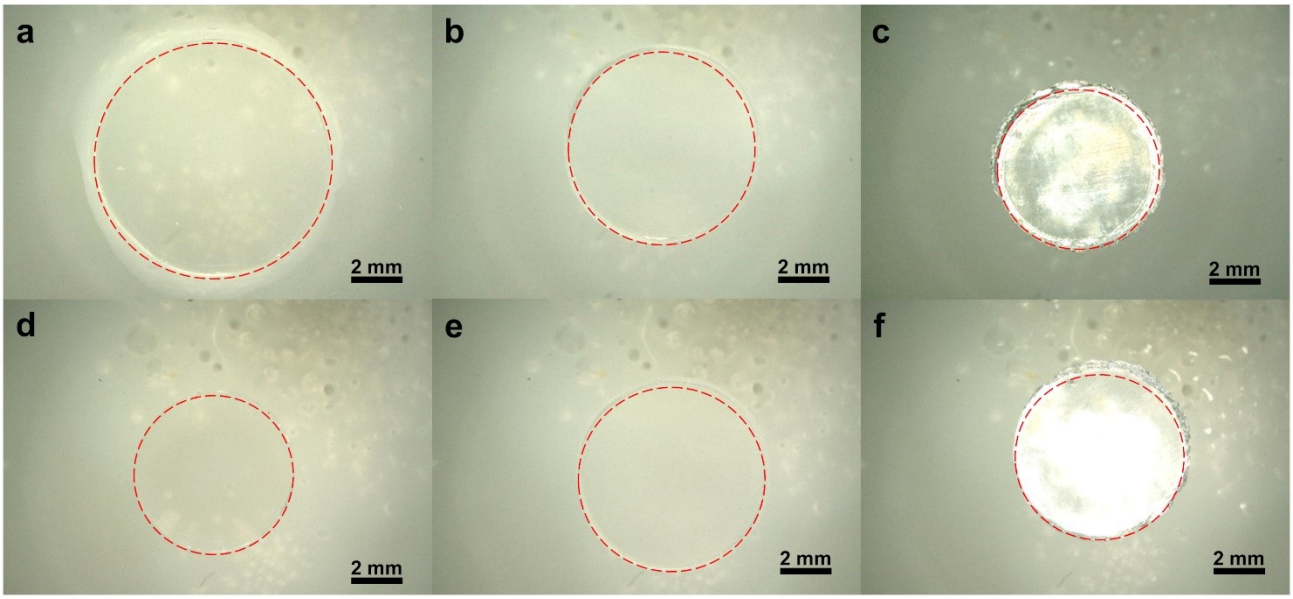

Figure S3. Comparison of the transparency of (a) NC-3-S, (b) NC-10-S and (c) NC-17-S samples with (d) NC-3-RS1, (e) NC-10-RS1, and (f) NC-17-RS1, respectively.

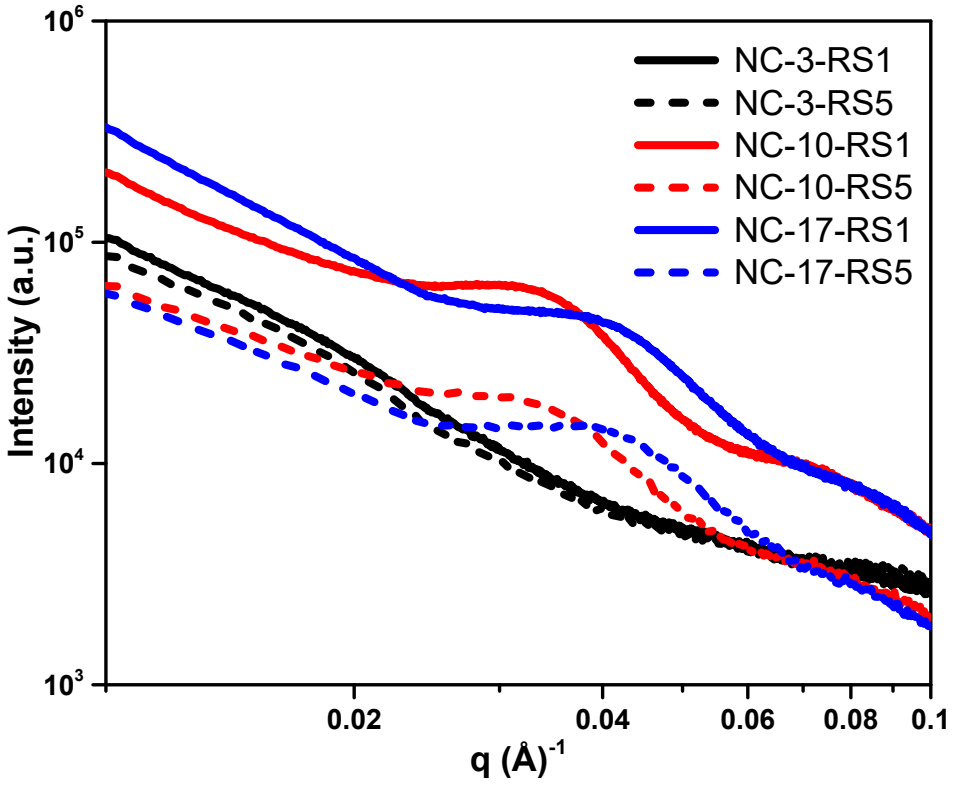

Figure S4 Small angle X-ray scattering (SAXS) for NC-PNIPAM hydrogels after one and five reswelling, denoted as RS1 and RS5, respectively.

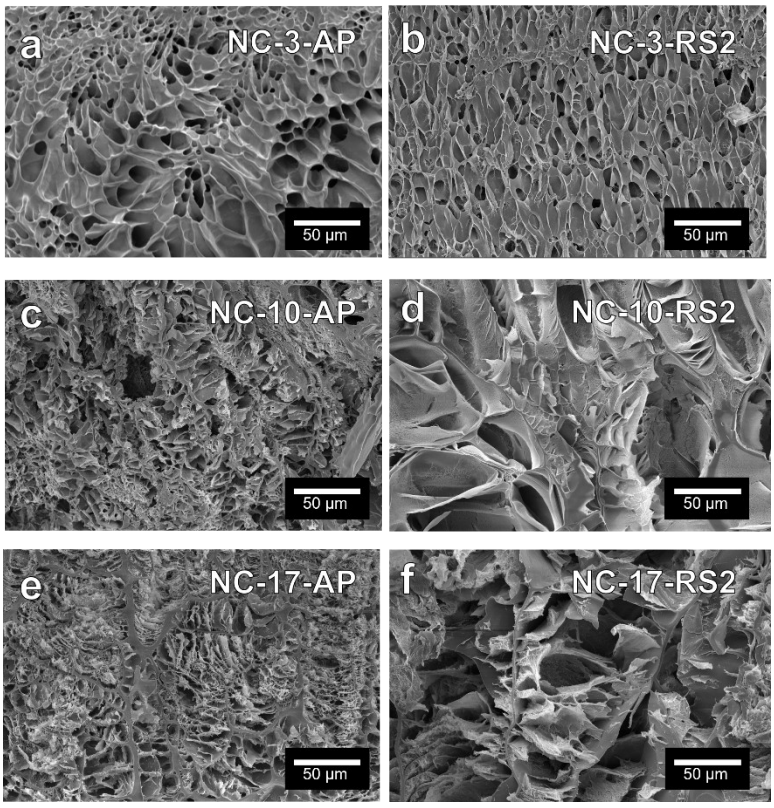

Figure S5. SEM images of the as-prepared (AP) states and second reswelled states (RS2) for hydrogels (a, b) NC-3, (c, d) NC-10, and (e, f) NC-17, respectively.

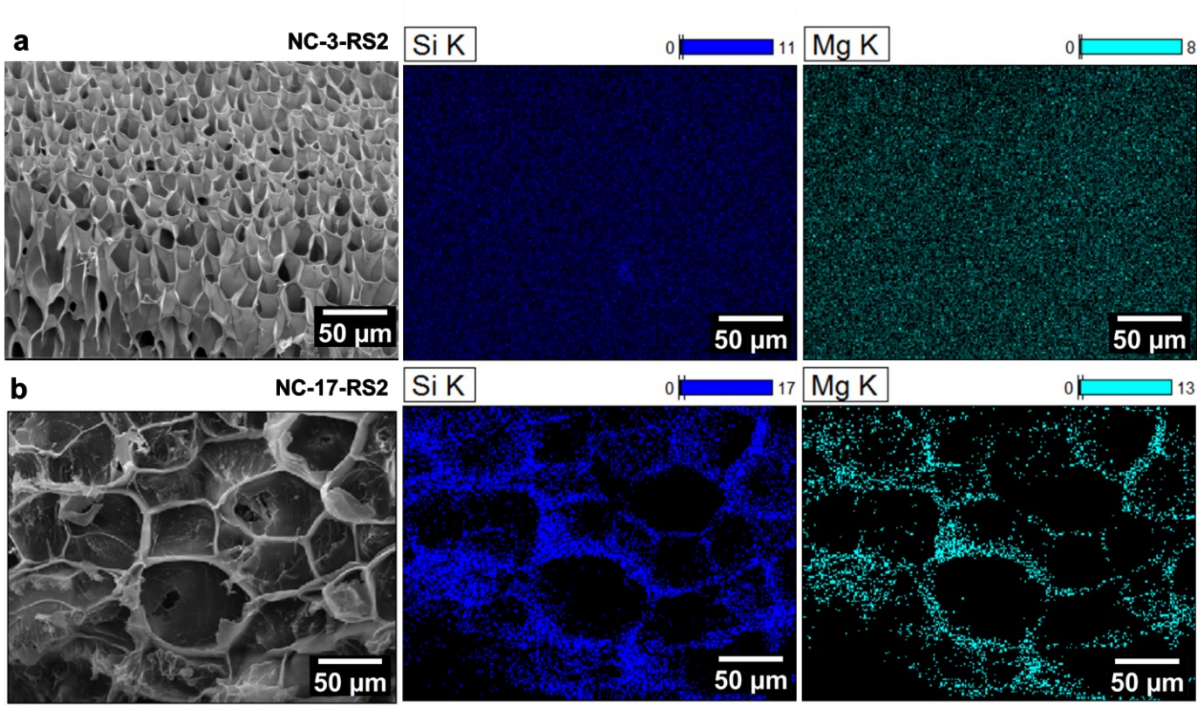

Figure S6. SEM images and corresponding EDX images of (a) NC-3-RS2 and (b)NC-17-RS2. The detected elements are Si and Mg.