Supporting Information for

Gold nanorod impact on mechanical properties of stretchable hydrogels

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1. Supplementary Table

2. Supplementary Figures

1. Supplementary Tables

AuNR Surface Chemistry	AuNR Concentration (nM)	Young's Modulus (kPa)	Maximum Elongation %
N/A	0.0	3.83 ± 0.50	2,040 ± 310
CTAB	0.1	3.67 ± 0.05	2,153 ± 560
CTAB	0.5	3.46 ± 0.34	1,600 ± 620
CTAB	1.0	2.83 ± 0.14	2,130 ± 480
CTAB	2.0	2.76 ± 0.40	2,200 ± 460
PEG-SH	0.1	3.64 ± 0.09	1,950 ± 590
PEG-SH	0.5	3.50 ± 0.30	1,270 ± 240
PEG-SH	1.0	2.79 ± 0.05	2,710 ± 690
PEG-SH	2.0	2.66 ± 0.31	2,130 ± 500
MUA	0.1	3.64 ± 0.10	3,545 ± 350
MUA	0.5	3.43 ± 0.22	3,051 ± 770
MUA	1.0	2.79 ± 0.08	3,567 ± 730
MUA	2.0	2.58 ± 0.33	2,675 ± 210

Table S1: Summary of Na-alginate/PAAM hydrogel mechanical testing results for each type of AuNR hydrogel synthesized. The Young's modulus and elongation results for the hydrogel without AuNRs was comparable to what was previously reported.[1]

CTAB	0.1 nM	0.5 nM	1.0 nM	2.0 nM
0.0 nM	0.4905	0.0718	0.0003	0.0003
0.1 nM		0.2042	0.0001	0.0010
0.5 nM			0.0025	0.0061
1.0 nM				0.7215

PEG-SH	0.1 nM	0.5 nM	1.0 nM	2.0 nM
0.0 nM	0.4660	0.0997	0.0020	0.0010
0.1 nM		0.3924	0.0001	0.0005
0.5 nM			0.0003	0.0005
1.0 nM				0.3817

MUA	0.1 nM	0.5 nM	1.0 nM	2.0 nM
0.0 nM	0.4158	0.0425	0.0002	0.0001
0.1 nM		0.0726	0.0001	0.0001
0.5 nM			0.0001	0.0001
1.0 nM				0.1857

Table S2: Calculated p-values to determine statistical significance between the Young's modulus values of various AuNR concentrations for each surface chemistry tested. The p-values are listed in the table with colors (green) corresponding to a statistically significant difference and (red) corresponding to not statistically different.

AuNR Surface Chemistry	AuNR Concentration (nM)	Young's Modulus (kPa)
N/A	0.0	64 ± 19
CTAB	0.1	83 ± 13
CTAB	1.0	38 ± 6 *
PEG-SH	0.1	81 ± 16
PEG-SH	1.0	86 ± 13
MUA	0.1	85 ± 30
MUA	1.0	84 ± 2 *

Table S3: Young's modulus values for Ca-alginate/PAAm hydrogels. *Denotes values that are statistically different ($p < 0.05$) than the hydrogel sample without AuNRs.

2. Supplementary Figures

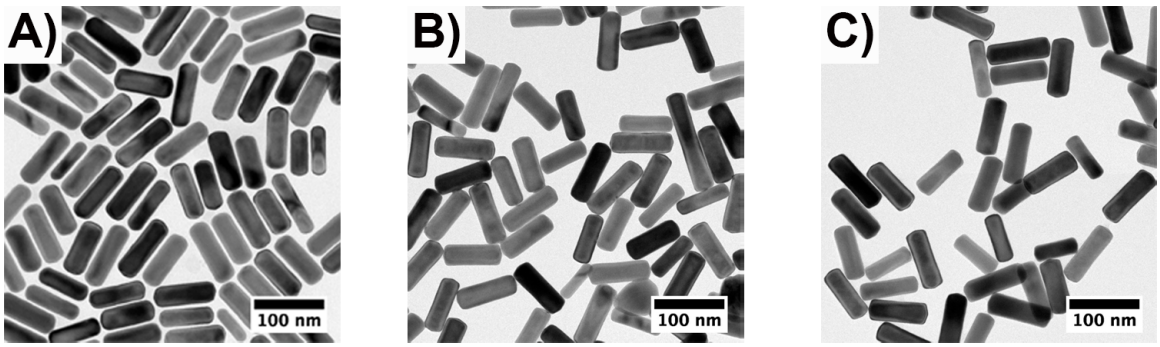

Figure S1: TEM images of AuNRs with varying surface chemistries. (A) CTAB (B) PEG-SH and (C) MUA. Scale bars are 100 nm.

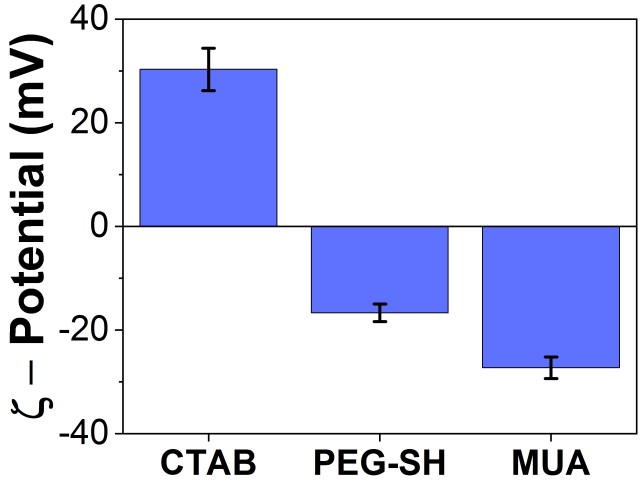

Figure S2: Zeta – potential results for the three different surface chemistries tested.

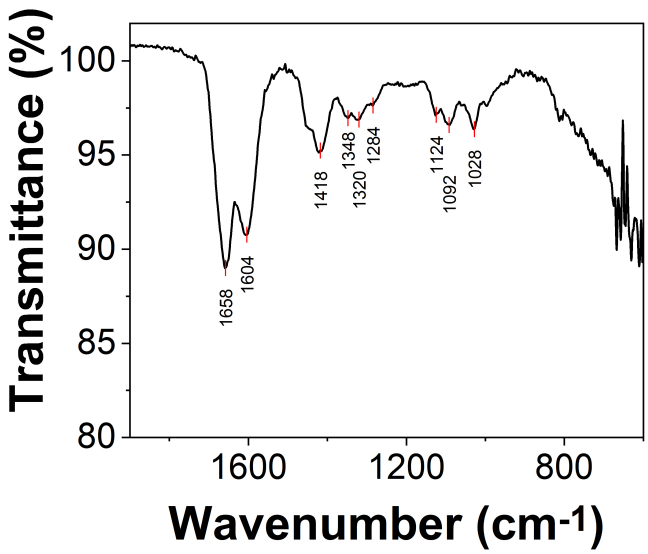

Figure S3: ATR-FTIR of Na-alginate/PAAm hydrogel. Sample was prepared by lyophilizing hydrogel and then grinding into a powder. Peak at 1284 cm^{-1} is the C-N stretching of the secondary amide formed between the alginate chains and polyacrylamide.[2] (1658 cm^{-1}: C = O stretching, 1604 cm^{-1}: N-H deformation, 1418 cm^{-1}: C-N stretching, 1348 cm^{-1}: C-H deformation, 1320 cm^{-1}: C-H deformation, 1124 cm^{-1}: NH_2 in-plane rocking, 1092 cm^{-1}: C-O stretching, 1028 cm^{-1}: C-O stretching).

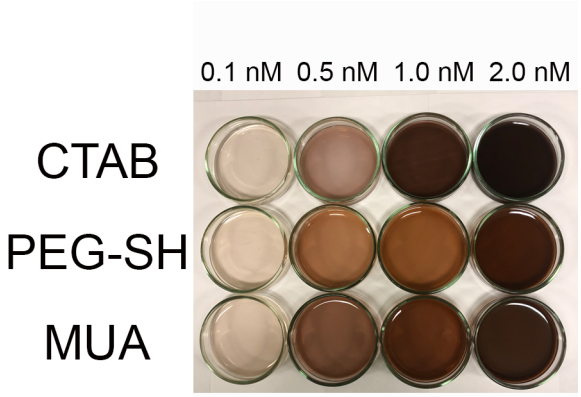

Figure S4: Photograph of a representative batch of synthesized Na-alginate/PAAm hydrogels with AuNRs.

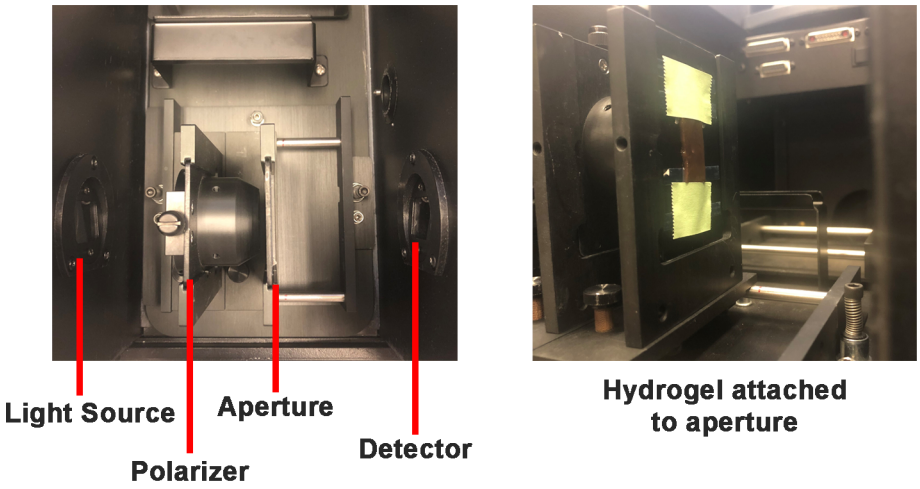

Figure S5: Measurement setup for UV-vis polarization measurements. Polarizer was placed between the light source and the aperture; the hydrogel was attached to the aperture plate in a stretched or unstretched position such that the hydrogel sample was completely covering the aperture.

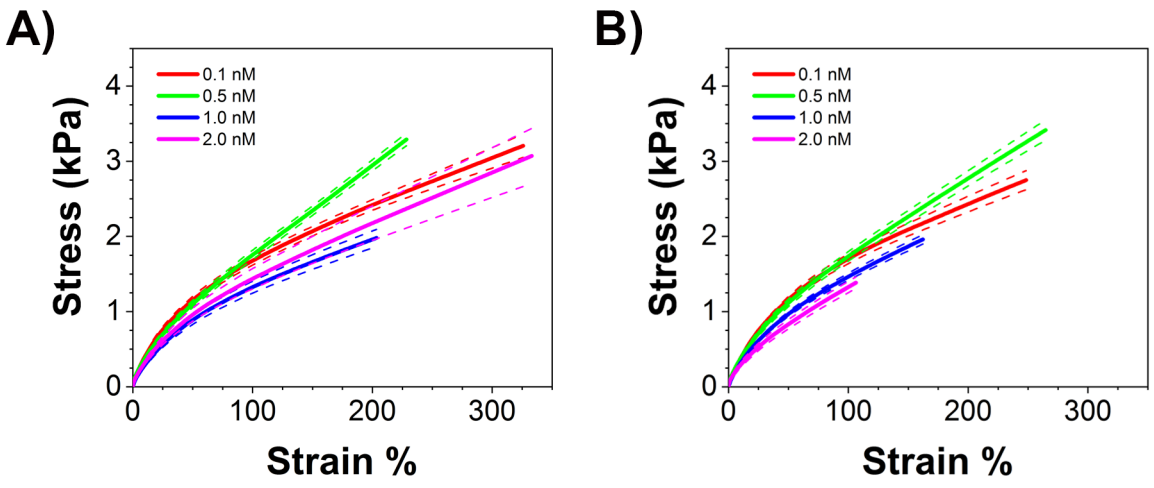

Figure S6: Averaged stress versus strain curves obtained from DMA for (A) CTAB AuNR Na-alginate/PAAm hydrogels and (B) PEG-SH AuNR Na-alginate/PAAm hydrogels. The solid line is the average of multiple curves and the dotted line is the standard error in the average curve.

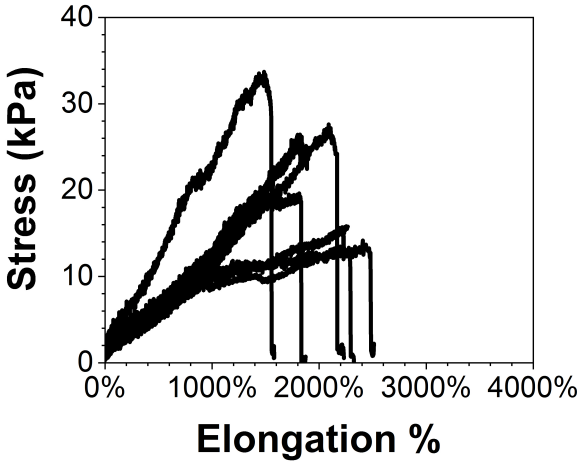

Figure S7: Stress versus elongation percentage (normalized elongation length) for Na-alginate/PAAm hydrogels without AuNRs.

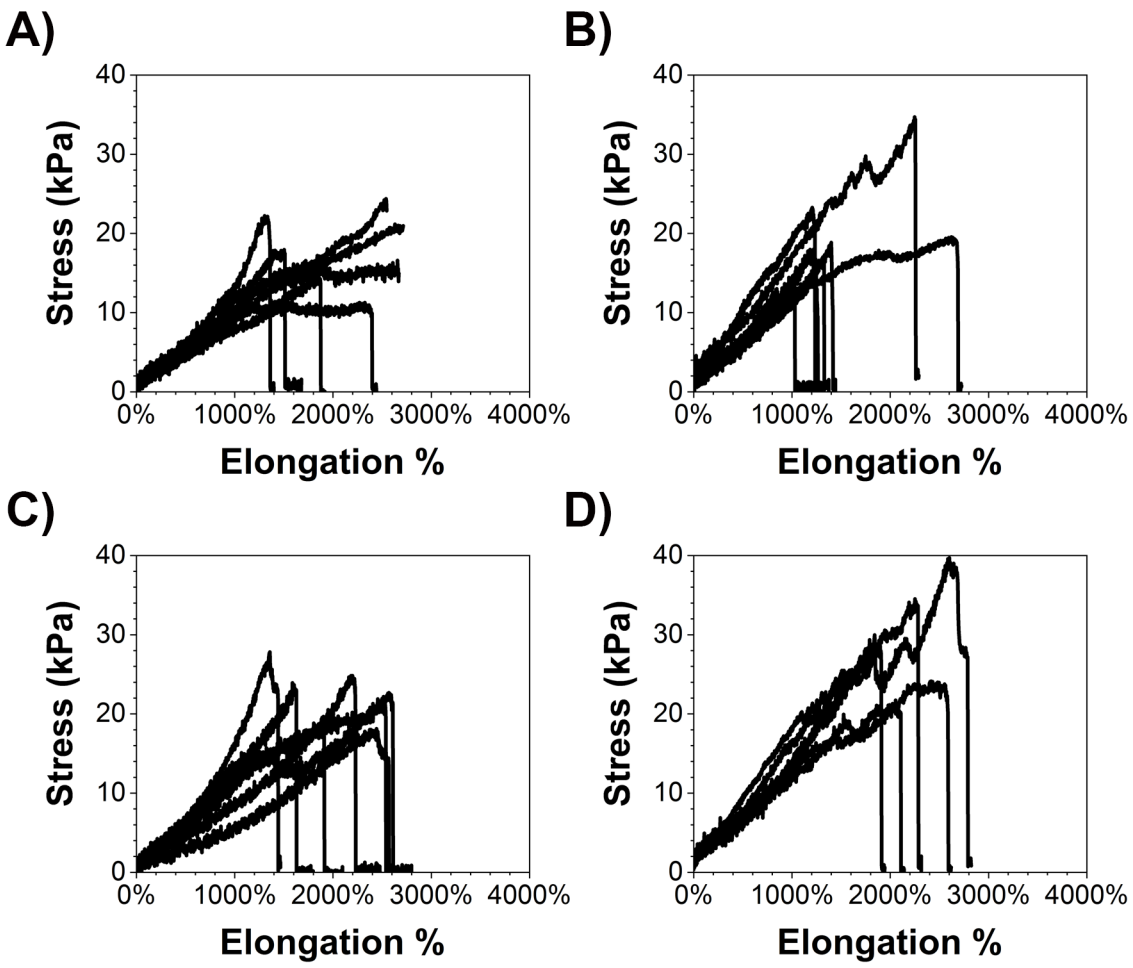

Figure S8: Stress versus elongation percentage (normalized elongation length) for Na-alginate/PAAm hydrogels with (A) 0.1 nM CTAB AuNRs and (B) 0.5 nM CTAB AuNRs (C) 1.0 nM CTAB AuNRs (D) 2.0 nM CTAB AuNRs.

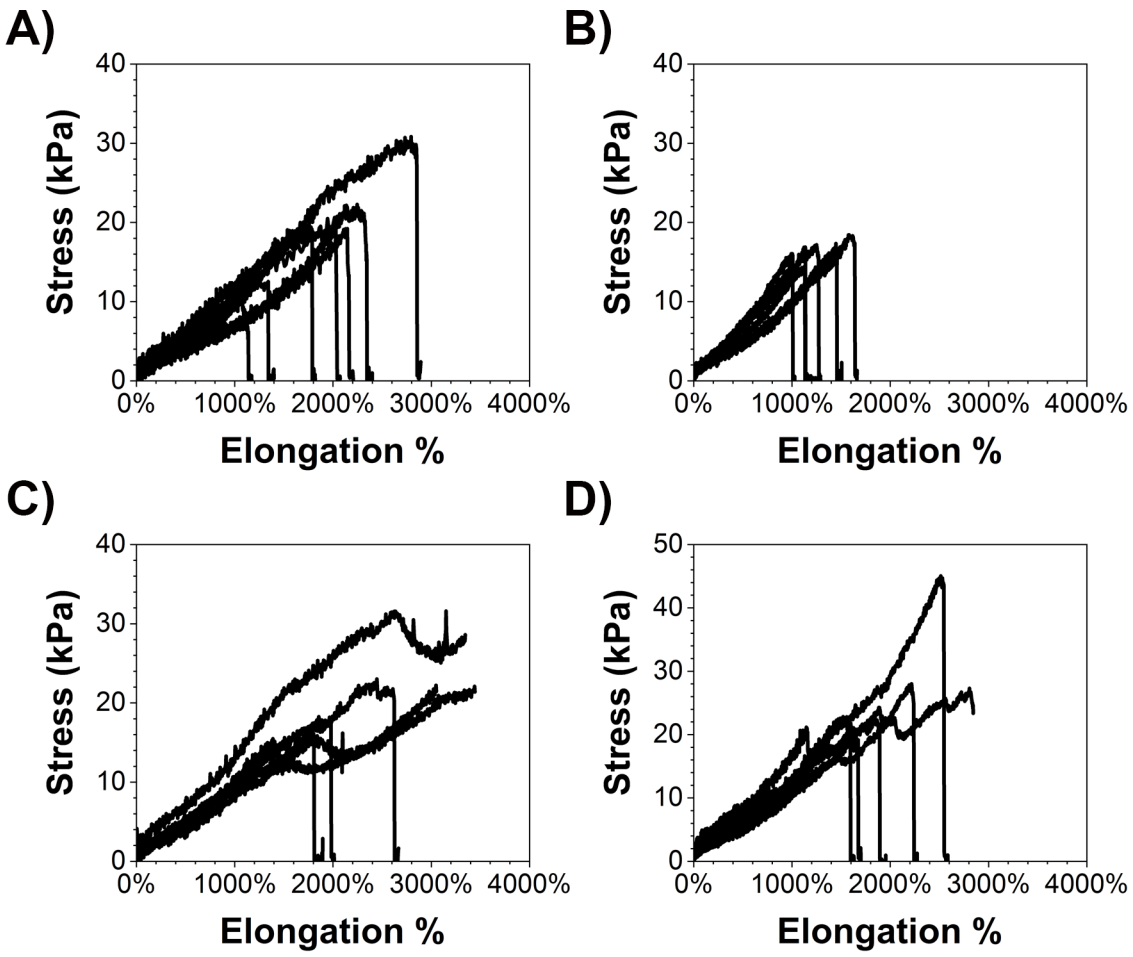

Figure S9: Stress versus elongation percentage (normalized elongation length) for Na-alginate/PAAm hydrogels with (A) 0.1 nM PEG-SH AuNRs and (B) 0.5 nM PEG-SH AuNRs (C) 1.0 nM PEG-SH AuNRs (D) 2.0 nM PEG-SH AuNRs.

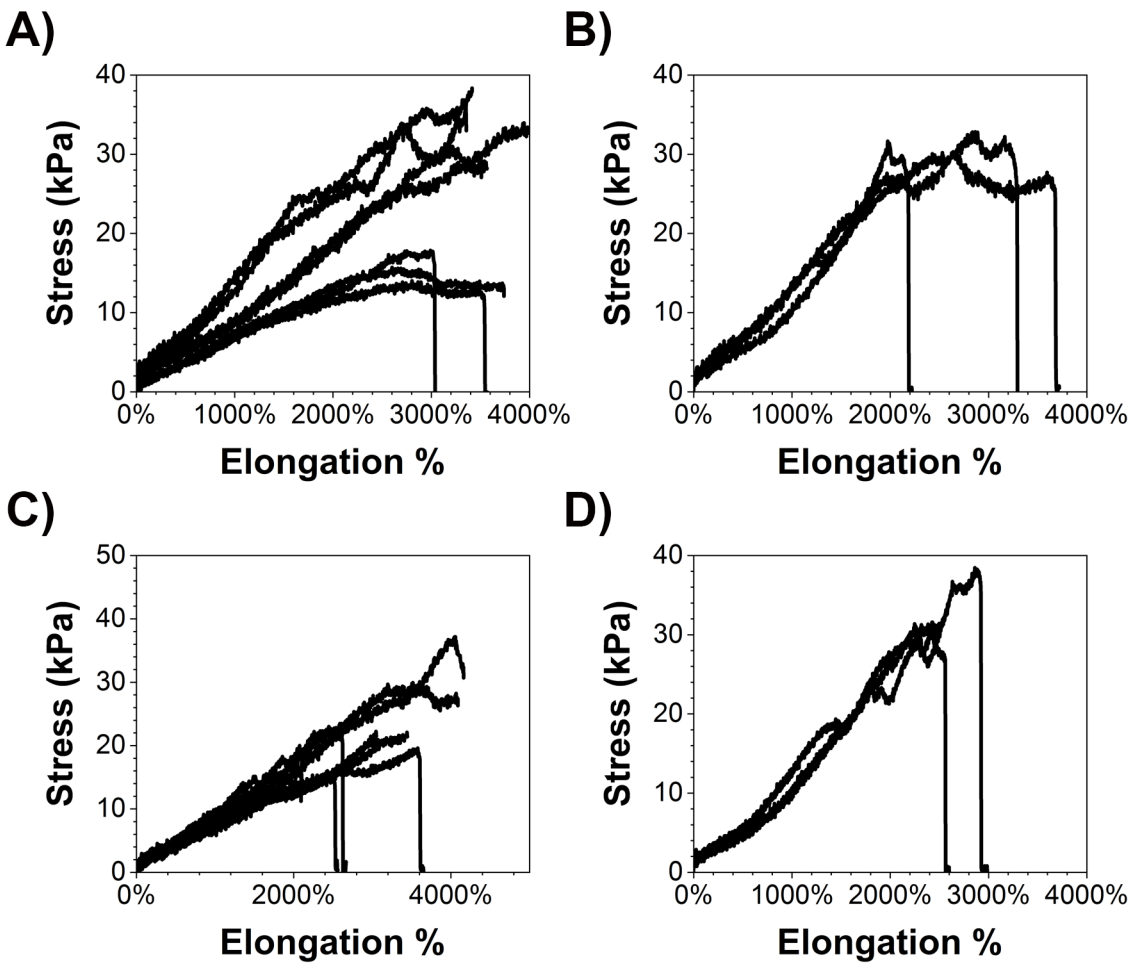

Figure S10: Stress versus elongation percentage (normalized elongation length) for Na-alginate/PAAm hydrogels with (A) 0.1 nM MUA AuNRs and (B) 0.5 nM MUA AuNRs (C) 1.0 nM MUA AuNRs (D) 2.0 nM MUA AuNRs.

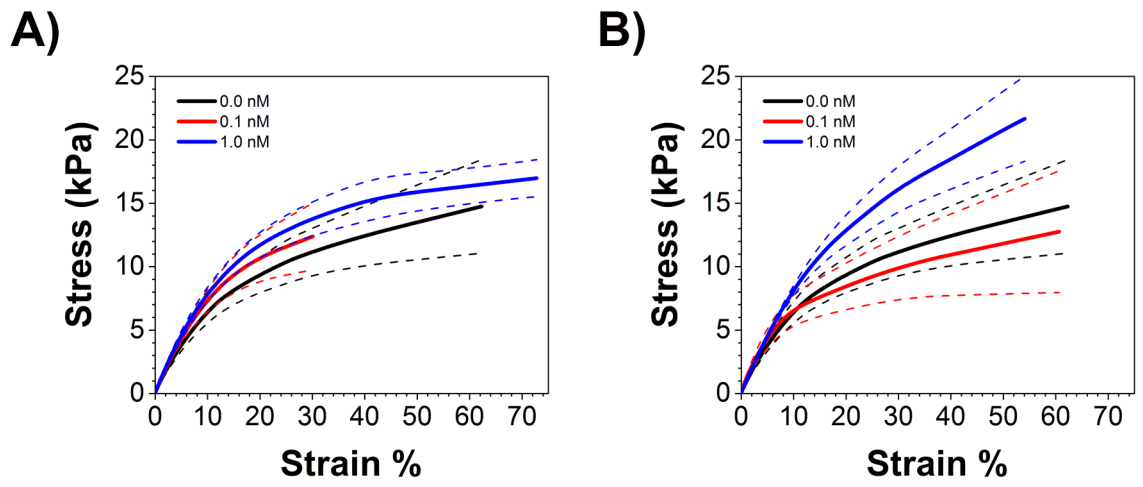

Figure S11: Averaged stress versus strain curves obtained from DMA for (A) PEG-SH AuNR Ca-alginate/PAAm hydrogels and (B) MUA AuNR Ca-alginate/PAAm hydrogels. The solid line is the average of multiple curves and the dotted line is the standard error in the average curve.

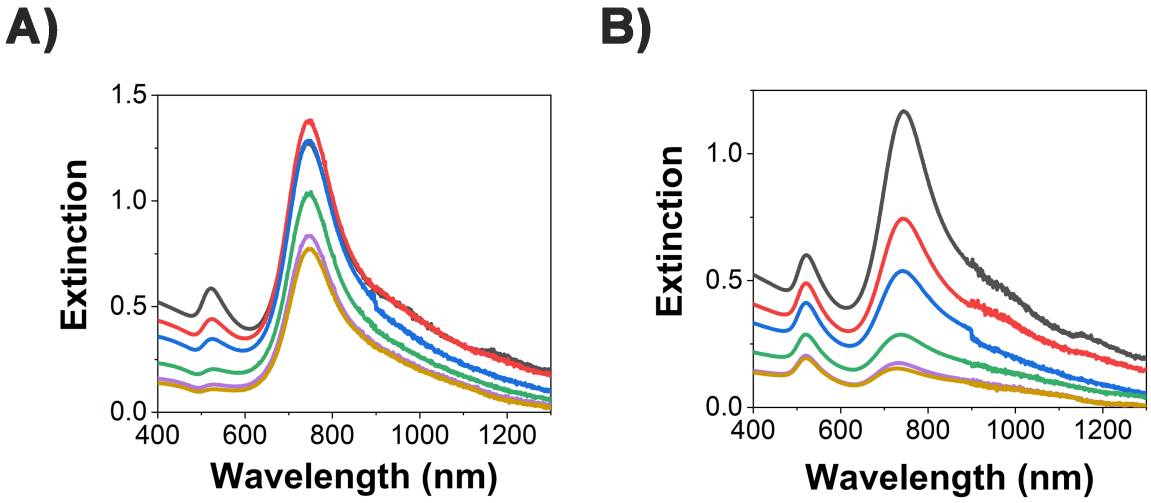

Figure S12: Polarized UV-vis extinction spectra of Na-alginate/PAAm hydrogels with 1.0 nM CTAB AuNRs stretched varying amounts. (A) Polarized parallel to the stretch direction (0°). (B) Polarized perpendicular to the stretch direction (90°). Colors represent different elongation percentages in relation to the initial length of the hydrogel (black: 0%, red: 100%, blue: 200%, green: 300%, purple: 400%, and gold: 500%).

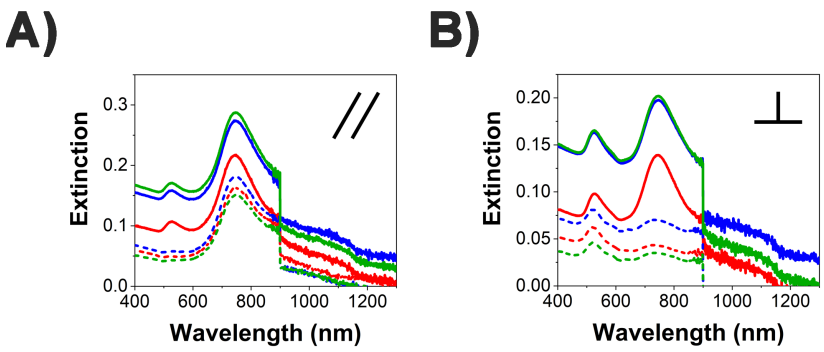

Figure S13: Polarized UV-vis extinction spectra of a Na-alginate/PAAm hydrogel with 0.1 nM CTAB AuNRs. (A) Polarized parallel to the stretch direction (0°). (B) Polarized perpendicular to the stretch direction (90°). Colors represent different stretch/relax cycles (red: 1st, blue: 2nd, green: 3rd). Solid lines represent the spectra of a relaxed hydrogel and dotted lines represent the spectra of the hydrogel stretched 500% its initial length.

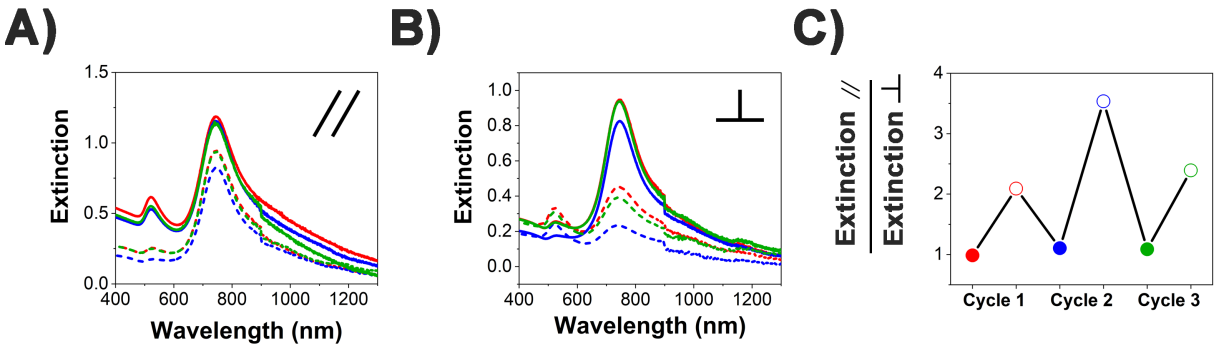

Figure S14: Polarized UV-vis extinction spectra of a Na-alginate/PAAm hydrogel with 1.0 nM CTAB AuNRs. (A) Polarized parallel to the stretch direction (0°). (B) Polarized perpendicular to the stretch direction (90°). Colors represent different stretch/relax cycles (red: 1st, blue: 2nd, green: 3rd). Solid lines represent the spectra of a relaxed hydrogel and dotted lines represent the spectra of the hydrogel stretched 500% its initial length. (C) Plot of the ratio of the extinction at the longitudinal plasmon for light polarized parallel over light polarized perpendicular for each stretch/relax cycle. Colors represent different stretch/relax cycles, while filled circles represent the ratio the relaxed hydrogel, and open circles represent the ratio of the stretched hydrogel.

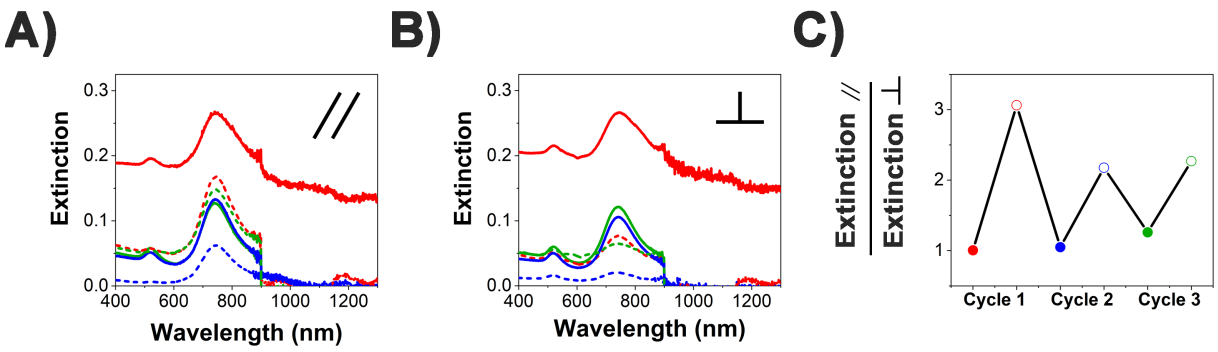

Figure S15: Polarized UV-vis extinction spectra of a Na-alginate/PAAm hydrogel with 0.1 nM PEG-SH AuNRs. (A) Polarized parallel to the stretch direction (0°). (B) Polarized perpendicular to the stretch direction (90°). Colors represent different stretch/relax cycles (red: 1st, blue: 2nd, green: 3rd). Solid lines represent the spectra of a relaxed hydrogel and dotted lines represent the spectra of the hydrogel stretched 500% its initial length. (C) Plot of the ratio of the extinction at the longitudinal plasmon for light polarized parallel over light polarized perpendicular for each stretch/relax cycle. Colors represent different stretch/relax cycles, while filled circles represent the ratio the relaxed hydrogel, and open circles represent the ratio of the stretched hydrogel.

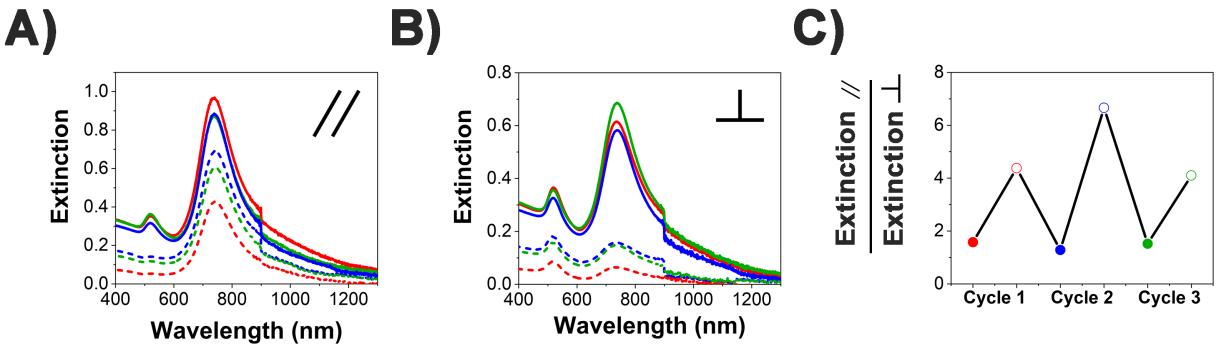

Figure S16: Polarized UV-vis extinction spectra of a Na-alginate/PAAm hydrogel with 1.0 nM PEG-SH AuNRs. (A) Polarized parallel to the stretch direction (0°). (B) Polarized perpendicular to the stretch direction (90°). Colors represent different stretch/relax cycles (red: 1st, blue: 2nd, green: 3rd). Solid lines represent the spectra of a relaxed hydrogel and dotted lines represent the spectra of the hydrogel stretched 500% its initial length. (C) Plot of the ratio of the extinction at the longitudinal plasmon for light polarized parallel over light polarized perpendicular for each stretch/relax cycle. Colors represent different stretch/relax cycles, while filled circles represent the ratio the relaxed hydrogel, and open circles represent the ratio of the stretched hydrogel.

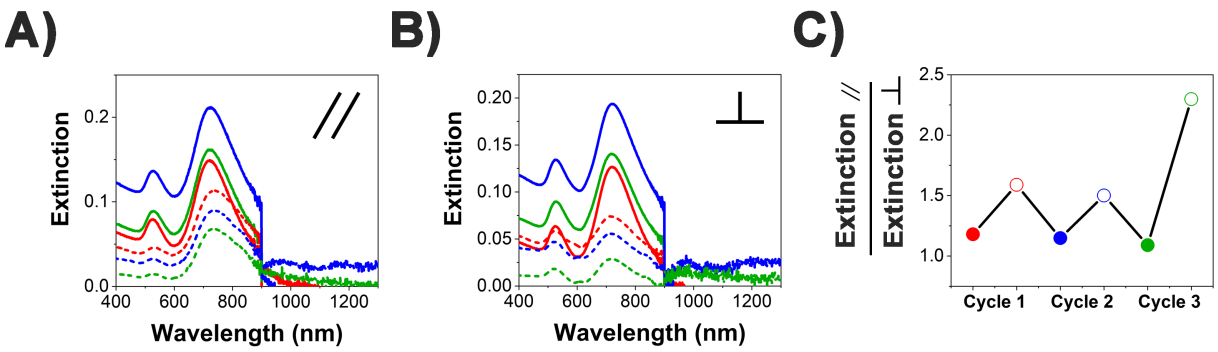

Figure S17: Polarized UV-vis extinction spectra of a Na-alginate/PAAm hydrogel with 0.1 nM MUA AuNRs. (A) Polarized parallel to the stretch direction (0°). (B) Polarized perpendicular to the stretch direction (90°). Colors represent different stretch/relax cycles (red: 1st, blue: 2nd, green: 3rd). Solid lines represent the spectra of a relaxed hydrogel and dotted lines represent the spectra of the hydrogel stretched 500% its initial length. (C) Plot of the ratio of the extinction at the longitudinal plasmon for light polarized parallel over light polarized perpendicular for each stretch/relax cycle. Colors represent different stretch/relax cycles, while filled circles represent the ratio the relaxed hydrogel, and open circles represent the ratio of the stretched hydrogel.

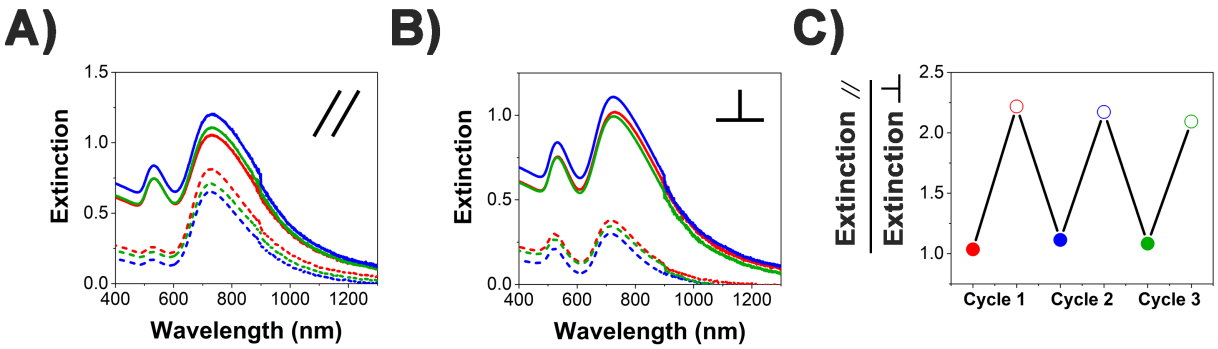

Figure S18: Polarized UV-vis extinction spectra of a Na-alginate/PAAm hydrogel with 1.0 nM MUA AuNRs. (A) Polarized parallel to the stretch direction (0°). (B) Polarized perpendicular to the stretch direction (90°). Colors represent different stretch/relax cycles (red: 1st, blue: 2nd, green: 3rd). Solid lines represent the spectra of a relaxed hydrogel and dotted lines represent the spectra of the hydrogel stretched 500% its initial length. (C) Plot of the ratio of the extinction at the longitudinal plasmon for light polarized parallel over light polarized perpendicular for each stretch/relax cycle. Colors represent different stretch/relax cycles, while filled circles represent the ratio the relaxed hydrogel, and open circles represent the ratio of the stretched hydrogel.

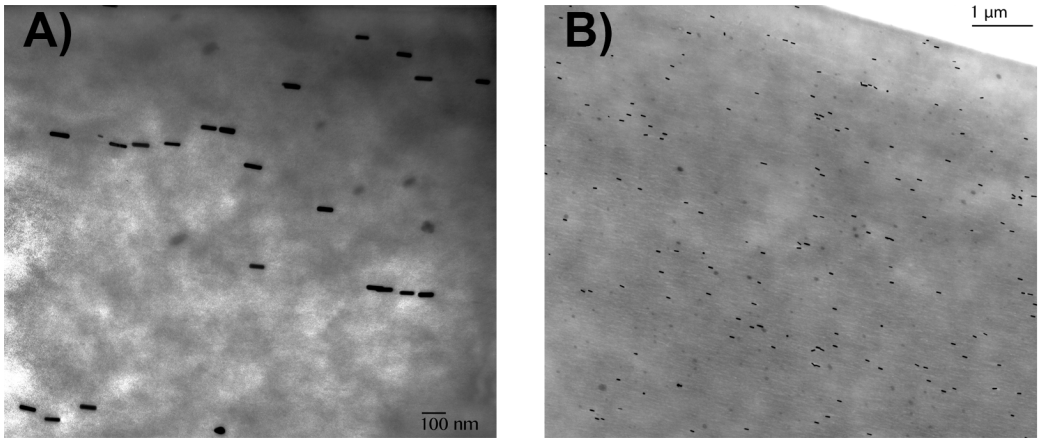

Figure S19: TEM images of AuNRs aligned in a stretched 2.0 nM PEG-SH Na-alginate/PAAm hydrogel at different magnifications (A) 40,000x and (B) 10,000x.

3. References

(1) Yang, C. H.; Wang, M. X.; Haider, H.; Yang, J. H.; Sun, J.-Y.; Chen, Y. M.; Zhou, J.; Suo, Z. Strengthening Alginate/Polyacrylamide Hydrogels Using Various Multivalent Cations. *ACS Appl. Mater. Interfaces* **2013**, *5* (21), 10418–10422.

(2) Sun, J.-Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. Highly Stretchable and Tough Hydrogels. *Nature* **2012**, *489* (7414), 133–136.