Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Near-infrared Light Triggerable Deformation-free Polysaccharide Double Network Hydrogel

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Supporting information1:

Materials

Poly (vinyl alcohol) (PVA) (M_w 9000–10,000), $FeCl_3 \cdot 6H_2O$ (97% purity), pyrrole monomer (98% purity), alginate (alginic acid sodium salt, viscosity = 15-20 cP in 1% H_2O), agarose (type IX-A, ultra-low gelling temperature), tetramethylrhodamine isothiocyanate-dextran (TRITC-dextran, average molecular weight = 65,000-85,000 Da) and ethylenediaminetetraacetic acid (EDTA) were obtained from Sigma-Aldrich (Singapore) and used without further purification.

Supporting information 2:

Synthesis and characterization of polypyrrole nanoparticles

Polypyrrole (PPy) nanoparticles were prepared in an aqueous solution that contained PVA, $FeCl_3 \cdot 6H_2O$ and pyrrole monomer. First, 0.75 g of PVA was dissolved in 10 ml of deionized water by stirring on a 60°C hotplate for 20 minutes. After the mixture cooled, 0.63 g of $FeCl_3 \cdot 6H_2O$ was added to the PVA solution and the mixture was stirred for 1 hour to fully dissolve the $FeCl_3 \cdot 6H_2O$. Subsequently, 69 µl of pyrrole monomer was added dropwise to the reaction mixture. The reaction mixture was maintained at 4°C while stirring for 24 hours during the polymerization reaction. The resulting black PPy nanoparticle solution was centrifuged at 13,000×*g* and at 4°C for 40 minutes to separate the PPy nanoparticles. The PPy nanoparticles were then washed twice with deionized water. The centrifugation and washing processes were repeated three times to remove excess PVA.[1]

Scanning electron microscopy (SEM, JEOLJSM-6430F, JEOL, Japan) was used to investigate the morphology of the PPy nanoparticles. One drop of the PPy nanoparticle suspension was placed on a clean silicon wafer, dried, coated with Pt and observed under an accelerating voltage of 5 keV.

To determine the hydrodynamic diameter and polydispersity index of the PPy nanoparticles, dynamic light scatting (DLS) measurements were performed using a Malvern Zeta-sizer (Malvern Zetasizer Nano, UK). First, 1 ml of a dilute PPy

nanoparticle aqueous solution was placed in a disposable cuvette and tested three times. The absorption spectrum of the PPy nanoparticle suspension in a quartz cuvette was measured using a UV–Vis spectrophotometer (UV-2401PC, Shimadzu, Japan) over the wavelength range of 250 to 1000 nm.

To investigate the ability of PPy nanoparticles to convert NIR light into heat, the PPy nanoparticle suspension was heated using NIR irradiation. One milliliter of an aqueous solution of PPy nanoparticles at different concentrations (0, 200 and 400 μg/ml) was placed in a 4 ml cuvette (1 cm path length), which was stirred magnetically. The thermocouple of a digital thermometer with a precision of 0.1°C (Fluke 51-II) was immersed in the solution. The PPy nanoparticle solution was then irradiated with a 915 nm continuous-wavelength (CW) laser (BWT Beijing, Ltd., China) at an intensity of 2 W/cm^2 for 10 minutes. The laser intensity was calculated using the following equation provide by the power meter supplier: (250 / d^2) × Power, where d is the diameter of the laser beam in millimeters. The laser beam diameter was determined using an IR indicator card. Power was determined with a model 841-PE power/energy meter (Newport Opto-Electronics Technologies, Singapore), and temperature changes were recorded every 10 seconds.

References

[1] J. Y. Hong, H. Yoon and J. Jang, *Small*, 2010, **6**, 679.

Supporting information 3:

Fabrication of agarose/alginate double-network composite hydrogels

Three grams of agarose with an ultra-low gelation temperature was dissolved in 100 ml of deionized water (DI H_2O) by heating at 50°C for 30 minutes. The pre-heated agarose solution was mixed with an equal volume of 3% (w/v %) alginate solution and maintained at 50°C for further use. One milliliter of the agarose/alginate solution was mixed thoroughly with 400 μg PPy nanoparticles and subsequently injected into a plastic mold. The solution-filled mold was placed in a covered Petri

dish and cooled in a 4°C refrigerator for 30 minutes to induce the gelation of agarose. The mold was subsequently immersed in 10 ml 0.5 M $CaCl_2$ solution for 15 min to induce the gelation of alginate. The hydrogel shapes were removed from the mold and washed once with DI H_2O.

In this study, we chose agarose with an ultra-low gelling temperature, which has a melting point of approximately 40°C and a gelation point of approximately 25°C. Once melted, this agarose will remain in the liquid phase until the temperature decreases to less than 25°C, which ensures its easy manipulation at room temperature. Once gelled, this agarose will remain solid unless the temperature increases to greater than 40°C, and it can be used as a template for subsequent alginate gelation and to trap reagents. When PPy nanoparticles were used at concentrations greater than 400 μg/ml, the solution temperature reached 40°C or above during irradiation with an NIR laser. Thus, with this type of agarose in a thermal-responsive hydrogel matrix, PPy nanoparticles can be used as effective photothermal nano-transducers to induce the sol-gel transition of the agarose for pulsatile release of reagents when triggered by NIR laser switching.

To investigate the effects of NIR laser irradiation on hydrogel properties, samples of agarose composite hydrogel and double-network composite hydrogel were suspended in water, placed onto a slide and viewed with a microscope equipped with a CW 915 nm laser source (Nikon ECLIPSS TE2000-U, Singapore) to examine the response behavior of the composite hydrogel to NIR laser irradiation for various times and at various intensities. The sizes and morphological changes of these composite hydrogels before and after irradiation with an NIR laser were recorded.

Supporting information 4:

Rheological measurements of the composite hydrogel

An amplitude-sweep test of the composite hydrogel was performed with a controlled-stress rheometer (Anton Paar, PP25/TG-SN6539, Singapore) to investigate its storage (G′) and loss (G″) moduli. An oscillating deformation was applied, and

G′/G″ were measured as functions of the applied strain between 0.1% and 20% at a constant frequency (f = 1 Hz) and temperature (T = 25°C). The composite hydrogel samples were flat disks, and they were measured in plate-plate rheometer geometry, with an upper plate diameter of 25 mm. It is important to make sure that adequate contact between the hydrogel samples and plates without significantly compressing the hydrogel should be maintained.

Supporting information 5:

NIR-laser-directed release of TRITC-dextran from composite hydrogels

TRITC-dextran was used as a model compound to characterize the NIR-laser-triggered release profile of these composite hydrogels. TRITC-dextran was dissolved in the agarose solution and loaded into the composite hydrogel. The TRITC-dextran-loaded composite hydrogel was made into a flat disk with a diameter of 5 mm and a thickness of 2 mm. These TRITC-dextran-loaded composite hydrogels were immersed in 1 ml of H_2O and irradiated with the NIR laser (915 nm, 2 W/cm^2). A 0.5 ml aliquot of the supernatant was removed for fluorescence spectroscopy analysis, and equivalent amounts of fresh H_2O were added at designated time intervals. The concentration of released TRITC-dextran was analyzed using excitation light with a wavelength of 550 nm and emission light with a wavelength of 570 nm.

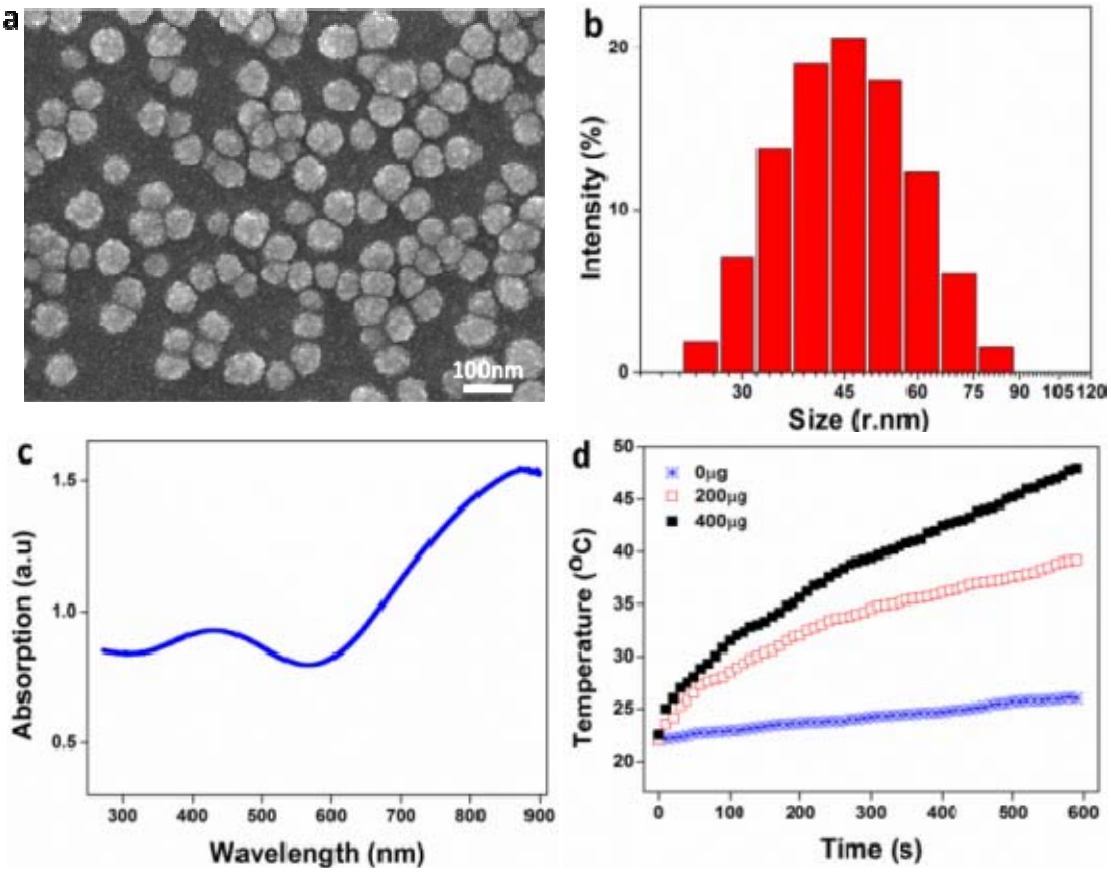

Figure S1. (a) SEM micrograph of PPy nanoparticles; (b) DLS results showing the hydrodynamic diameters of the PPy nanoparticles; (c) UV-vis-NIR absorption spectrum of the PPy nanoparticles; and (d) heating effects of PPy nanoparticles after irradiation with NIR laser, which increased the water temperature.

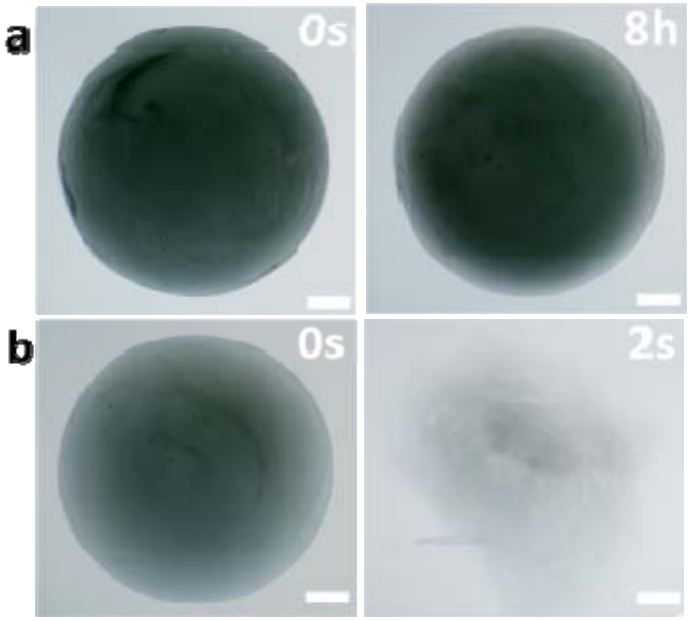

Figure S2. Microscope observations showing the morphology of (a) an agarose/alginate double-network composite hydrogel before (0s) and after (8h) boiling and (b) an agarose hydrogel before (0 s) and after (2 s) boiling treatment; the scale bar is 200 μm.

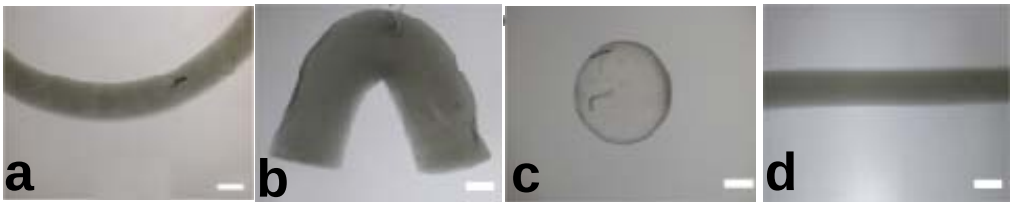

Figure S3. Different shapes of hydrogels prepared from agarose/alginate hydrogel with various concentration.

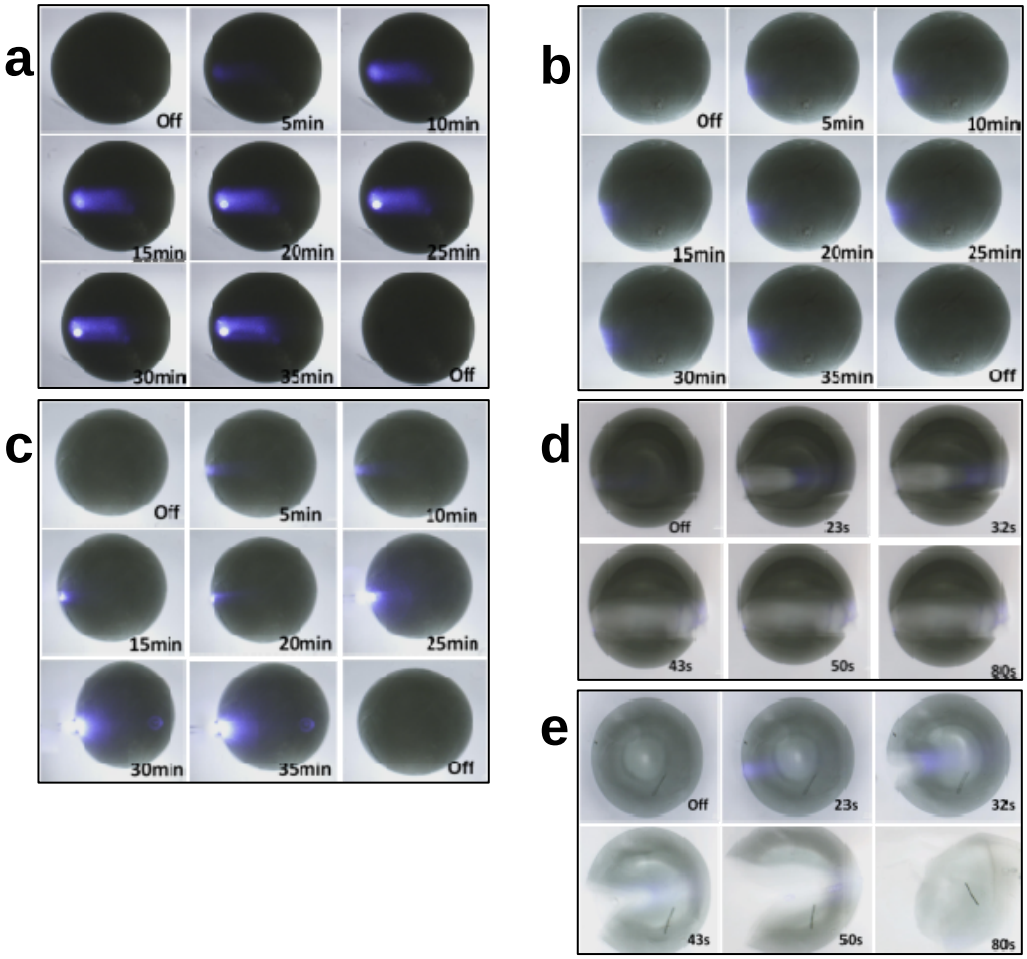

Figure S4. Microscope observations showing the shape integrity of various agarose/alginate hydrogels (a) agarose / alginate (0.2 / 1.8) (b) agarose / alginate (1 / 1) (c) agarose / alginate (1.4 / 0.6); The shape integrity of these hydrogels during the laser irradiation (2 W/cm2, 915 nm) process was maintained, indicating that these agarose/alginate double network hydrogel with different stoichiometry ratios of agarose and alginate remained integrated during the laser irradiation process. (d) agarose/alginate (1.8 / 0.2) (e) agarose/alginate (2 / 0); these two hydrogels can not maintain the shape integrity during the laser irradiation process.

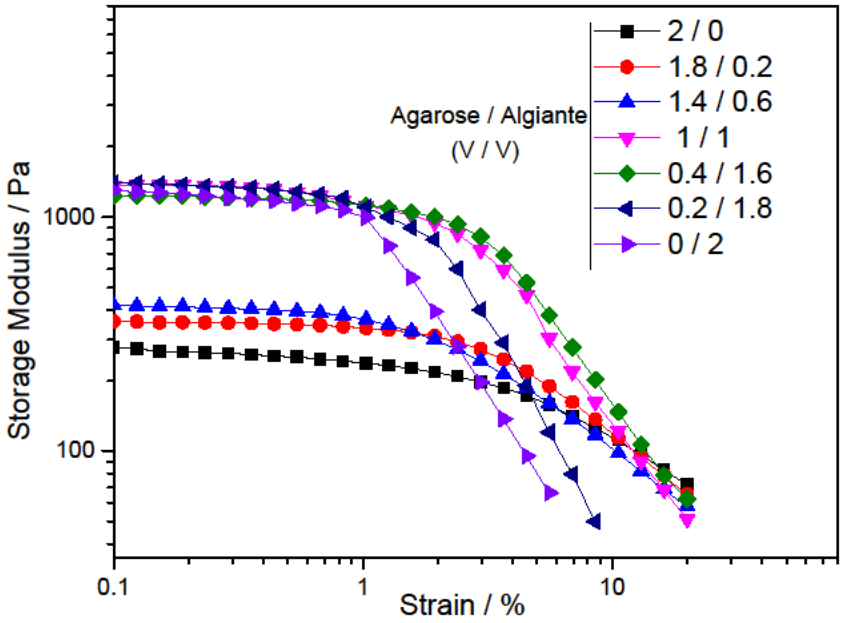

Figure S5. Rheological properties characterization of agarose/alginate double network hydrogel with different stoichiometry

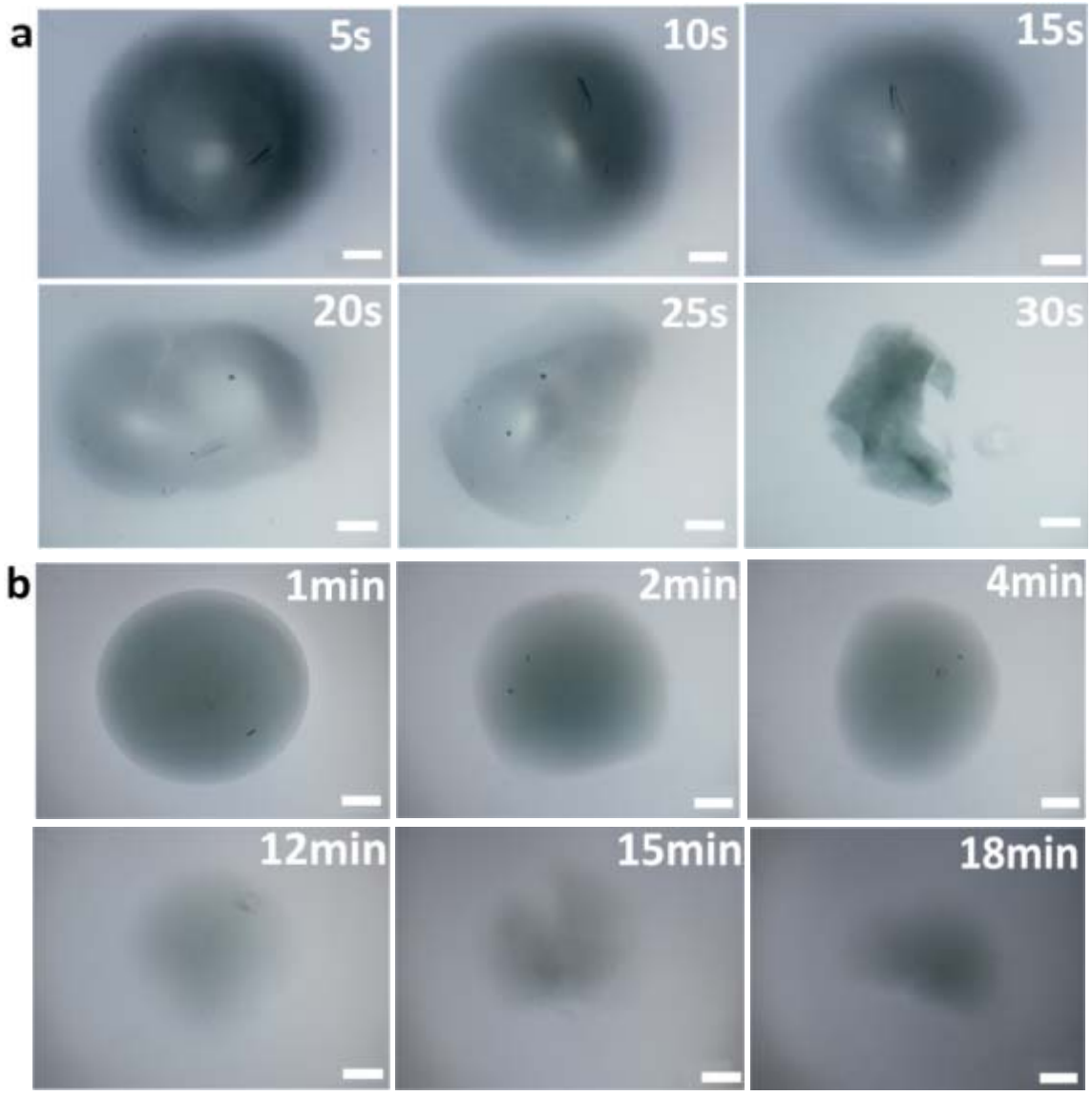

Figure S6. (a) Serial microscope observations showing the heating (40^{o}C) induced dissociation of the shaped hydrogel structure for EDTA treated Agarose/Alginate double network composite hydrogel (b) serial microscope observation showing the EDTA (0.1M) induced dissociation of the shaped hydrogel structure for heating treated Agarose/Alginate double network composite hydrogel; the scale bar is 200μm.

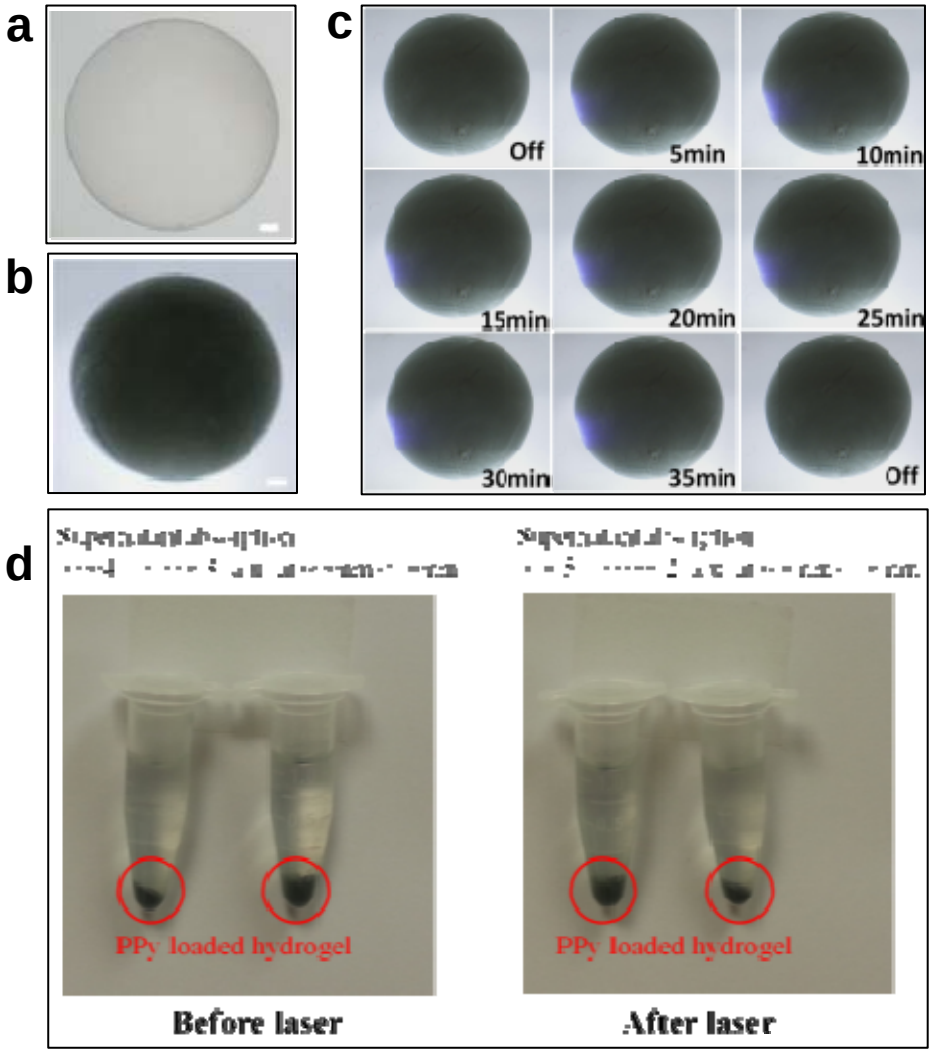

Figure S7. (a) agarose/alginate hydrogel without PPy nanoparticles; (b) agarose/alginate hydrogel with PPy nanoparticles loading, indicating the fine distribution of PPy nanoparticles within the hydrogel; (c) microscope observation showing the effects of laser irradiation on the agarose/alginate hydrogel loaded with PPy nanoparticles, indicating that PPy nanoparticles did not release out during laser irradiation process; (d) PPy nanoparticles loaded agarose/alginate hydrogel was incubated with 1ml H_2O before laser irradiation, the supernatant (pure H_2O) was analyzed with UV-Vis spectrometer, showing an absorption value of 0.004 ±0.0003 (a.u) at 600nm~900nm; after laser irradiation on the hydrogel, the supernatant was analyzed with UV-Vis spectrometer, showing an absorption value of 0.005 ±0.0002 (a.u), indicating that PPy nanoparticles did not release out during the laser-triggered TRITC-dextran releasing process.

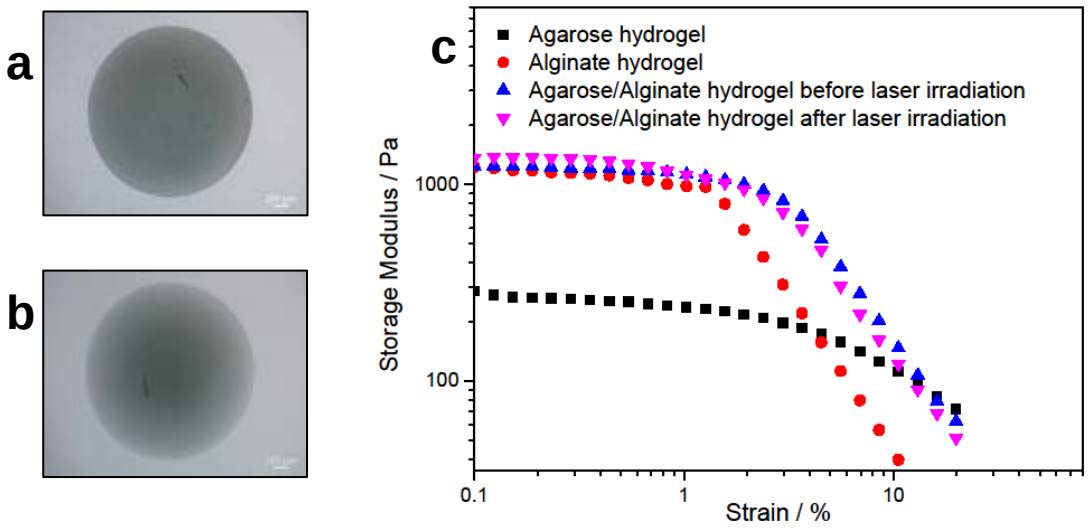

Figure S8. Microscope observation showing the effects of EDTA treatment on the morphologies of agarose/alginate hydrogel after laser irradiation (a) agarose/alginate hydrogel after laser irradiation and before EDTA treatment (b) agarose/alginate hydrogel after laser irradiation and after EDTA treatment. It was seen that the size and morphology of the hydrogel were maintained after laser irradiation and EDTA treatment, indicating that agarose did not release out during the laser-triggered TRITC-dextran releasing process; (c) Rheological properties of agarose hydrogel, alginate hydrogel, agarose/alginate hydrogel before and after laser irradiation, in which storage modulus of agarose/alginate hydrogel after laser irradiation remained similar to that of un-irradiated samples, indicating that agarose did not release out during the laser-triggered TRITC-dextran releasing process.