

Supporting Information

Light-triggered programming of hydrogel properties using sleeping photoactive polymer nanoparticles

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1. Additional experimental details

Writing/erasing patterns on PAAm/MBA-PBG(2) hydrogel film

Dyes were dissolved in water to reach concentration of 0.04 wt%. The UV irradiated samples (see Fig. 3) were left in 0.01 M HCl for 10 min then soaked in dye solution for 5 min followed by washing with water for 5 min.

Adsorption of oppositely charged particles onto PAAm/MBA-PBG(2) hydrogel

After UV irradiation, the PAAm/MBA-PBG(2) hydrogel film was soaked in 0.01 M HCl for 10 min then rinsed quickly with water. The sample was then placed in a gold nanoparticle (GNP) dispersion for 24 h and subsequently washed with water for 30 min.

The GNP dispersion was synthesised in-house according to the literature.¹ Briefly, HAuCl₄·3H₂O solution (95 ml, 0.25 mM) in a three-necked flask equipped with a reflux condenser was heated to ~ 100 °C and stirred vigorously. Then, Na₃Cit·2H₂O solution (5.0 mL, 19 mM) was rapidly added. The reaction was allowed to proceed for 40 min before cooling to room temperature. The final dispersion was collected and stored at 4 °C. The GNPs had a number-average diameter of 15 nm based on TEM analysis.

Post-polymerization within PAAm/MBA-PBG(4) network

For post-polymerization of 2-hydroxyethyl methacrylate (HEMA), the PAAm/MBA-PBG(4) gel was UV-irradiated for 1 h and then soaked in aqueous HCl solution (0.010 M) for 10 min. The gel was then placed in aqueous APS solution (1.0 mL, 6 mM) for 5 min. After this period the gel was washed with aqueous HCl (0.010 M) three times within 21 min (at 7 min intervals). A mixture of *N-N'*-methylene bisacrylamide (MBA, 0.0014g, 0.090 mmol) in HEMA (1.0 g, 7.1 mmol) was prepared and added to the vial containing the sample. The vial was purged with Ar, sealed and left in an oven at 80 °C. After 15 min the samples were removed and placed in water at 50 °C to swell.

The following procedure was employed for post-polymerization of polypyrrole. The hydrogel film was acid treated by soaking in aqueous HCl solution (0.10 M) for 10 min before being placed in aqueous FeCl₃ solution (1.0 mL, 0.1 wt%). After 5 min the FeCl₃ solution was removed and the sample was washed with HCl (0.010 M) three times within 15 min (5 min intervals). A mixture of pyrrole (0.0150 g, 0.020 mmol) and p-toluenesulfonic acid monohydrate (0.010 g, 0.058 mmol) in water (1 mL) was prepared and purged with Ar and hydrogel film was left in this mixture for 1 h. After this period the sample was washed consecutively with water to remove unreacted monomer and reagents.

Hydrogels containing PAG and PBG particles

PAAm/MBA-PAG(1)/PBG(1) was prepared as follows and used for rheology measurements. AAm (0.0220 g, 0.31 mmol) and MBA (0.70 mg, 0.045 mmol) was dissolved in a mixture of PAG/PBG dispersion (500 µL) with volume ratio of 1:1 and solid content of 2.0 wt%. Then TEMED solution (11 µL, 0.24 M) and APS (15 µL, 0.23 M) was added. In order to prepare disc-like samples for rheological measurement an O-ring with internal diameter of 20 mm and height of 2 mm was sandwiched between two glass slides, and used as a mold.

The PAAm/MBA-PAG(3)/PBG(3) hydrogel film used for the actuator was prepared as follows. AAm

(0.030 g, 0.42 mmol) and MBA (0.7 mg, 0.045 mmol) was dissolved in 500 μL mixture of PAG/PBG dispersion with volume ratio of 1:1 and a concentration of 6 wt%. Then TEMED solution (17 μL , 0.24 M) and APS (19 μL , 0.23 M) was added and the precursor was injected into a mold as described in section Section 2.5 of the main paper. Both the hydrogel film and disc were cured in an oven at 50 $^{\circ}\text{C}$ for 10 min.

UV-irradiation of PAAm/MBA-PAG/PBG hydrogel

Both the hydrogel film and disc were initially irradiated by UV light (300 nm) for 1 h and then they were irradiated for a further 1 h. The actuator half of hydrogel film was masked with Al foil. During UV irradiation samples were kept wet by dripping water on the surface of the hydrogel as described in Section 2.4 of the main paper.

Hydrogel actuator and grabber preparation

For the actuator and grabber the hydrogel film (from above) was cut into a rectangular shape for actuator and a cross shape for the grabber, respectively, and then UV-irradiated and left in pH adjusted water. Aqueous NaOH (0.01 M) and HCl (0.01 M) solutions were used to adjust the pH. Universal pH indicator was used to visualize the pH change.

2. Supporting Movies

Movie S1. Illustration of electrical conductivity in two different regions of PAAm/MBA-PBG(4) hydrogel film. Post-polymerization of pyrrole caused an increase in electrical conductivity in the masked area.

Movie S2. Gripper response to pH. The gripper is grabbing a low density object (paraffin colored in pink for better visualization). The initial pH (time 00:00 mm:ss) was 4.8 as the universal pH indicator had orange color. The pH was increased to 10 at time 01:00 by addition of NaOH 0.1 M which caused color of pH indicator turned pink. The size is shown in Figure 6b.

3. Supporting Figures and Discussion

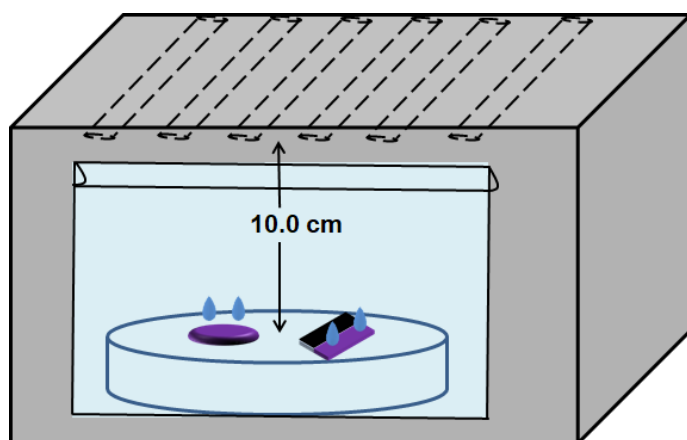


Figure S1. Depiction of the experimental geometry used for the UV-irradiation of the gels. Water was added to the top of the irradiated gels to keep them hydrated and prevent excessive heating. The black region for the system on the right-hand side depicts a photomask.

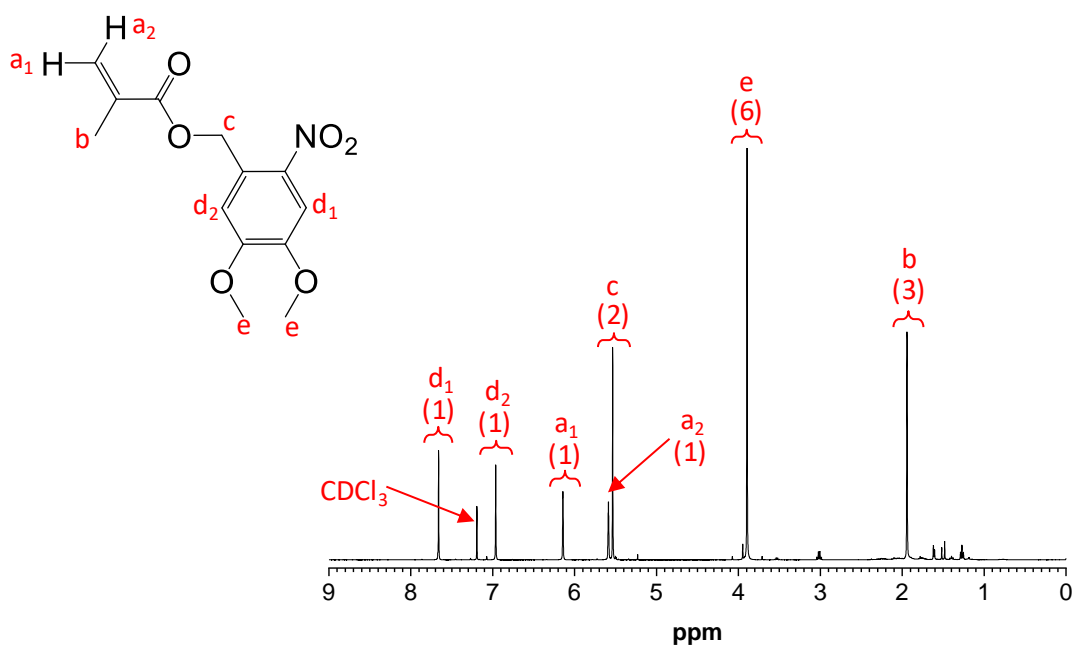


Figure S2. ^1H NMR spectrum of DMNBM. CDCl_3 was used as solvent.

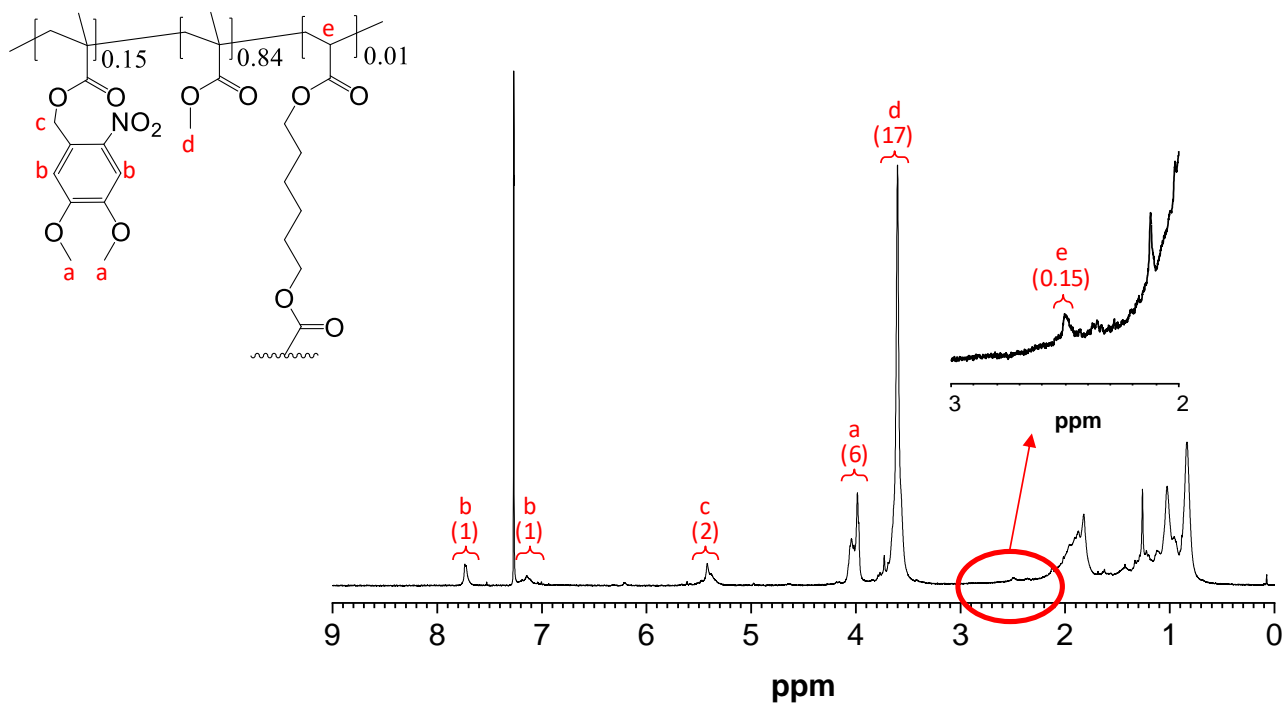


Figure S3. ^1H NMR spectrum of PAG particles. CDCl_3 was used as solvent. Peaks that were used for compositional analysis are identified.

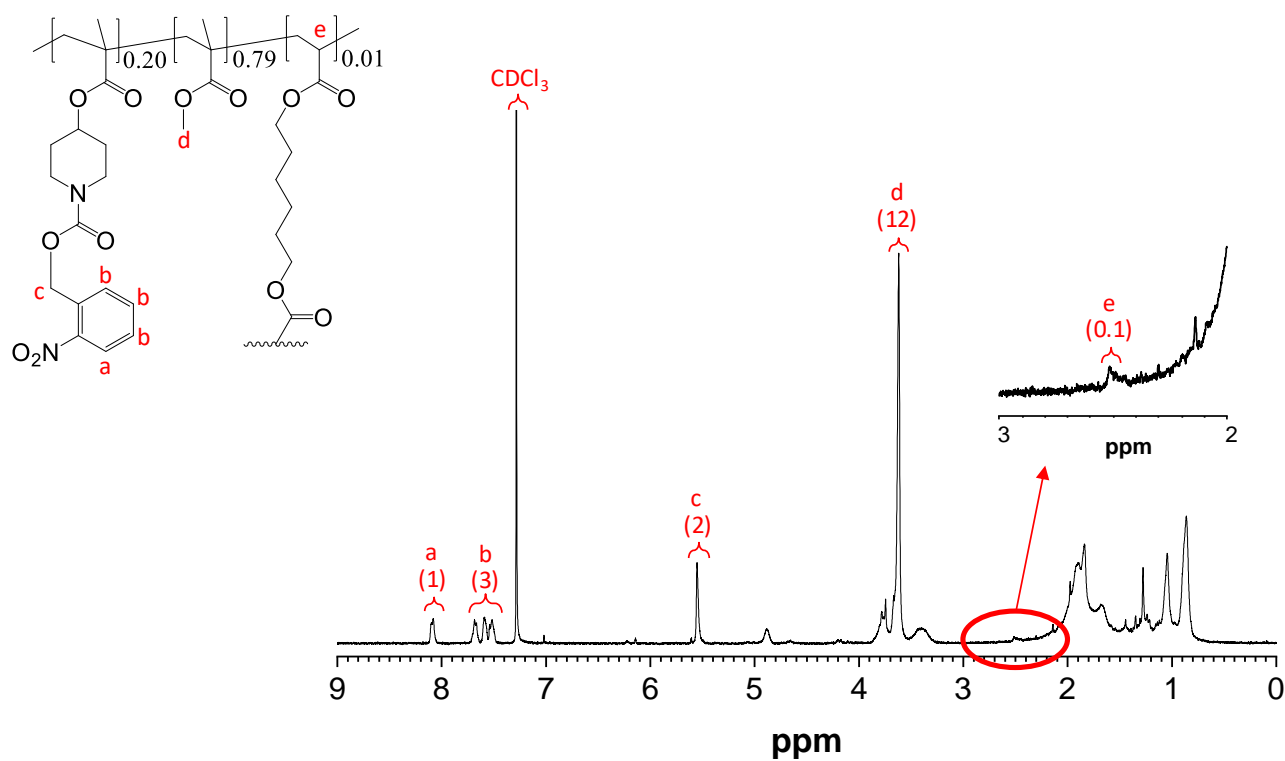


Figure S4. ^1H NMR spectrum of PBG particles. CDCl_3 was used as solvent. Peaks that were used for compositional analysis are identified.

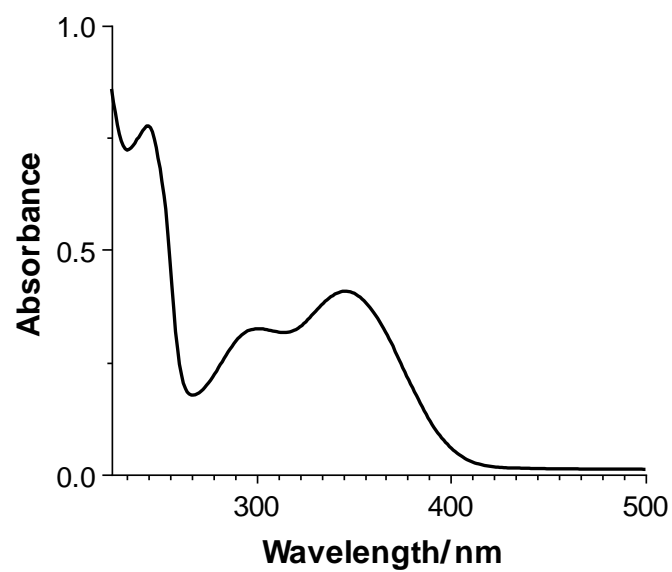


Figure S5. UV-visible spectrum for a 0.2 wt.% PAG dispersion.

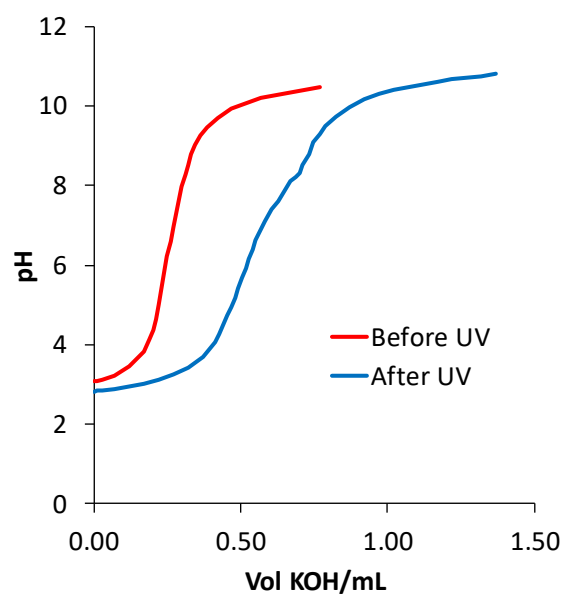


Figure S6. Potentiometric titration for PAG dispersion before and after UV exposure. For the latter the first and second inflection points belong to excess HCl and PAG particles respectively. The pK_a of PAG particles was calculated as 7.4.

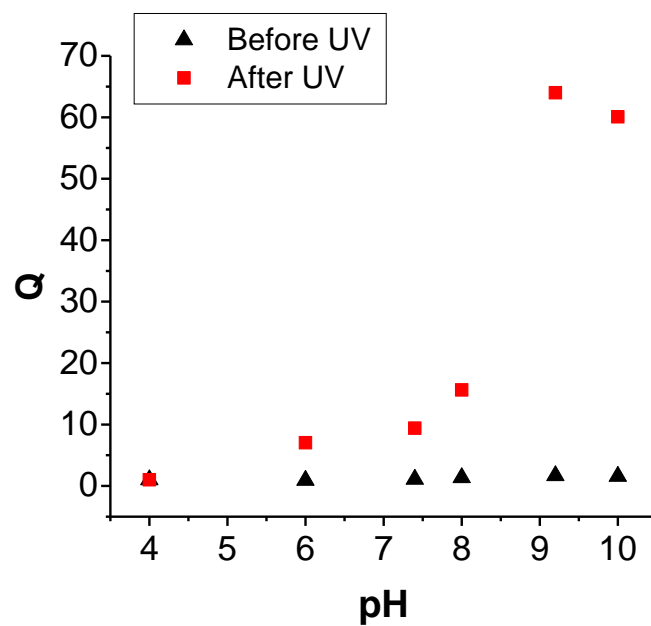


Figure S7. Volume swelling ratio at varied pH values for PAG nanoparticles before and after UV-irradiation.

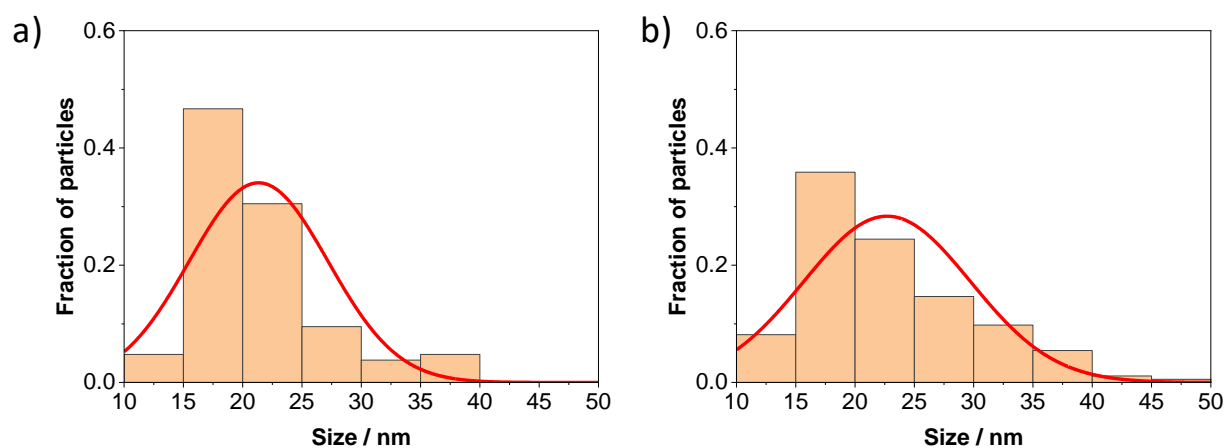


Figure S8. (a) and (b) show TEM size distribution of PAG particles before and after UV irradiation respectively.

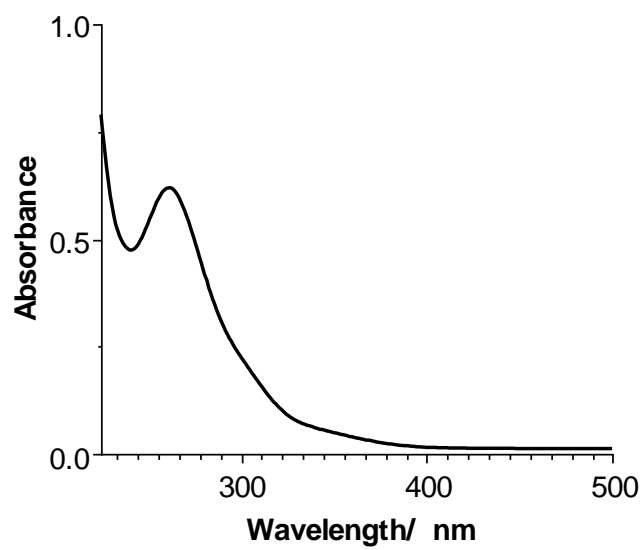


Figure S9. UV-visible spectrum for a 0.2 wt.% PBG dispersion

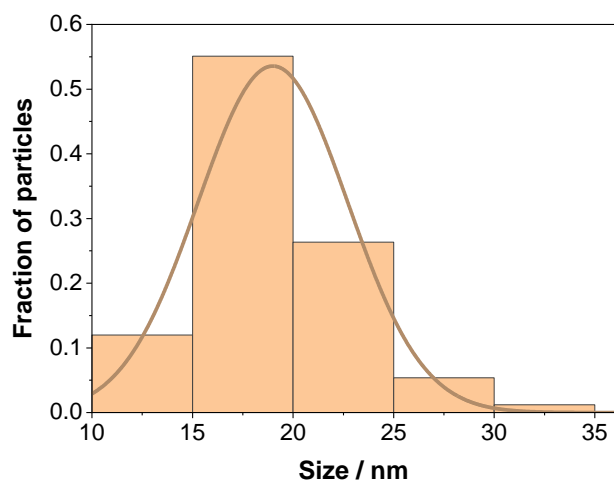


Figure S10. TEM size distribution of PBG particles before UV irradiation. The size distribution is not shown after UV irradiation because aggregation occurred as shown in Figure 1h.

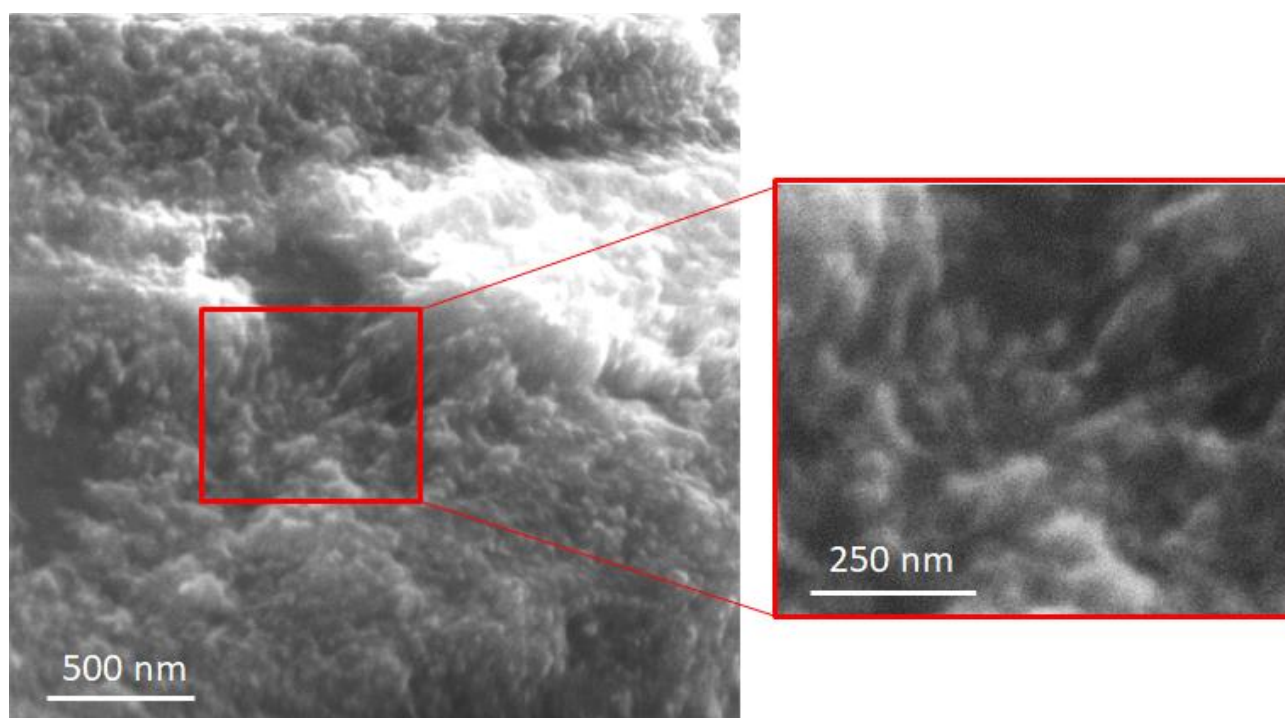


Figure S11. SEM images of freeze-dried PAAm/MBA-PAG(4) hydrogel.

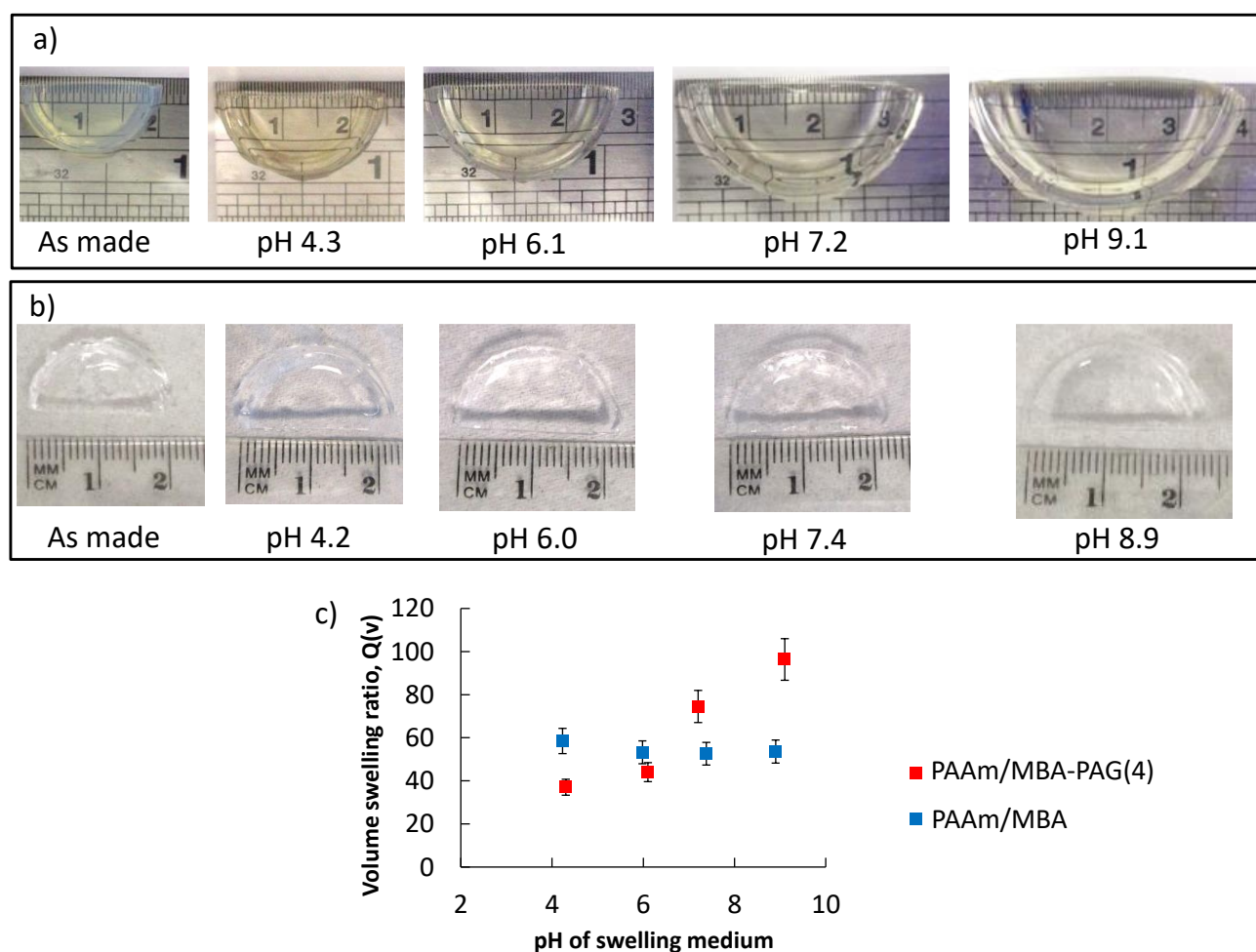


Figure S12. Photo-triggered transformation to a pH-responsive hydrogel for PAAm/MBA-PAG(4) is illustrated in (a). A PAAm/MBA control hydrogel is shown in (b). (c) shows the volume swelling ratio vs. pH for PAAm/MBA-PAG(4) and PAAm/MBA hydrogels.

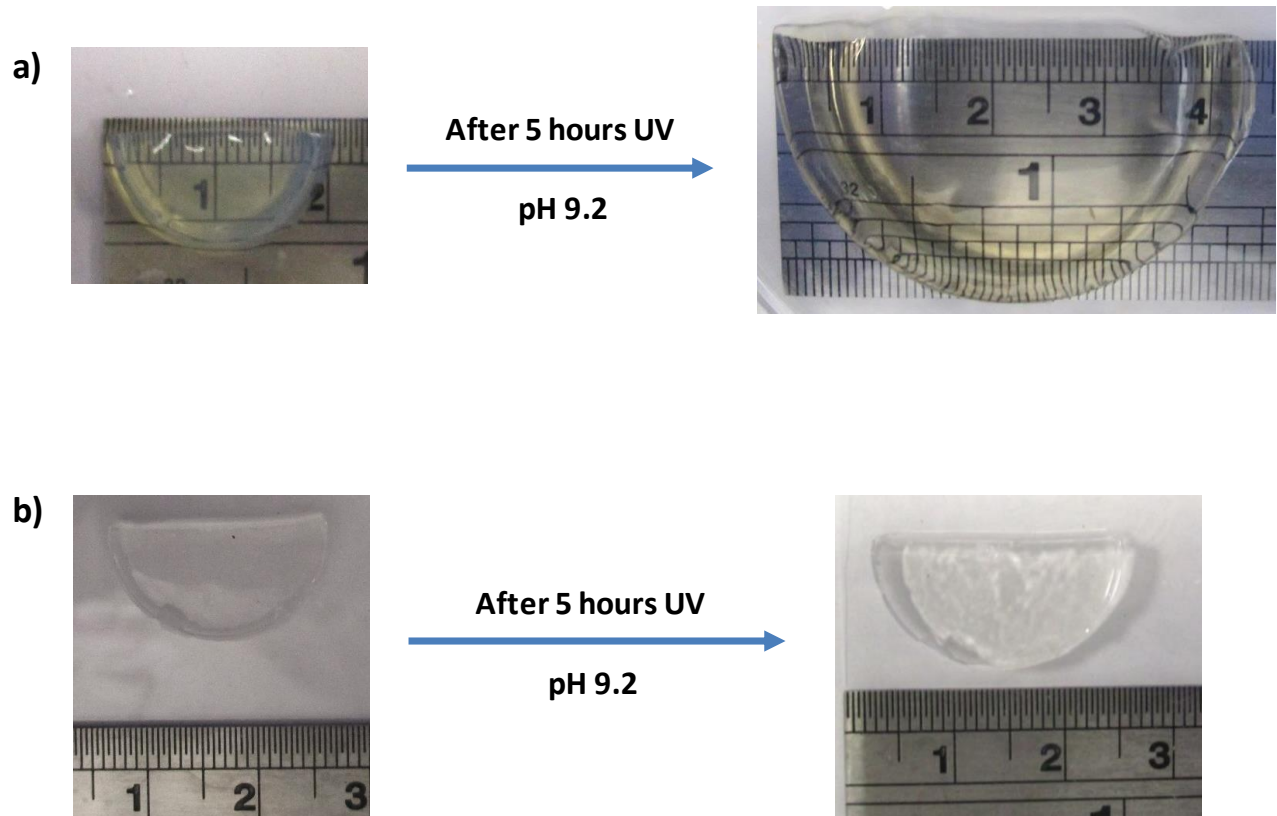


Figure S13. Photo-triggered swelling of PEGMA/PEGDA-PAG(4) hydrogel (a) and PEGMA/PEGDA as control.

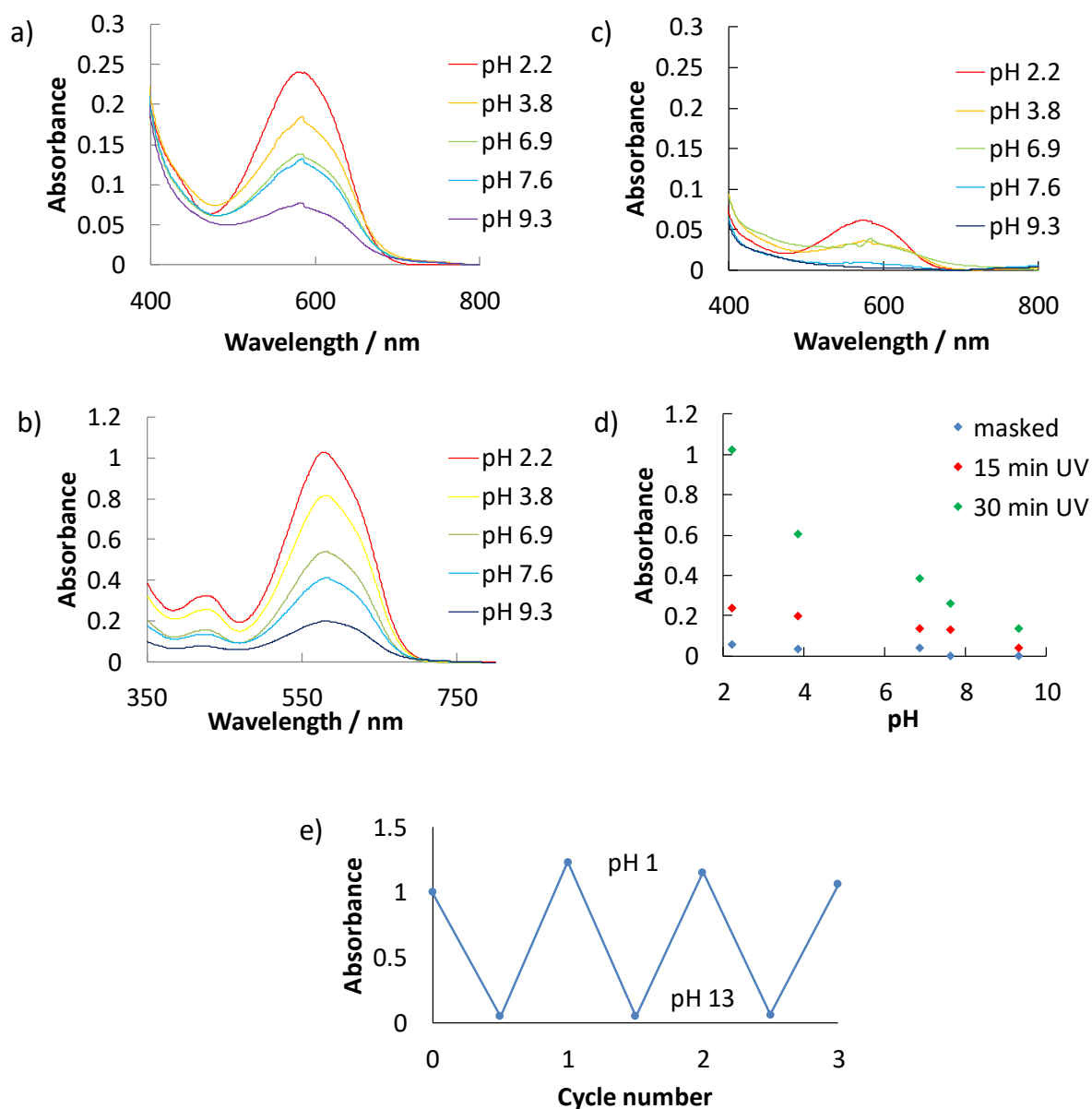


Figure S14. UV-visible measurements at different pH values for PAAm/MBA-PBG(2) hydrogel soaked in Brilliant Black BN dye. (a) and (b) were exposed to UV light 300 nm for 15 and 30 min respectively. (c) shows the control gel which was PAAm/MBA-PBG(2) and was photomasked during UV irradiation. (d) shows the maximum absorbance (580 nm) vs pH for (a), (b) and (c). Cyclic absorption at λ_{max} (580 nm) for dyed PAAm/MBA-PBG(2) at different pH values is shown in (e).

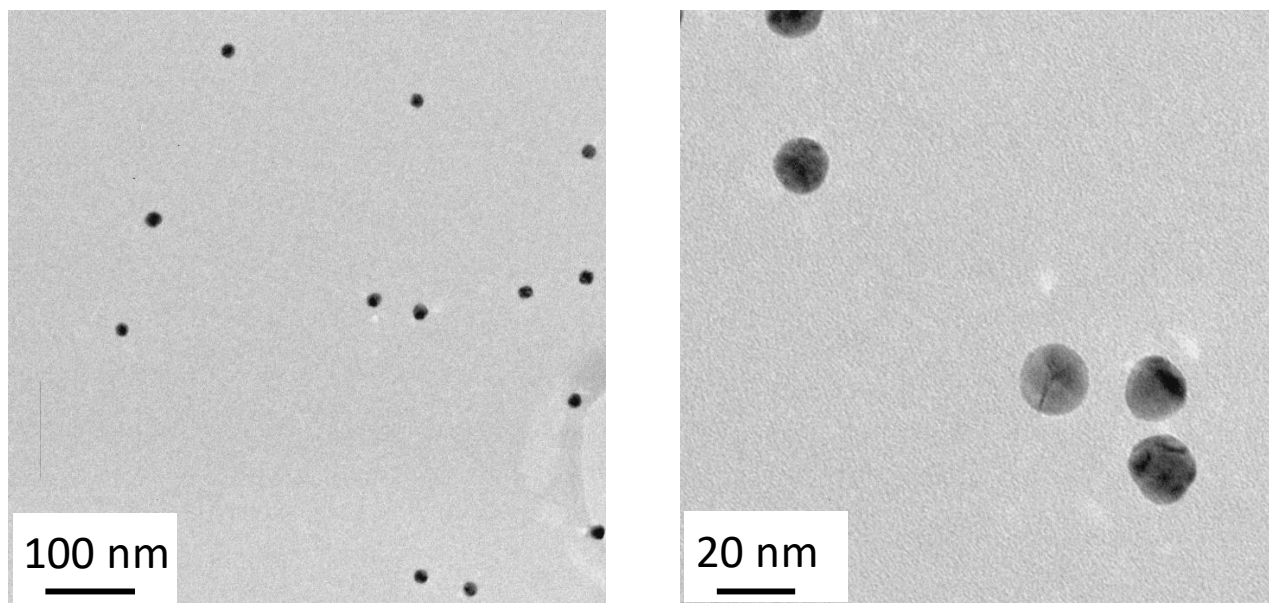


Figure S15. TEM images of GNPs at different magnifications

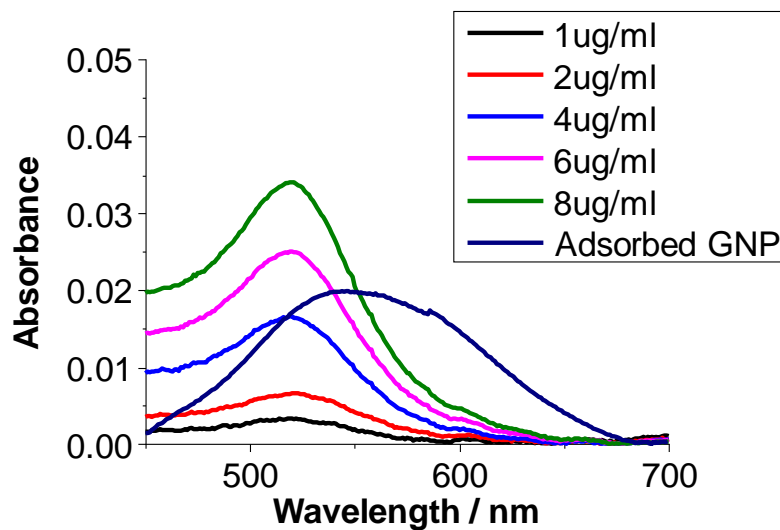


Figure S16. Corrected UV/vis spectrum of GNP coated PAAm/MBA-PBG(2) hydrogel film compared with spectra of pure GNPs at different concentrations. Formation of GNP aggregates is the reason for the red shift of λ_{max} observed for GNP-coated PAAm/MBA-PBG(2).

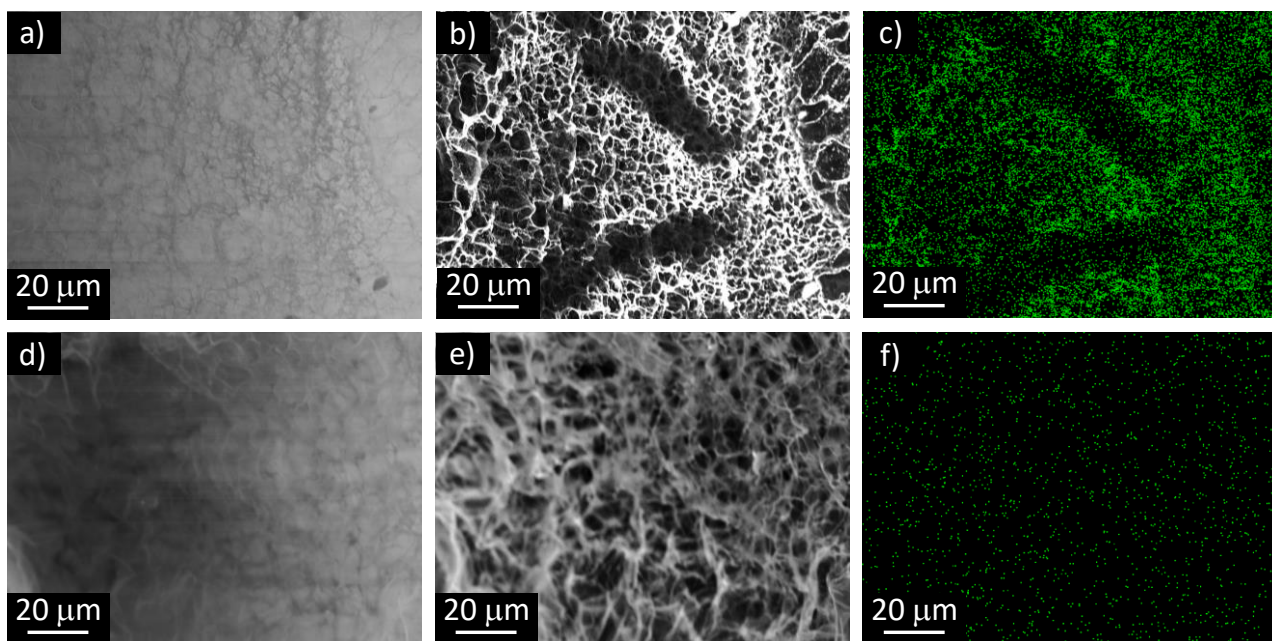


Figure S17. Adsorption of negatively charged GNPs onto UV-irradiated PAAm/MBA-PBG(2). (a), (b) and (c) are SEM images of UV-irradiated and GNP-coated area obtained by secondary electron, back scatter and energy-dispersive X-ray detector respectively. The green colour indicates gold signal. The gaps appeared in (b) and (c) are surface features. The images shown in (d), (e) and (f) were obtained using the same conditions as were used for (a), (b) and (c), respectively. However, they were captured from non-UV-irradiated areas.

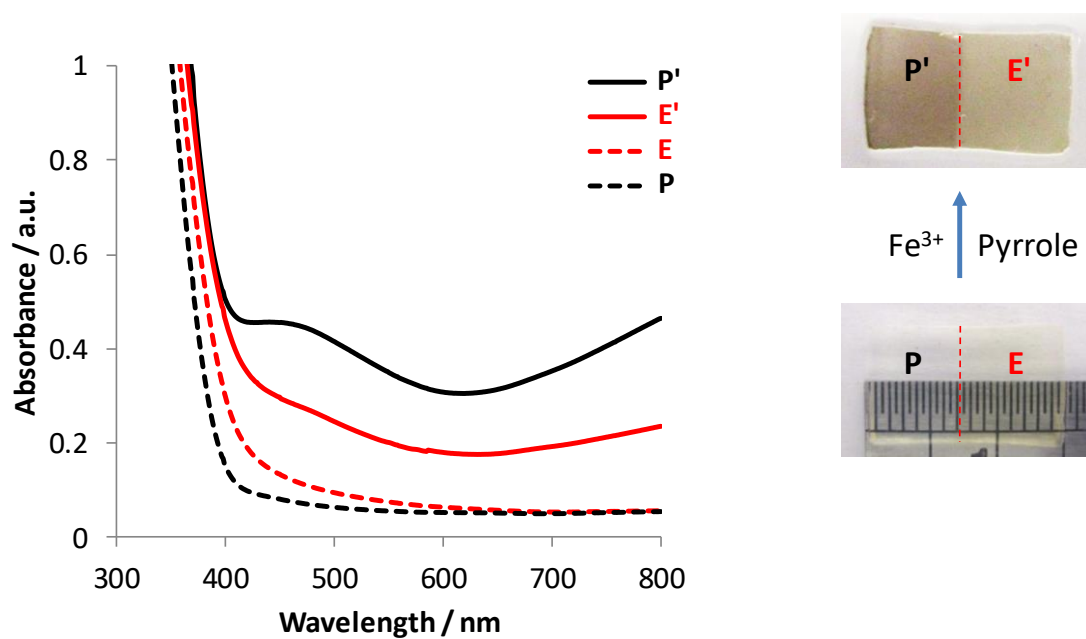


Figure S18. UV-visible spectra for PAAm/MBA-PBG(4) hydrogel. The digital images show the hydrogel film used for this measurement and the corresponding area for each curve is indicated. P is the photo-masked area while E is UV exposed area. P' and E' correspond to P and E after addition of Fe³⁺ and pyrrole. The maximum at 460 nm is due to polypyrrole.

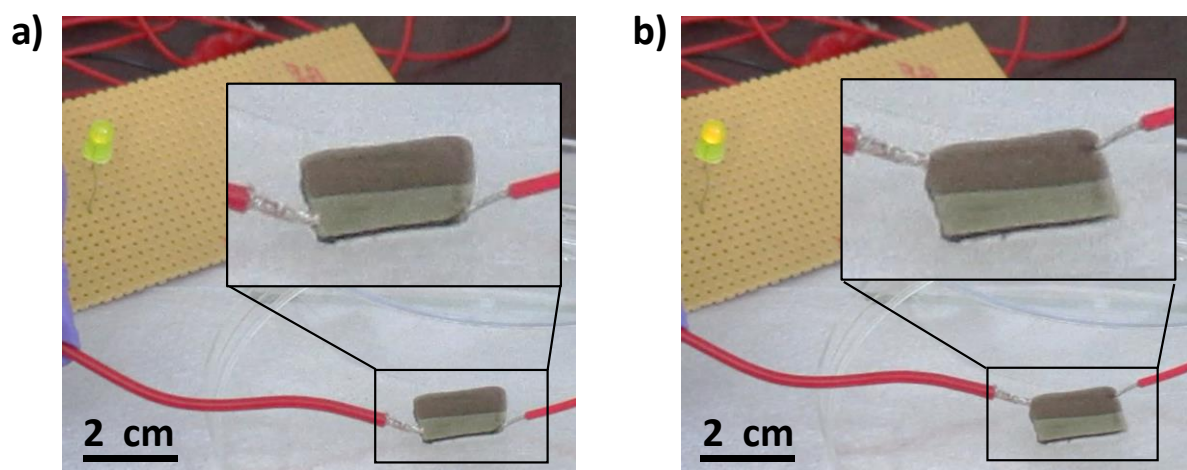


Figure S19. An LED circuit was used to demonstrate the difference in electrical conductivity of UV-irradiated and masked regions after space-selective post-polymerization of pyrrole in PAAm/MBA-PBG(4) hydrogel. (a) shows low electrical conductivity in the UV irradiated region. Higher electrical conductivity was observed in the masked area due to formation of polypyrrole (b). See also Movie S1.

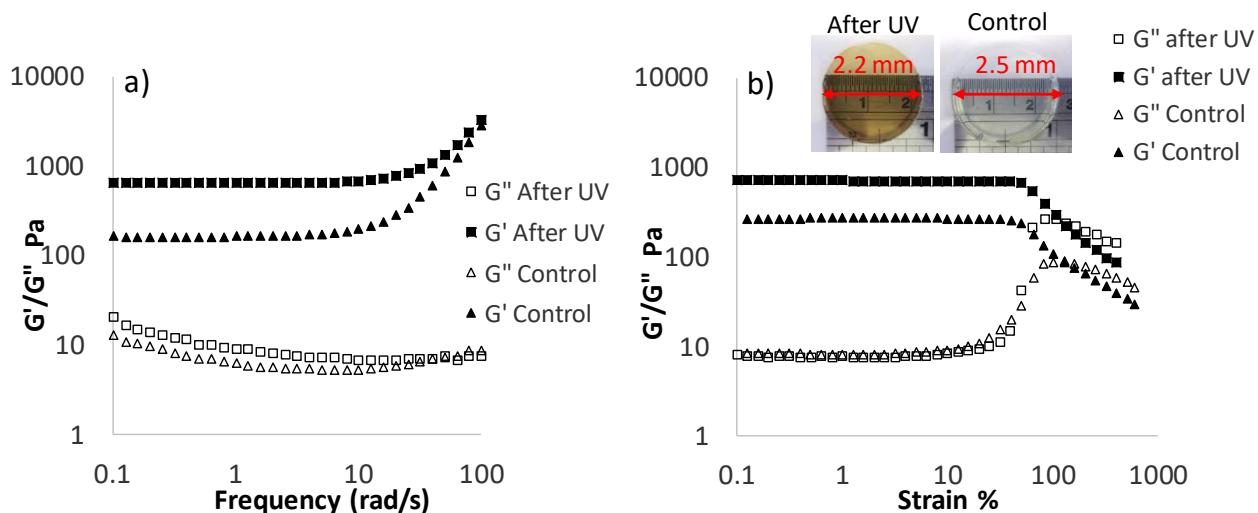


Figure S20. Rheology data for PAAm/MBA-PAG(1)/PBG(1) hydrogel. G' and G'' are the storage and loss modulus values, respectively. (a) and (b) show frequency-sweep and strain-sweep data before and after UV-irradiation, respectively. After UV-irradiation, both samples were left in water to swell for 24 h. The UV-irradiated sample at pH 5 swelled less and showed higher storage modulus values.

Assessment of light penetration within the gels

The absorbance at 300 nm (A_{300}) is used to assess light penetration in the gels because that wavelength was employed for the irradiation of most of the gels and the actuator (PAAm/MBA-PAG(3)/PBG(3)). We first consider light absorption by the nanoparticles. The A_{300} values obtained from the spectra of the PAG and PBG dispersions in figures S5 and S9, respectively, are 0.32 and 0.23. Assuming Beer's law applies the extinction coefficients at 300 nm (ϵ_{300}) for the PAG and PBG particles can be estimated as $0.16\%^{-1} \text{ mm}^{-1}$ and $0.12\%^{-1} \text{ mm}^{-1}$, respectively. Because these values are reasonably close it follows that the nature of these particles does not have a major effect on the absorption of light.

We now consider the gels. The value of A_{300} for the PAAm/MBA-PBG(2) at pH 9.3 (from Figure S14c) was 0.55. The light penetration through this gel film can be assessed using:

$$\frac{I(x)}{I(0)} = e^{-\alpha x} \quad (\text{S1})$$

where $I(x)$ and $I(0)$ and α are the light intensity at a distance x , incident light intensity and the film absorption coefficient (mm^{-1}), respectively. The value of α at 300 nm can be calculated using A_{300} ($= \log_{10}(I(0)/I(t))$, where t = the film thickness) and $\alpha = 2.303(A_{300}/x)$. The absorption depth (α^{-1}), is the penetration depth required for the light intensity to fall to 37% of the incident value. Using a gel film thickness of 1 mm, $\alpha^{-1} \sim 0.8 \text{ mm}$. Hence, there was good light penetration for this gel.

The PAAm/MBA-PAG(3)/PBG(3) actuator gel had a total particle concentration that was three times that for the PAAm/MBA-PBG(2) gel. We therefore expect a significantly higher α value and lower α^{-1} . Indeed, the experimental image from Fig. 6a shows that most of the colour developed within the top 130 μm of the surface irradiated which is consistent with this expectation. Our experimental data show that increasing the particle concentration decreases the light penetration for these gels.

4. Supporting Tables

Table S1. Physical and chemical characteristics of PAG and PBG nanoparticles

	DMNBM [mol%]	NPMPC [mol%]	MMA [mol%]	HDODA [mol%]	pK _a ^{a)}	d _z (pH 4) [nm] ^{b)}	d _z (pH4 ,UV) [nm] ^{c)}	d _{TEM} [nm] ^{d)}	d _{TEM} (UV) [nm] ^{e)}
PAG	15	-	84	1.0	7.4	36	42	21 ± 6	23 ± 7
PBG	-	20	79	1.0	-	21	-	18 ± 4	-

a) Apparent pK_a value; *b)* z-average diameter measured by DLS at pH 5.4; *c)* z-average diameter measured by DLS at pH 5.4 after UV-irradiation; *d)* TEM number-average diameter; *e)* TEM number-average diameter after UV irradiation. The ± value is the standard deviation.

Table S2. Chemical composition of hydrogels

Code	AAM [wt%]	MBA [wt%]	PEGMA [wt%]	PEGDA [wt%]	PAG [wt%]	PBG [wt%]	TSC of hydrogel ^{a)} [%]
PAAm/MBA-PAG(4)	49	2.0	-	-	49	-	8.0
PAAm/MBA	98	2.0	-	-	-	-	4.0
PAAm/MBA-PBG(2)	65	2.0	-	-	-	33	6.0
PAAm/MBA-PBG(4)	49	2.0	-	-	-	49	8.0
PAAm/MBA-PAG(1)/PBG(1)	66	2.0	-	-	16	16	6.0
PAAm/MBA-PAG(3)/PBG(3)	49	1.0	-	-	25	25	12
PEGMA/PEGDA-PAG(4)	-	-	75	2.0	23	-	17

^{a)} Total solid content including polymer network and nanoparticles

Reference

(1) Turkevich, J.; Stevenson, P. C.; Hillier, J., A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discuss. Faraday Soc.* **1951**, 11, 55-75.