Supplementary Information

NIR-light-mediated Photocuring of Adhesive Hydrogels for Noninvasive Tissue Repair *via* Upconversion Optogenesis

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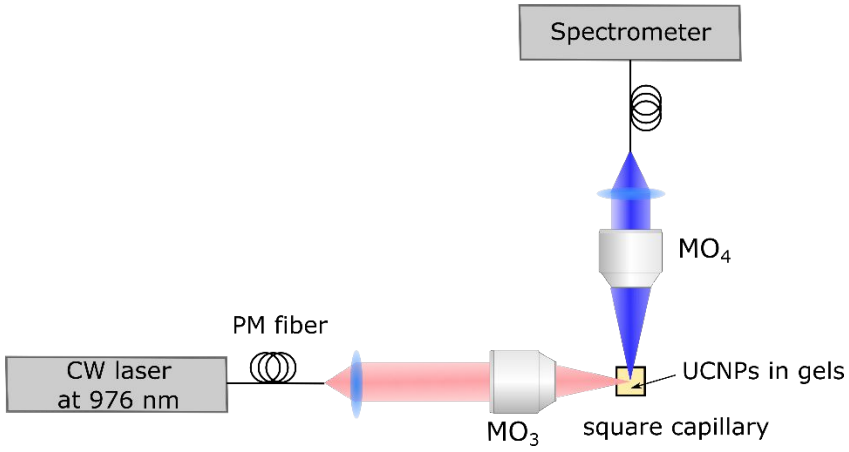
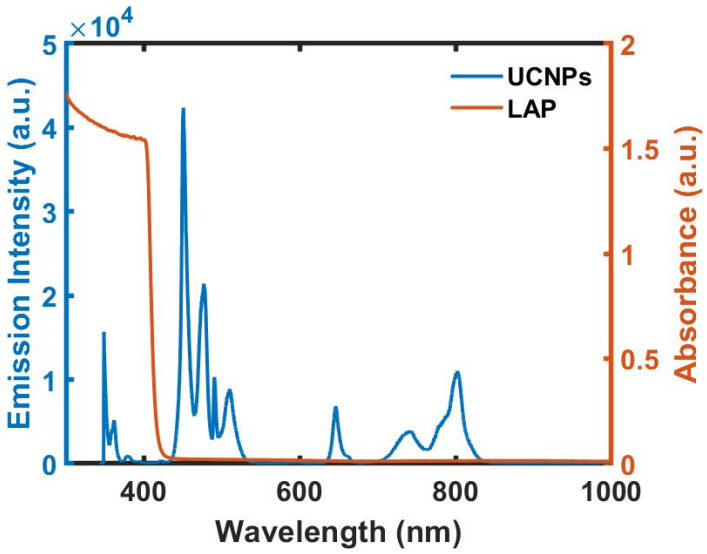
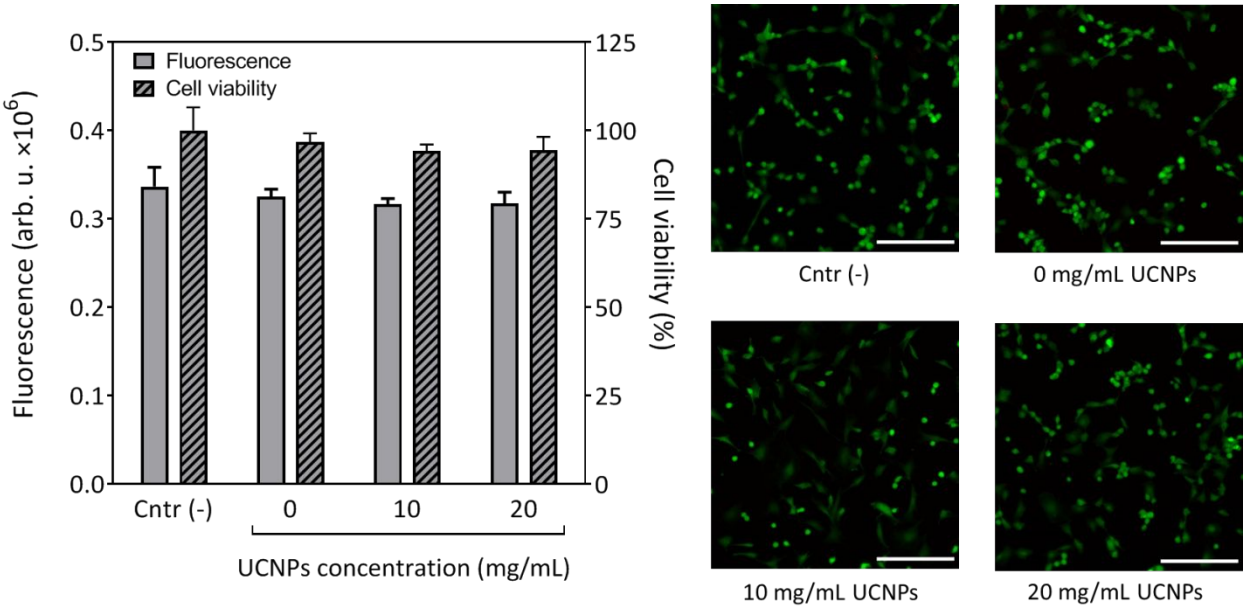
Spectra measurement. In order to include the environmental effect, the emission spectrum of UCNPs is measured in gelatin solution. A glass capillary is filled with hydrogels containing UCNPs (10 mg/mL) and polymer (15 wt%). The emission spectrum is recorded using the optical setup described above. The absorption spectrum of LAP (20 mg/mL) is recorded on a UV-Visible spectrophotometer (Varian Cary 50 Bio, Agilent).



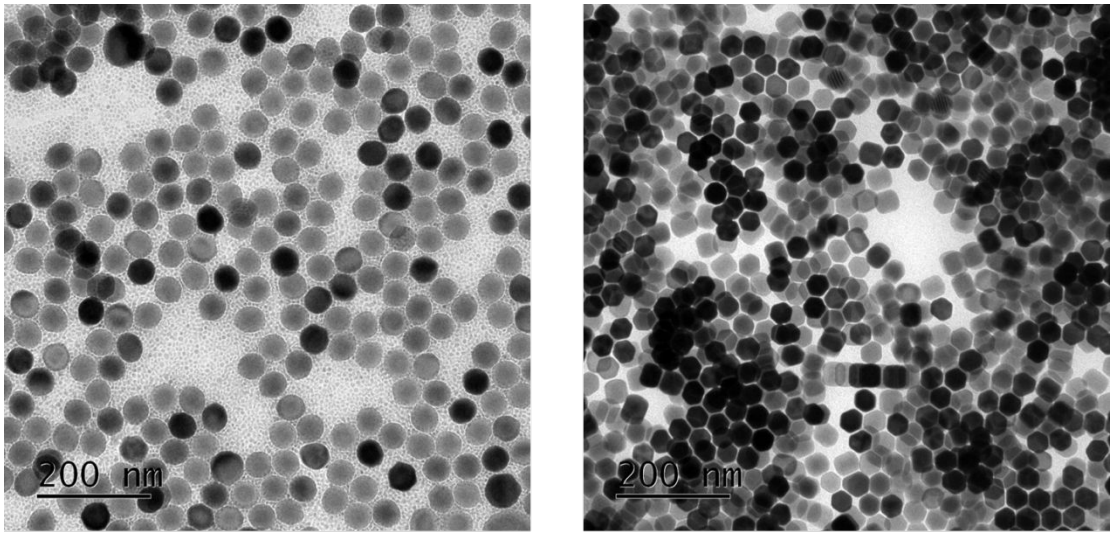
Supplementary Figure 1. Optical setup for emission spectrum measurement. A continuous-wave laser at 976 nm (900 mW, BL976-PAG900, Thorlabs) with a Polarization-Maintaining (PM) optical fiber is collimated by a lens (F230APC-980, Thorlabs, f = 4.55 mm). The beam is focused by a microscope objective MO3 (M Plan Apo NIR 20X, Mitutoyo) into a glass square capillary (0.10 x 0.10mm, CM Scientific). The fluorescence signal is then collected by a second objective MO4 (UApo/340 20x, Olympus) and coupled by a lens (LA4052-A-ML, Thorlabs) into a multi-mode fiber (QP400-025-SR/BX, Ocean Insight) and recorded by a spectrometer (Ocean Optics USB4000, Ocean Insight).



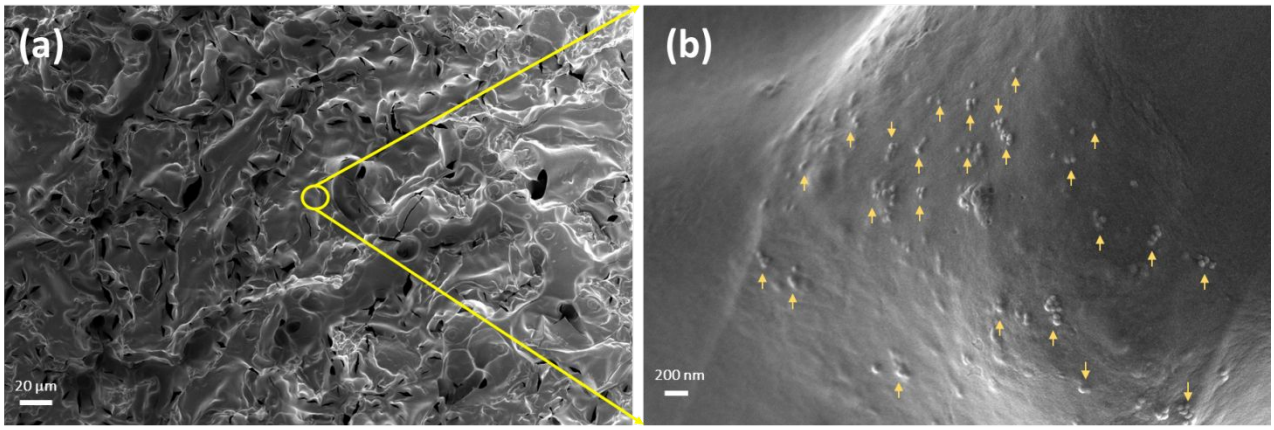
Supplementary Figure 2. The emission spectrum of UCNPs and the absorption spectrum of LAP. The LAP exhibits high absorption at wavelengths below 410 nm, and UCNPs have emission peaks at 349 and 362 nm, which should be responsible for the activation of the photoinitiator.



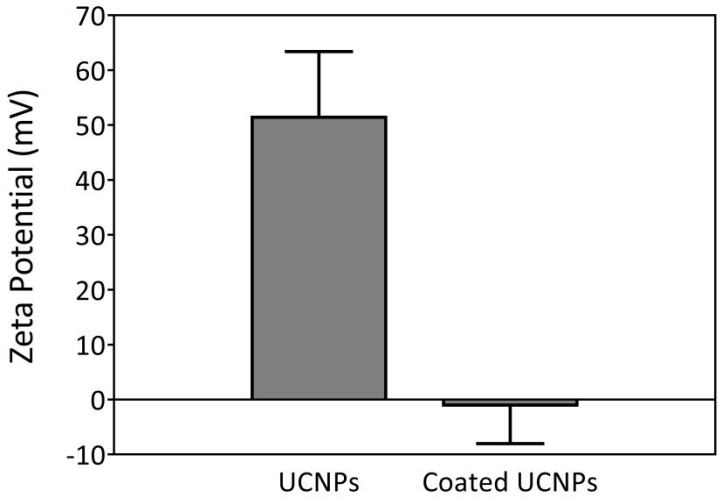
Supplementary Figure 3. Cytotoxicity test of the developed hydrogel system. No significant difference is observed in cells viability between test samples and control group (according to one-way ANOVA followed by Tukey's multiple comparison test, $p<0.05$), confirming the hydrogel composition are nontoxic to the cells as more than 90% of cells remained alive upon exposure to the extracts in all test groups compared to the control group. The cells viability was analyzed by the PrestoBlue assay (left hand side) and Live/Dead confocal imaging (representative images in right hand side), performed after 48 h exposure to the extracts. Live cells are imaged using the green stain, and dead cells are shown using the red stain. Scale bars show 200 μm. (n=3)



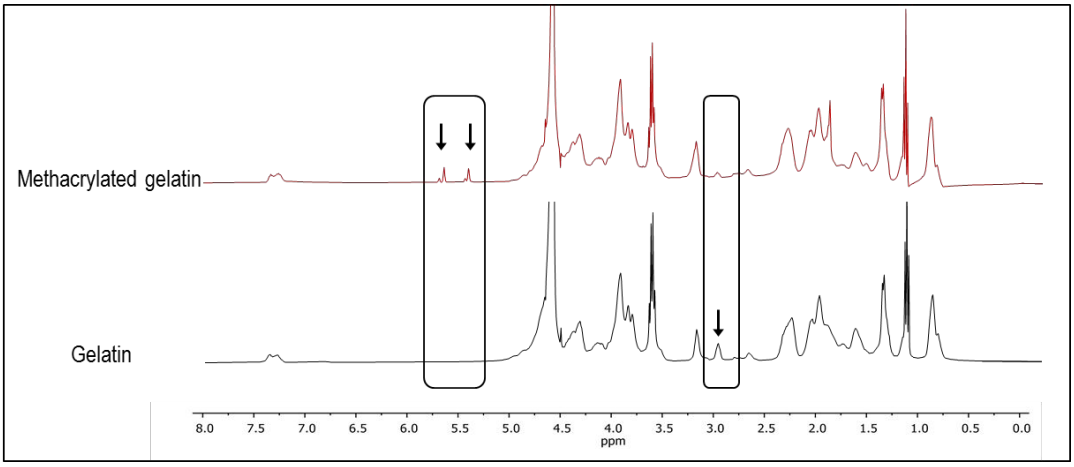
Supplementary Figure 4. (a) Seed UCNP particles. The particles are spherical in shape and the average diameter is 41.2 ± 2.78 nm. **(b)** Core-shell UCNP particles. They are hexagonal in shape and the average diameter is 44.11 ± 3.65 nm.



Supplementary Figure 5. Scanning electron microscopy (SEM) of freeze-dried adhesive hydrogel sample with 20 mg/mL UCNPs. (a) Confirms that the hydrogel has adequate porosity through the sample. (b) Proves that UCNPs are distributed randomly in framework of a hydrogel wall structures. The yellow arrows indicate the existence of UCNP particles in the hydrogel framework.



Supplementary Figure 6. Zeta (ζ) potential measurments of UCNPs and LAP-coated UCNPs. The zeta potential of uncoated UNCPs is 51.7 ± 11.4 mV whereas it was reduced to -1.3 ± 6.71 mV once LAP is coated to them which confirms the coating formation.



Supplementary Figure 7. ^{1}H NMR spectra of gelatin and methcrilated gelatin. The chemical structure and the modification degree of conjugates on the polymeric backbone were analyzed using ^{1}H NMR spectroscopy using a 400 MHz Bruker Avance NEO. The new signals at 5.4 and 5.7 ppm, corresponding to the acrylic protons of methacrylate vinyl group, and signal decrease at 2.9 ppm, corresponding to lysine methylene protons, demonstrates successful conjugation of methacrilate groups. Moreover, emergence of a new signal at 1.8 ppm correponds to the methyl function of methacrylate. The degree of methacrylation was calculted by comparing the lysine methylene signals in geltin and methcrilated gelatin which was around 60%. To prepare smaples for NMR characterization, 18 mg of the samples were dissolved in 500 µl of D_2O, and the NMR analysis was performed at 40°C.