High Modulus Carbon Nitride Reinforced Hydrogels via an Ethylene Glycol Co-solvent Route

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Experimental

Preparation of g-CN: 1.0 g of cyanuric acid (C) and 1.0 g of melamine (M) were mixed with 40 mL distilled water and shaked overnight. After centrifugation at 6000 rpm for 10 minutes, a precipitate was dried at 60 $^{\circ}$C under vacuum overnight. The dried product was transferred into a capped crucible and put into N_2 protected oven at 550 °C for 4 hours, with a heating rate of 2.3 °C /min^{-1}. CM must be well grinded prior to use.

Synthesis of Reference DMA Hydrogel with EG: 4.5 g of deionized water, 4.5 g ethylene glycol (EG), 0.8 g DMA and 0.06 g MBA crosslinker were mixed in a 20 mL glass vial. 0.1 g AscA was added to the mixture and mixed until dissolution. Addition of 1 mL 30% hydrogen peroxide was utilized to start the radical formation in the system. The glass vial was capped immediately after the hydrogen peroxide addition was completed. The reaction was left to stand for 1 hour until complete gelation occured. The gel was removed from the vial and transferred into a beaker with 40 mL distilled water; where it was left there to stand for 3 hours for purification.

Synthesis of 3% g-CN derived DMA Gels with EG: 4.45 g deionized water, 4.45 g EG and 300 mg of g-CN were mixed in a plastic centrifuge tube. The mixture was ultrasonicated at 50 amplitude for 40 minutes (2 minute portions, 20 times) to yield a dispersion. After the dispersion was transferred into a 20 mL glass vial, 0.8 g DMA and 0.06 g MBA were added. Nitrogen was flushed through the system for 3 minutes and the vial was capped. The mixture

was put between 2 50 W LED daylight source (20 cm apart from each other) to initiate gelation. After gelation was completed in 20 minutes, the gel was removed from the vial and put into 40 mL deionized water for 2 hours for purification.

Synthesis of 4% g-CN derived DMA Gels with EG: 4.4 g deionized water, 4.4 g EG and 400 mg of g-CN were mixed in a plastic centrifuge tube. The mixture was ultrasonicated at 50 amplitude for 40 minutes (2 minute portions, 20 times) to yield a dispersion. After the dispersion was transferred into a 20 mL glass vial, 0.8 g DMA and 0.06 g MBA were added. Nitrogen was flushed through the system for 3 minutes and the vial was capped. The mixture was put between 2 50 W LED daylight source (20 cm apart from each other) to initiate gelation. After gelation was completed in 14 minutes, the gel was removed from the vial and put into 40 mL deionized water for 2 hours for purification.

Synthesis of 2% g-CN Derived DMA Hydrogels Without Crosslinker: 4.5 g deionized water, 4.5 g EG and 200 mg of g-CN were mixed in a plastic centrifuge tube. The mixture was ultrasonicated at 50 amplitude for 40 minutes (2 minute portions, 20 times) to yield a dispersion. After the dispersion was transferred into a 20 mL glass vial, 0.8 g DMA was added. Nitrogen was flushed through the system for 3 minutes and the vial was capped. The mixture was put between 2 50 W LED daylight source (20 cm apart from each other) to initiate gelation and reaction was completed in 4 hours by yielding viscous liquid.

Performing Gelation on Tissue Paper: Small tissue paper sample was cut from Kimtech Science lab tissue papers. It was soaked in 2% g-CN-EG monomer solution until completely wet. Tissue paper then transferred into plastic petri dish and illuminated from top for 1 hour, and washed with deionized water for the removal of unreacted portions.

Performing Gelation Under Sunlight: 2% g-CN-EG monomer mixture was poured into a vial and nitrogen was flushed through system. After capped, on a sunny day, 21.07.2017, the vial was put on the balcony of the Max Planck Institute of Colloids and Interfaces in Potsdam-Golm, Germany on a sunny day and gelation was completed in 1 hour.

Table S1: Properties of g-CN synthesized from CM complex

	BET Surface Area (m^2/g)[a]	**Surface Zeta Potential (mV)**	**C:N ratio[b]**
g-CN	83.42	-35.5	0.6083

[a]Obtained by porosimetry and BET calculation. [b]Obtained by elemental analysis.

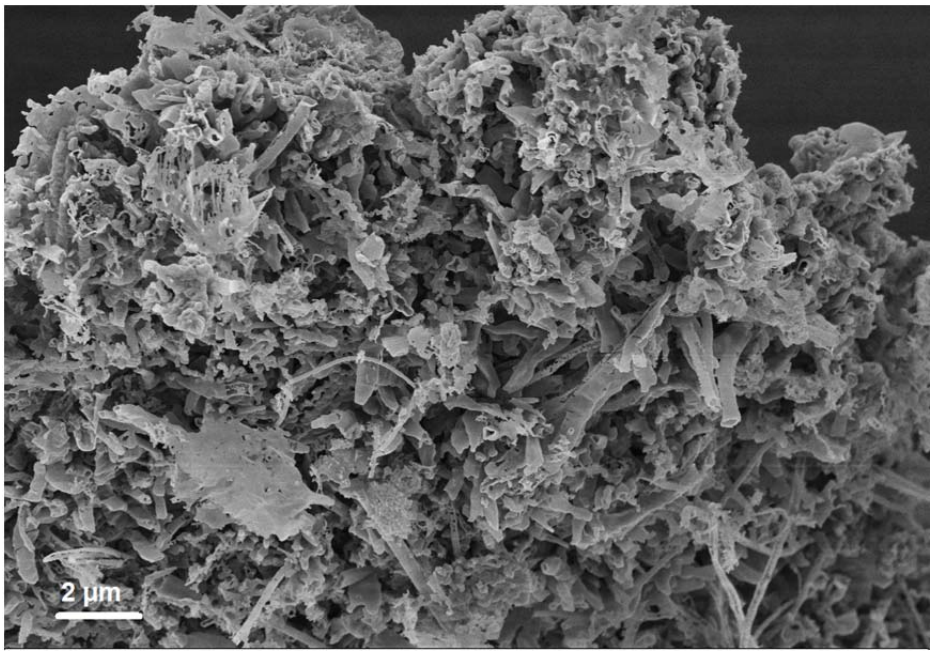


Figure S1. SEM image of utilized g-CN.

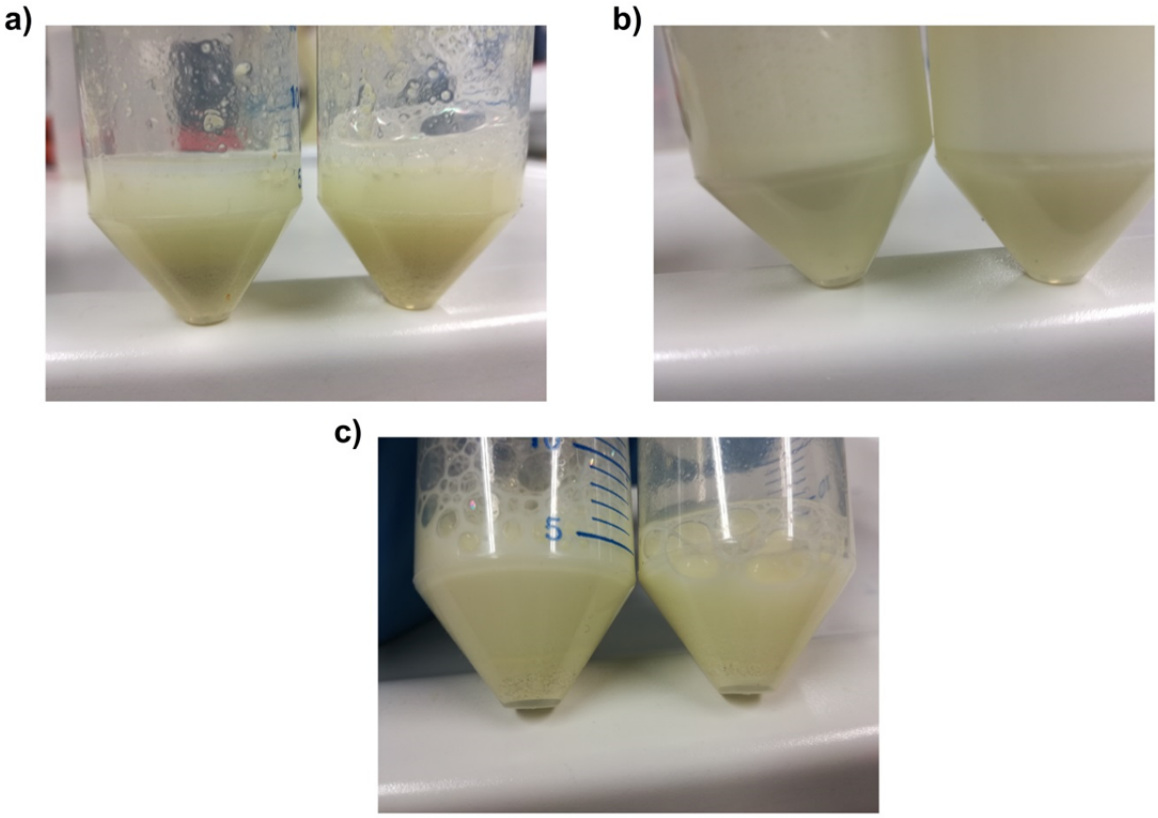
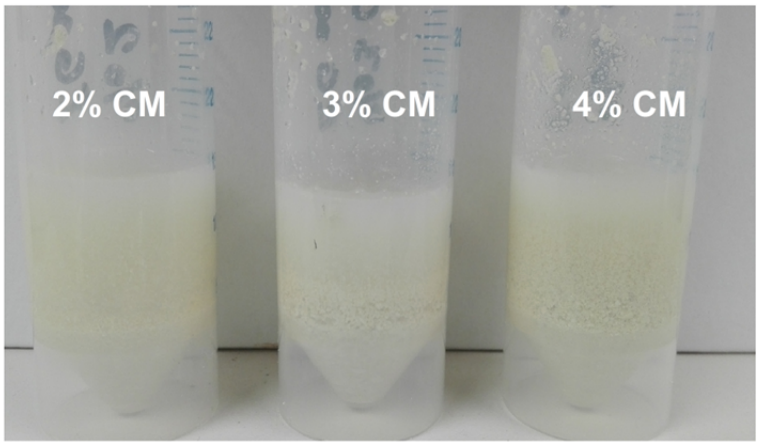


Figure S2. 2 wt.% g-CN in water with Triton X 305 (left tube) and Pluronic F127 (right tube) a) before ultrasonication, b) after ultrasonication and c) standing after 10 minutes.

a)



b)

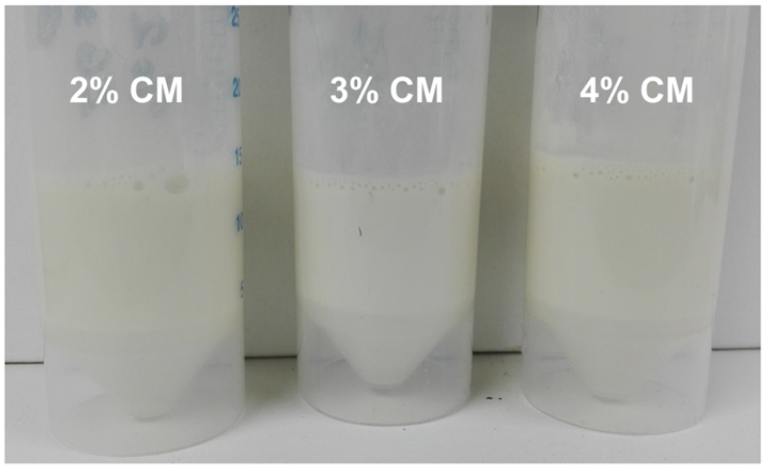


Figure S3. a) 2, 3 and 4 wt.% (from left to right) g-CN in 1:1 water:EG mixture before ultrasonication and b) 2, 3 and 4 wt.% (from left to right) g-CN dispersions in water:EG after ultrasonication for 40 minutes.

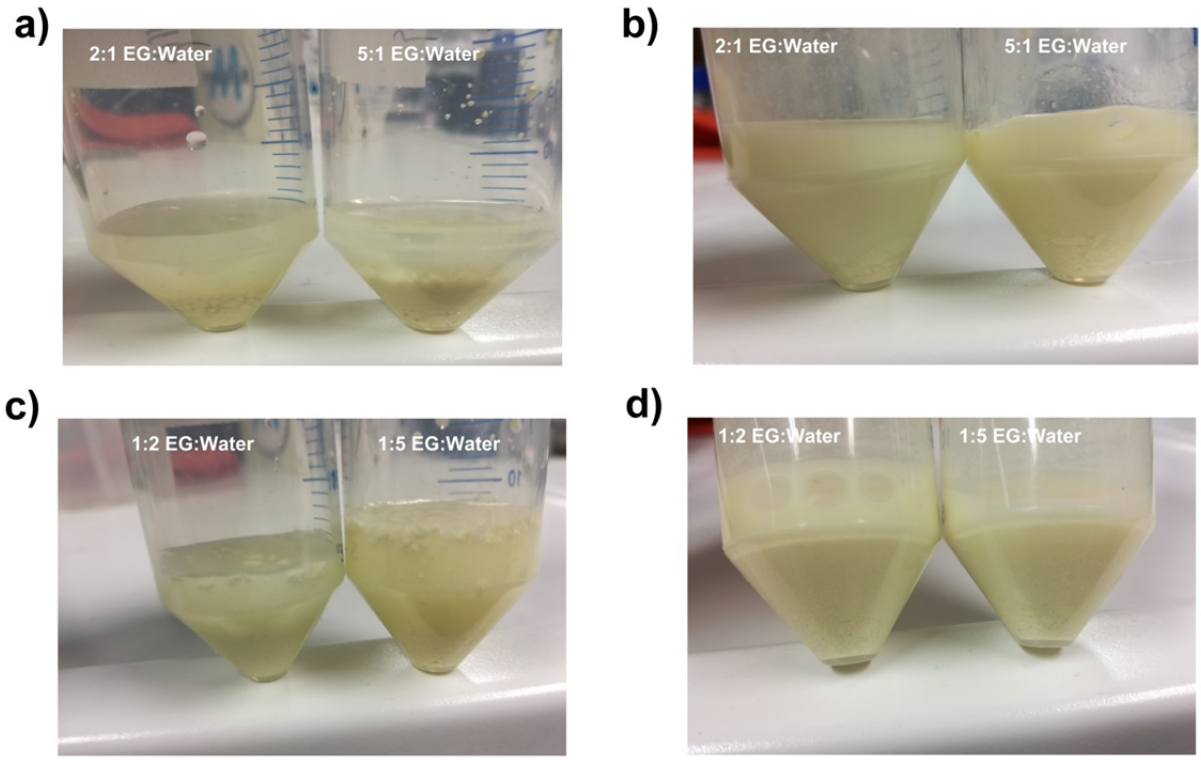


Figure S4. 2 wt.% g-CN a) in 2:1 and 5:1 EG:water solutions before ultrasonication, b) after ultrasonication, c) in 1:2 and 1:5 EG:water solutions before ultrasonication and d) after ultrasonication.

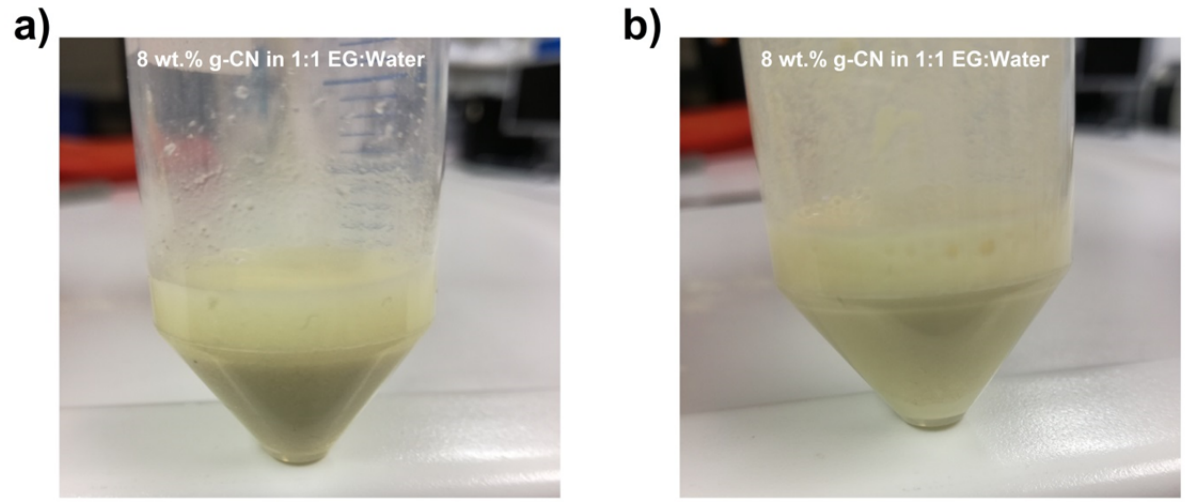


Figure S5. 8 wt.% g-CN in 1:1 EG:water solutions a) before and b) after ultrasonication.

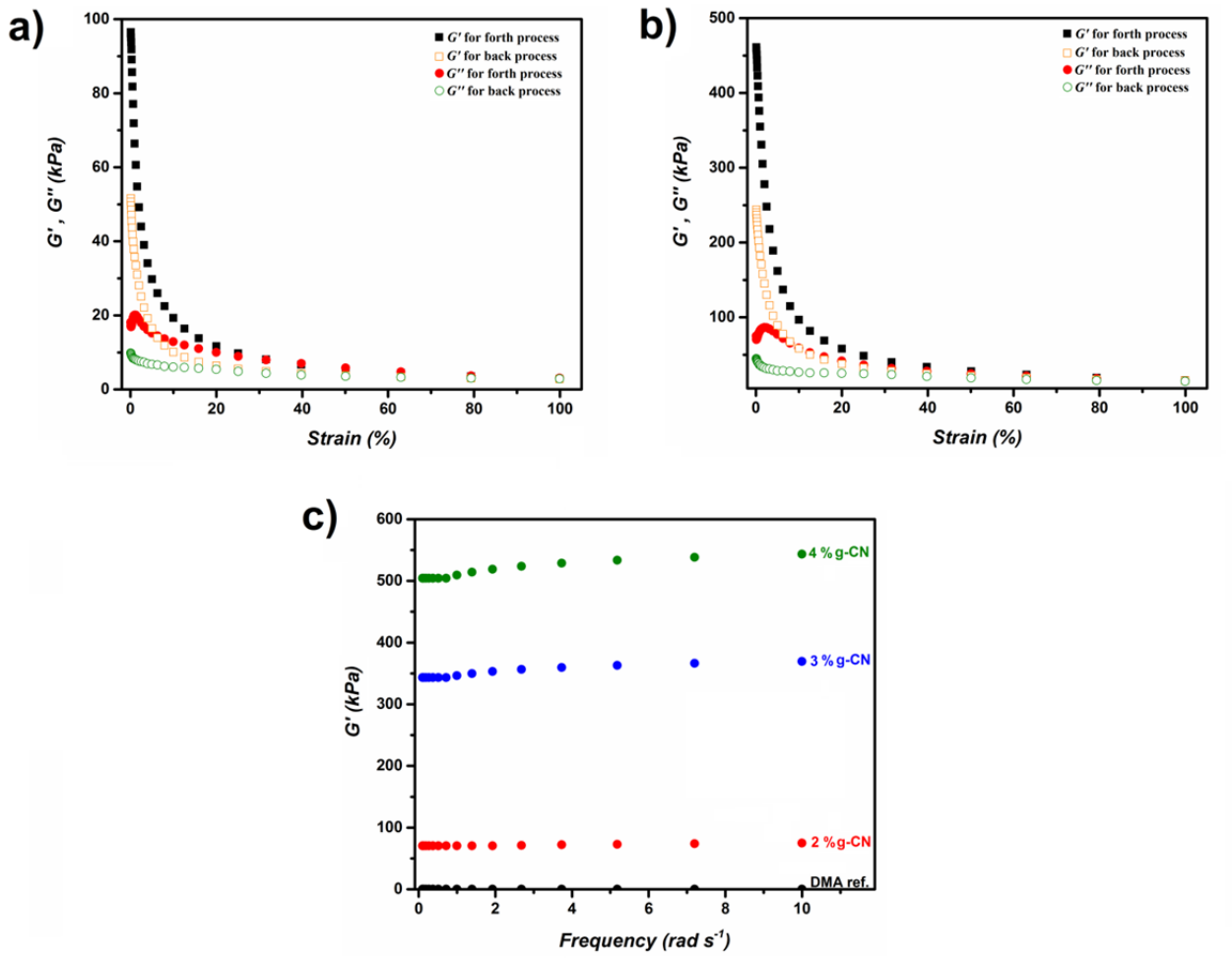


Figure S6. Comparison of storage (*G*', black and orange squares) and loss modulus (*G*'', red and green circles) of a) 2% and b) 3% g-CN-EG gels against strain, back (open) and forth (filled) process and d) storage moduli results of EG gels at constant strain (0.1%) against frequency.

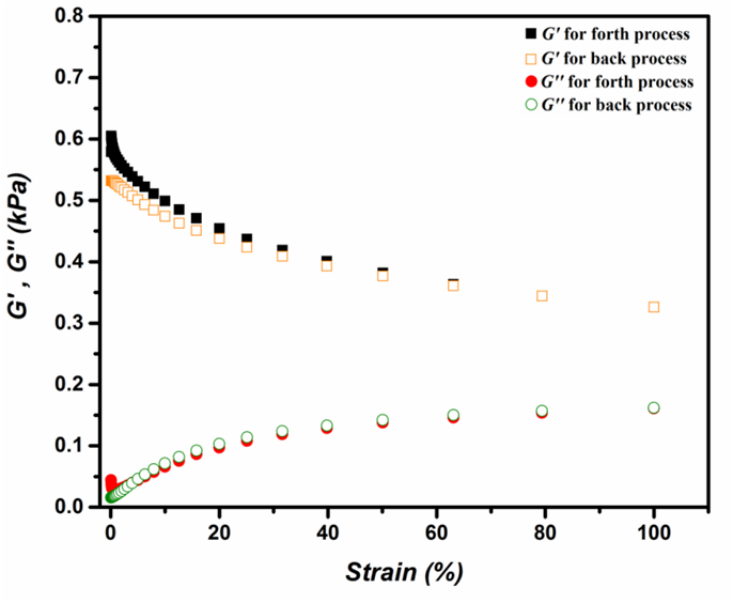


Figure S7. Rheology result of DMA reference EG gel, storage (*G'*, black and orange squares) and loss modulus (*G''*, red and green circles) against strain, back (open) and forth (filled) process.

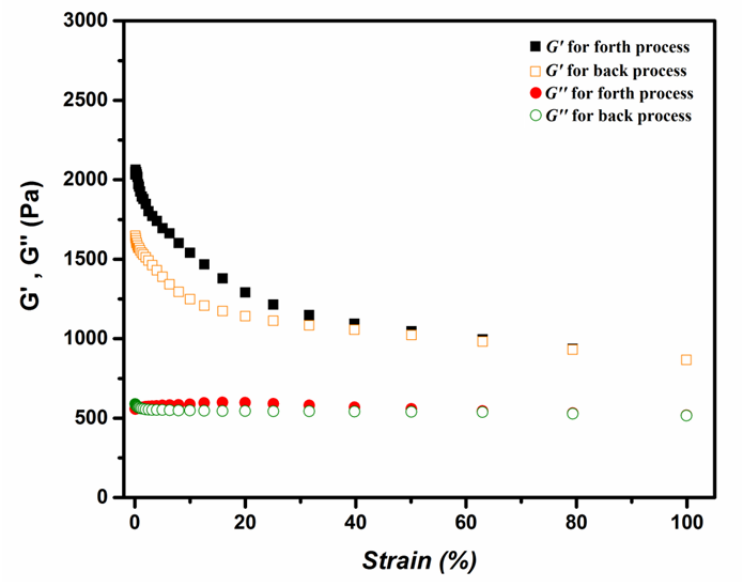


Figure S8. Rheology result of 2% g-CN EG gel without crosslinker, storage (*G'*, black and orange squares) and loss modulus (*G''*, red and green circles) against strain, back (open) and forth (filled) process.

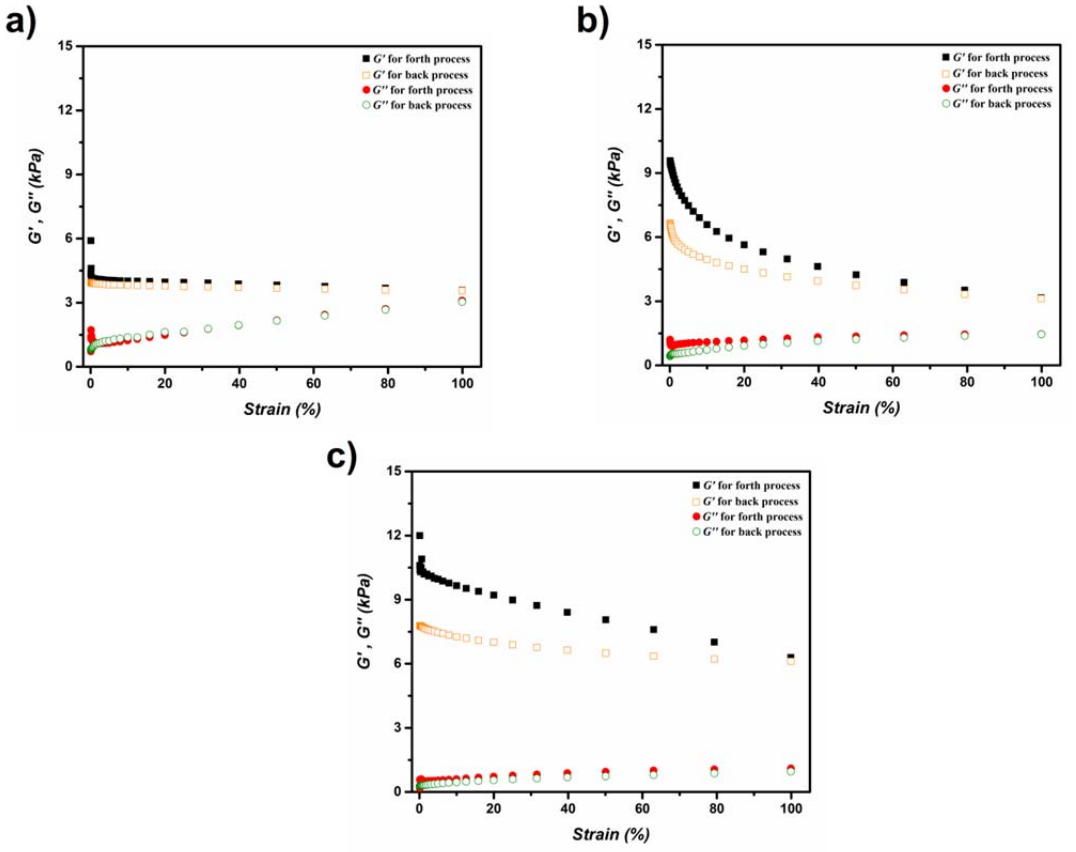


Figure S9. Comparison of storage (*G*', black and orange squares) and loss modulus (*G*'', red and green circles) of a) 2% and b) 3% and c) 4% g-CN EG gels initiated via redox in the dark, against strain, back (open) and forth (filled) process.

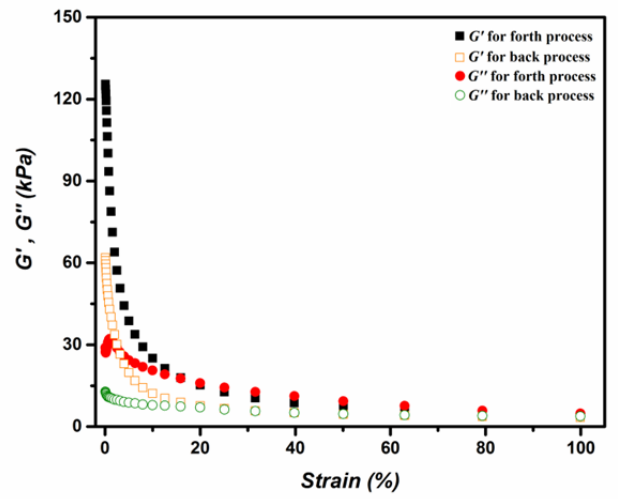


Figure S10. Rheology result of 8 wt.% g-CN EG gel, storage (*G*', black and orange squares) and loss modulus (*G*'', red and green circles) against strain, back (open) and forth (filled) process.

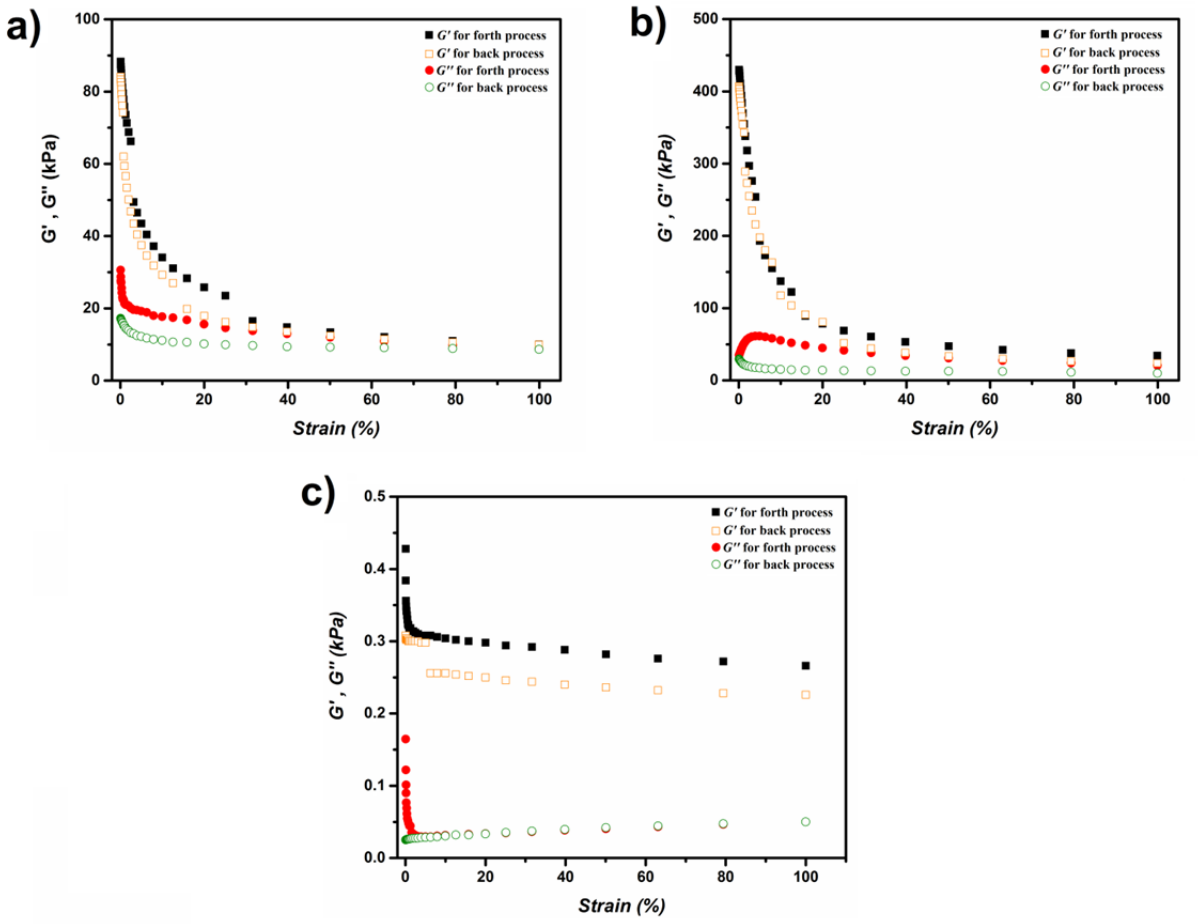


Figure S11: Comparison of storage (*G*', black and orange squares) and loss modulus (*G*'', red and green circles) of a) 2% and b) 3% g-CN and c) reference DMA hydrogels against strain, back (open) and forth (filled) process.

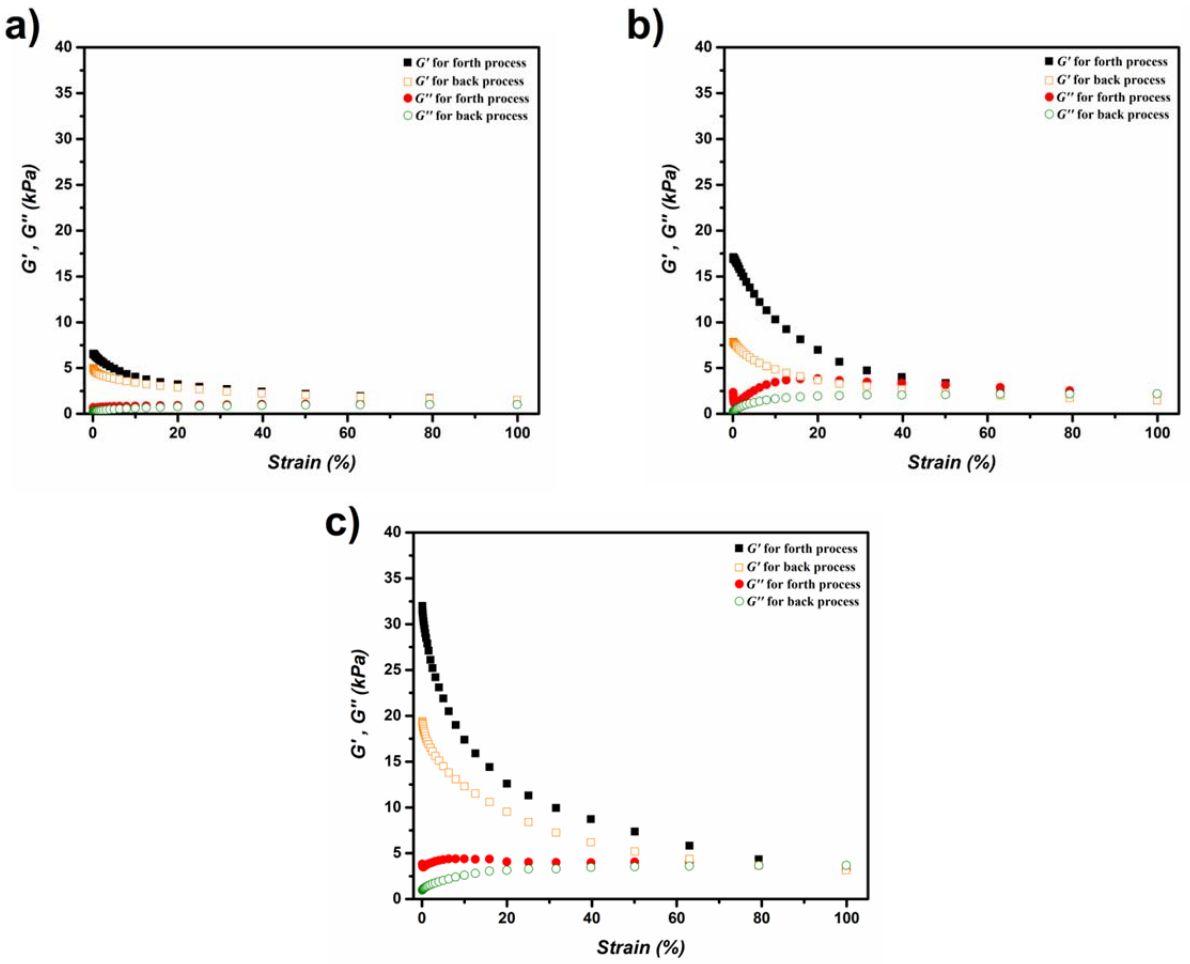


Figure S12. Comparison of storage (*G*', black and orange squares) and loss modulus (*G*'', red and green circles) of a) 2% and b) 3% and c) 4% g-CN hydrogels initiated via redox in the dark, against strain, back (open) and forth (filled) process.

Table S2: Comparison of storage modulus (*G*') values of reinforced hydrogels in literature with reinforcer type and content at strain of 0.1%.

Reinforcer Type	**Reinforcer Amount (wt.%)**	**Storage Modulus (*G*') (kPA)**
g-CN (this work)	4	720
g-CN [1]	0.6	6
Nanofiber-$CaCl_2$ [2]	5	12
Nanoclay [3]	1	1.23
Clay [4]	1	1
Titanate nanosheets [5]	0.8	2

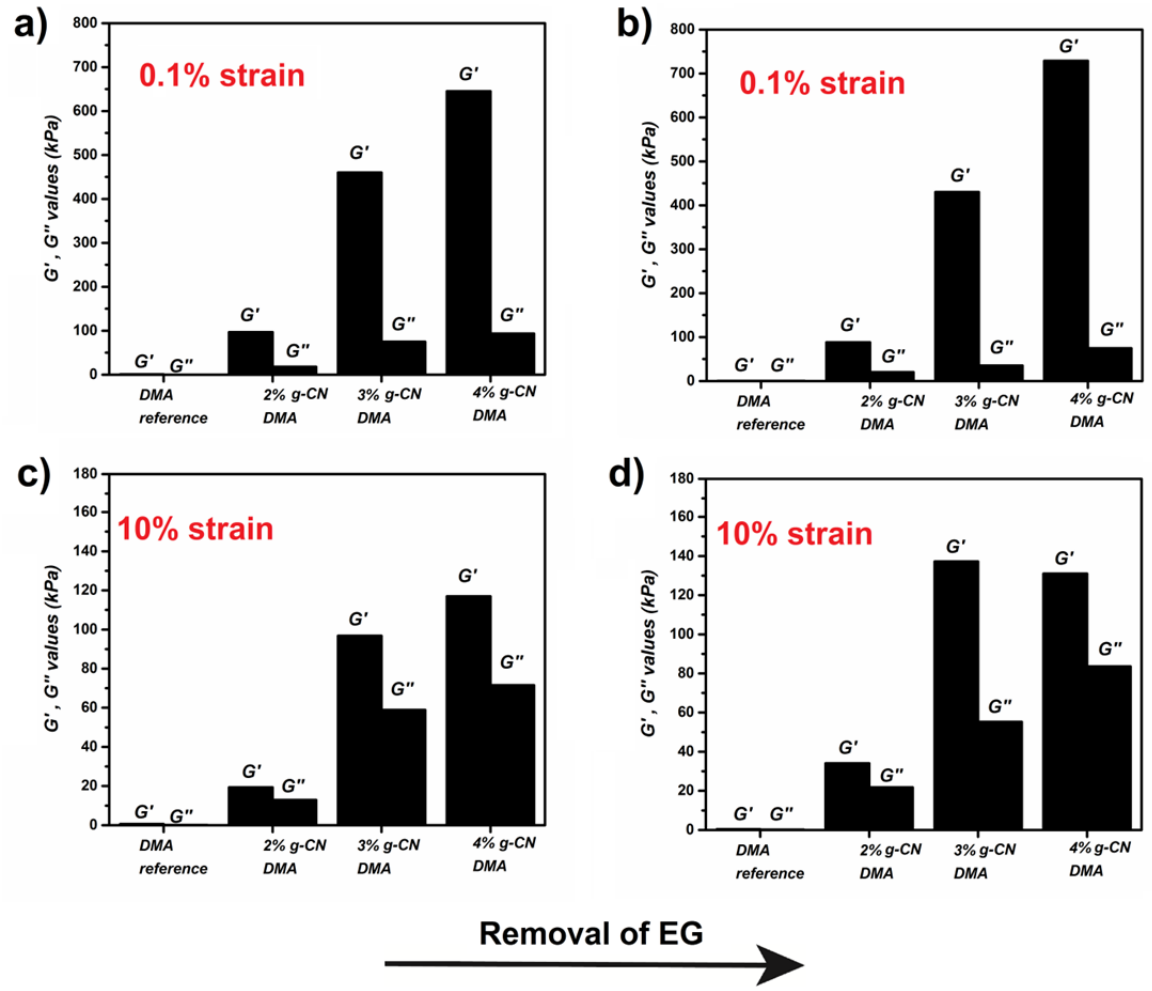


Figure S13. Comparison of storage and loss moduli for a) EG gels and b) hydrogels at 0.1% strain, c) EG gels and d) hydrogels at 10% strain.

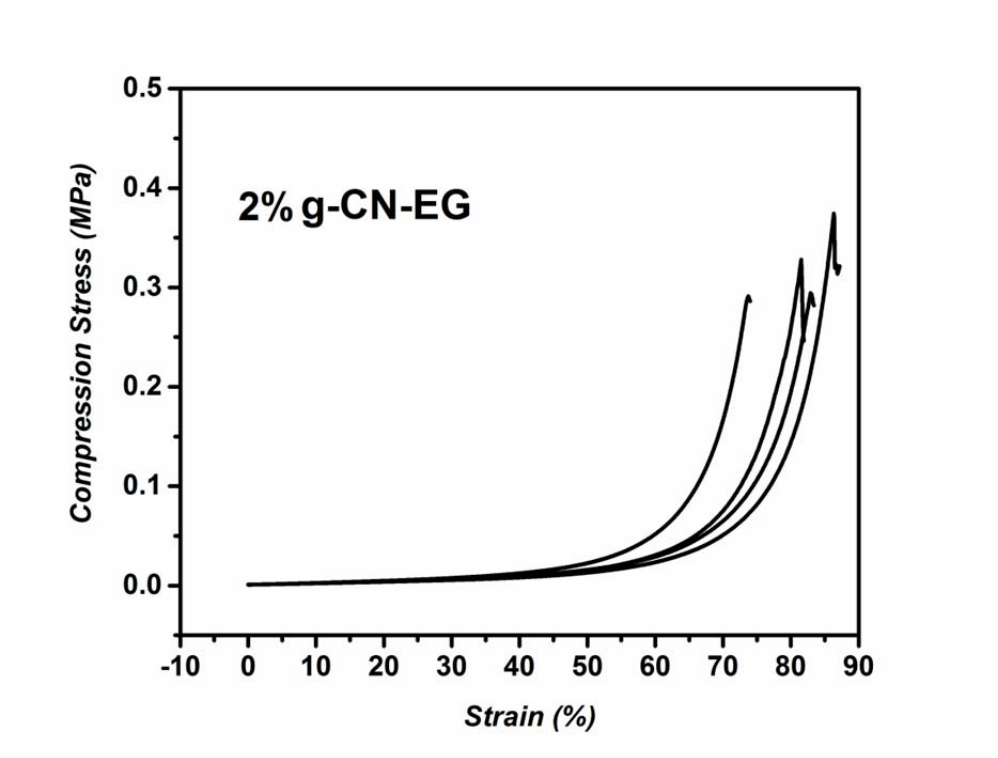


Figure S14. Compression test results of 2% g-CN EG gel samples.

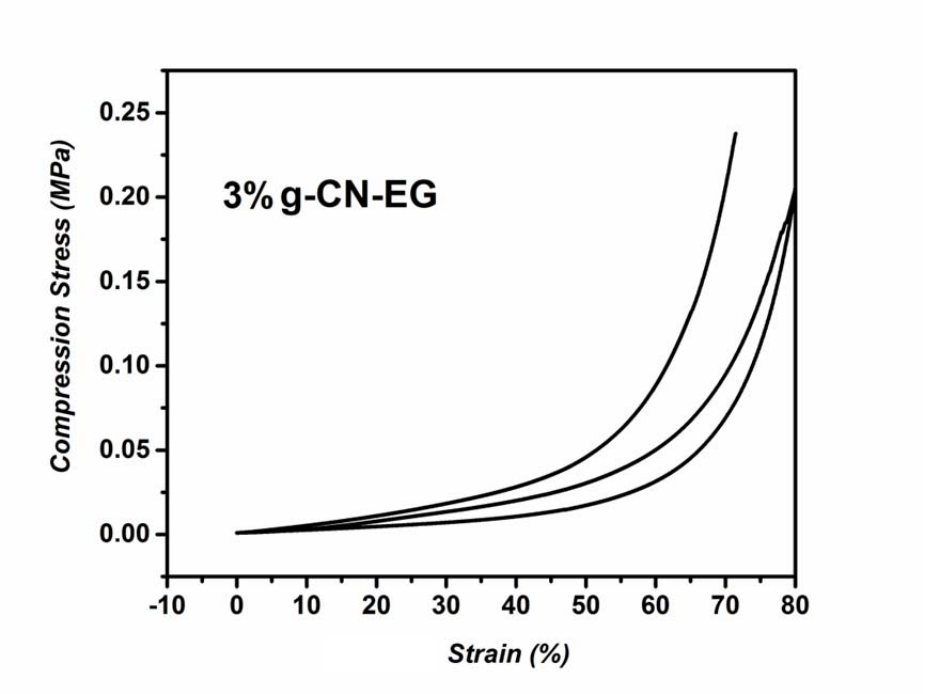


Figure S15. Compression test results of 3% g-CN EG gel samples.

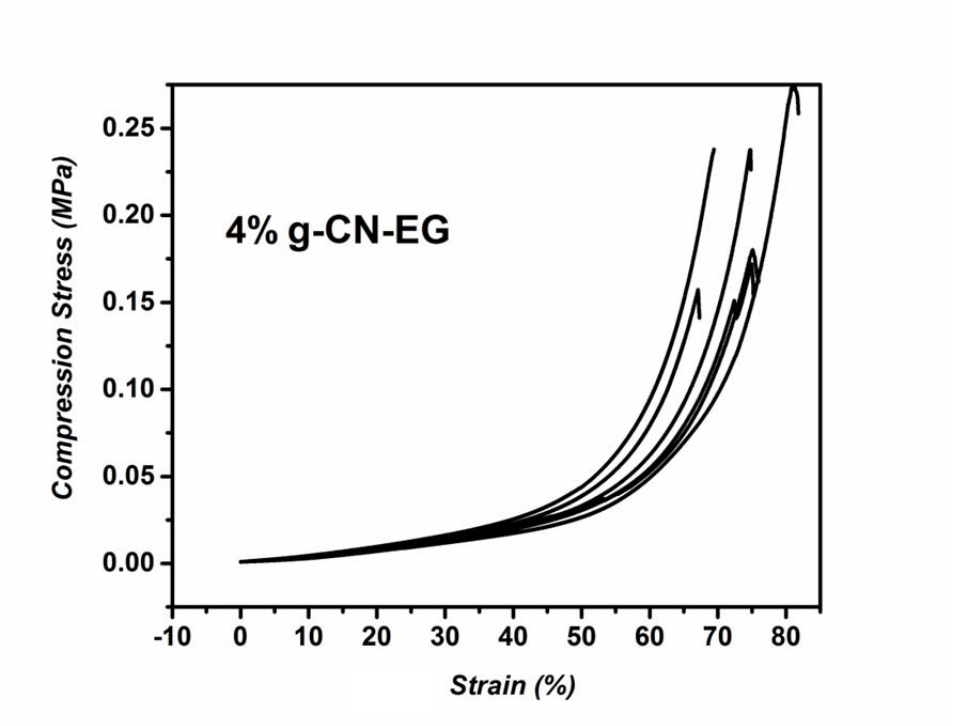


Figure S16. Compression test results of 4% g-CN EG gel samples.

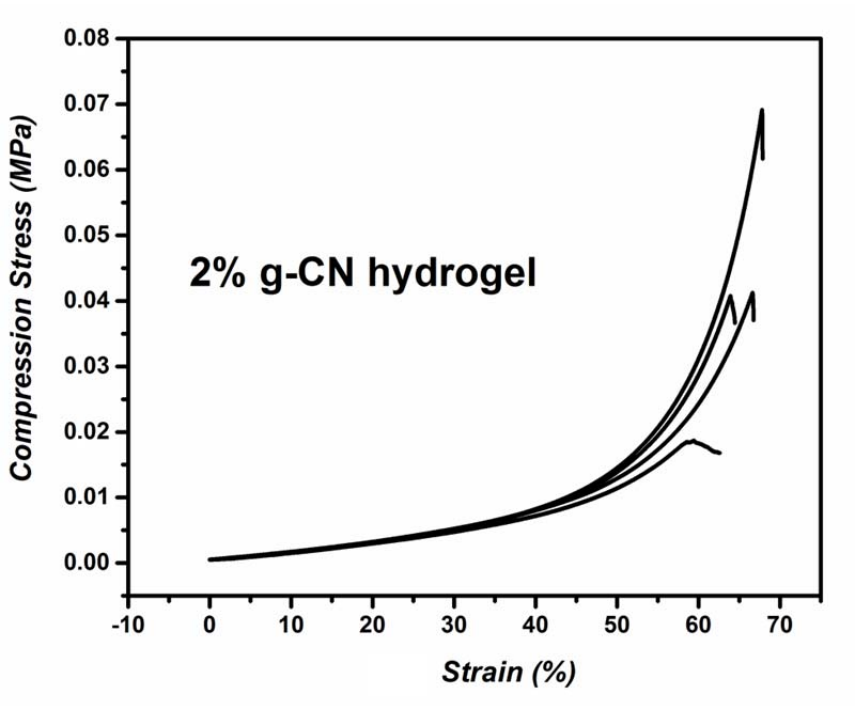


Figure S17. Compression test results of 2% g-CN hydrogel samples.

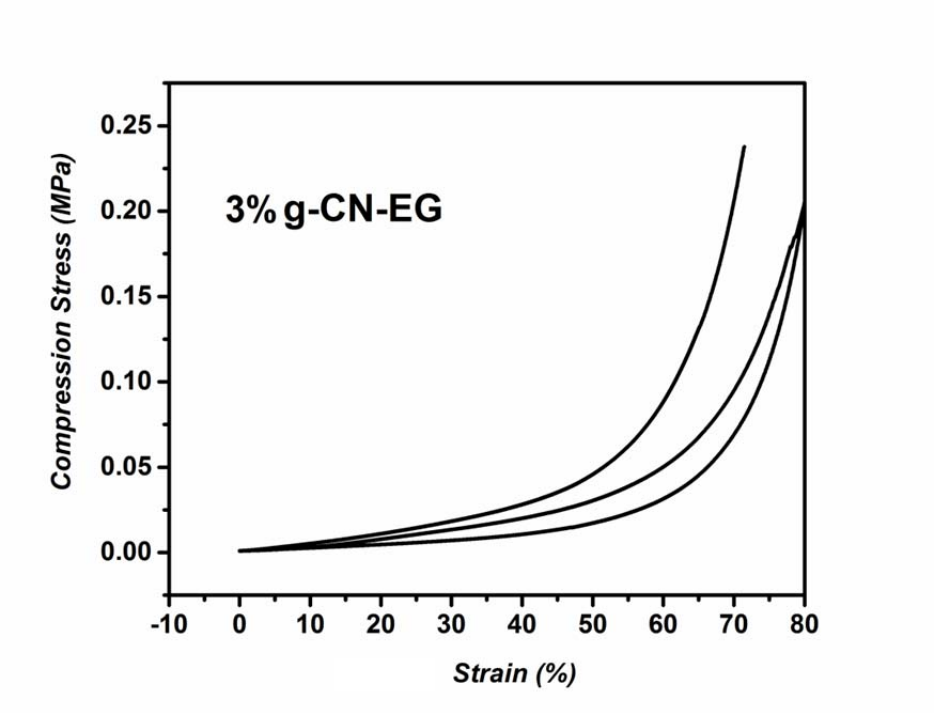


Figure S18. Compression test results of 3% g-CN hydrogel samples.

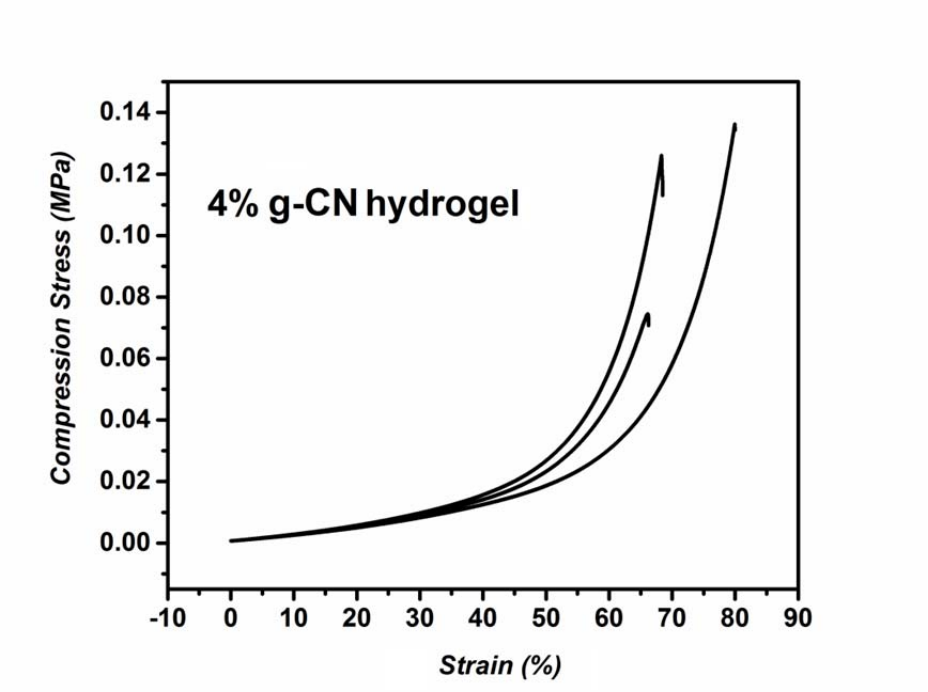


Figure S19. Compression test results of 4% g-CN hydrogel samples.

Table S3. Comparison of E_{mod} values from compression with literature.

Type of Hydrogel	**Compression Modulus (MPa)**
Presented Hydrogel (4 wt.%, covalent)	3.55
Double Network[6]	2.8
Double Network[7]	0.41
Silk composite[8]	0.521
Double Network[9]	0.33
Interpenetrating Network[10]	0.087
PVA-HA[11]	5.5

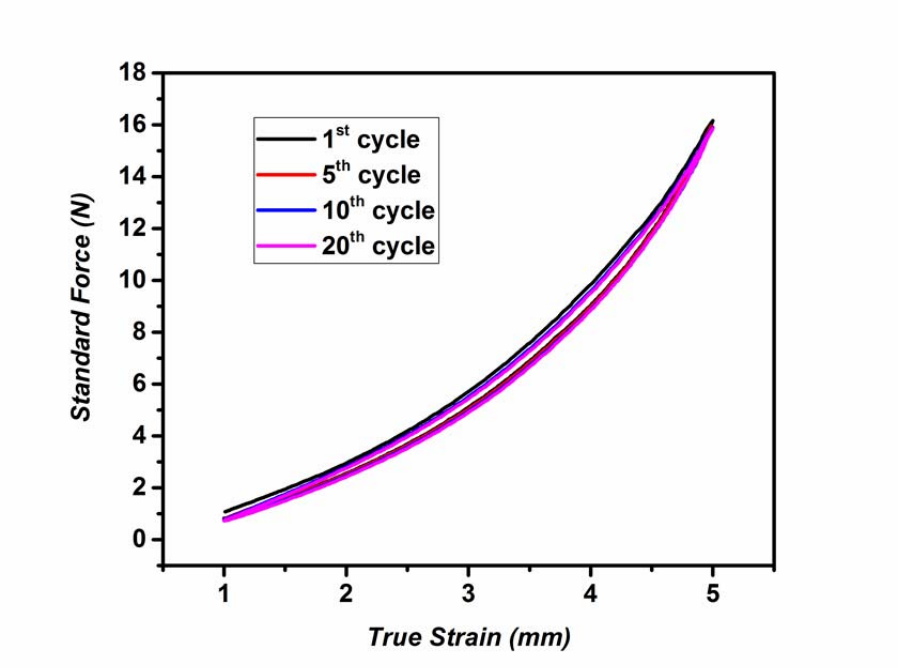


Figure S20. Cyclic compression test results of 3% g-CN EG gel.

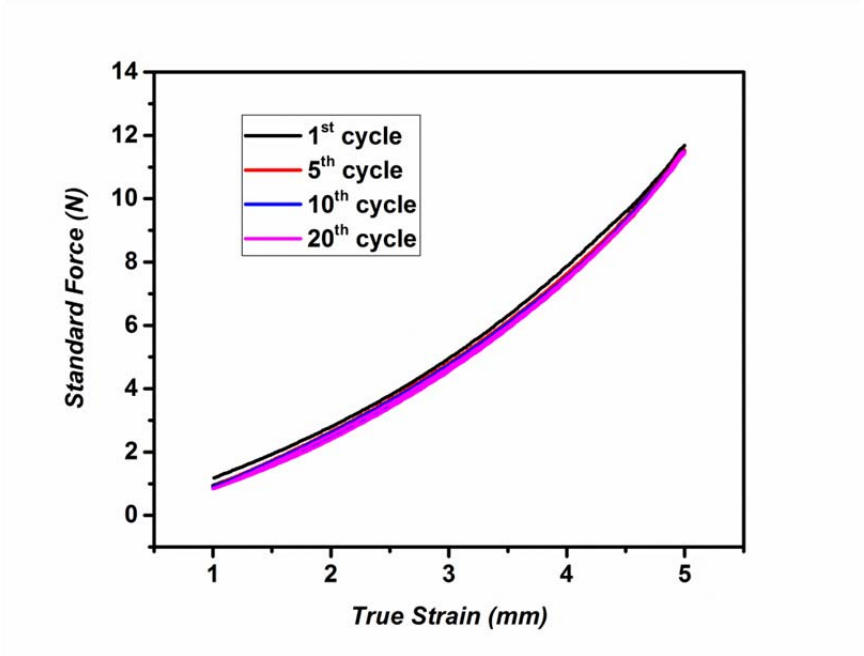


Figure S21. Cyclic compression test results of 4% g-CN EG gel.

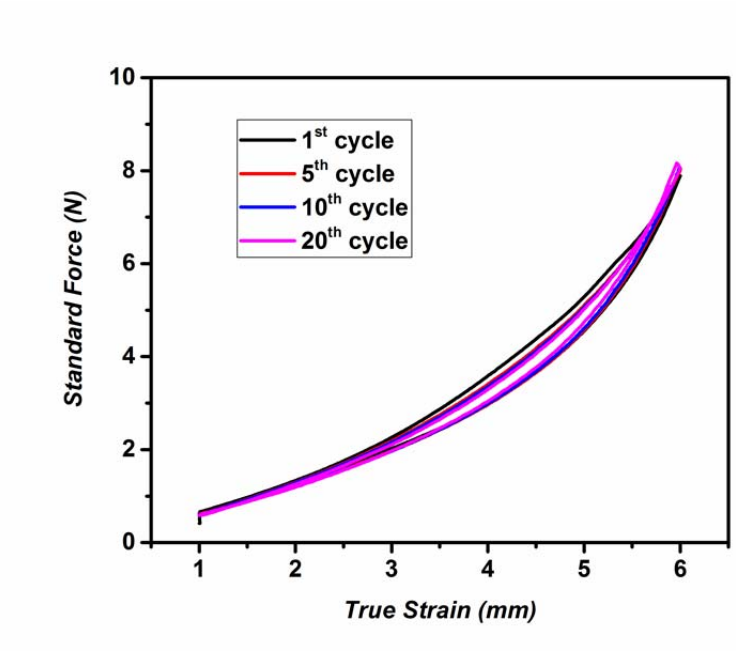


Figure S22. Cyclic compression test results of 3% g-CN hydrogel.

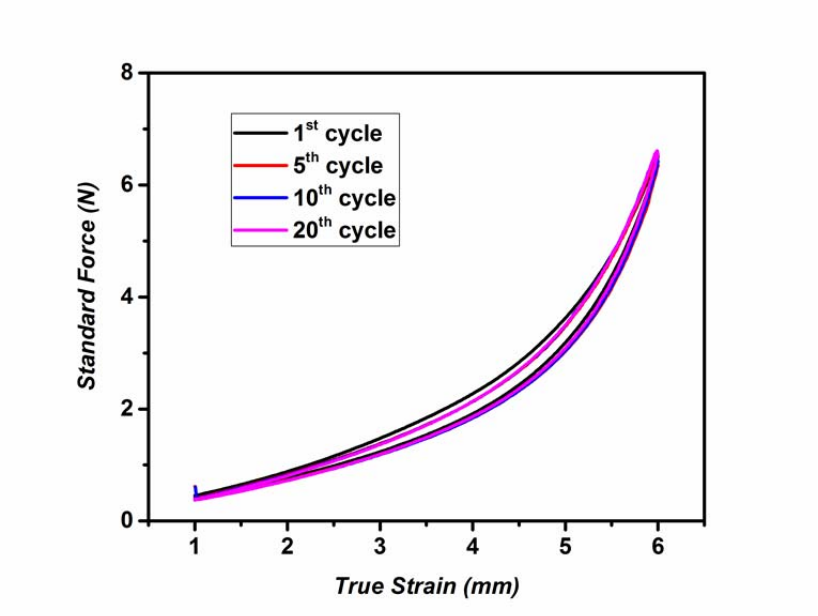


Figure S23. Cyclic compression test results of 4% g-CN hydrogel.

Figure S24. a) EG-based g-CN dispersion for gelation was put on a balcony receiving direct sun, b) complete gel formation after 1 hour.

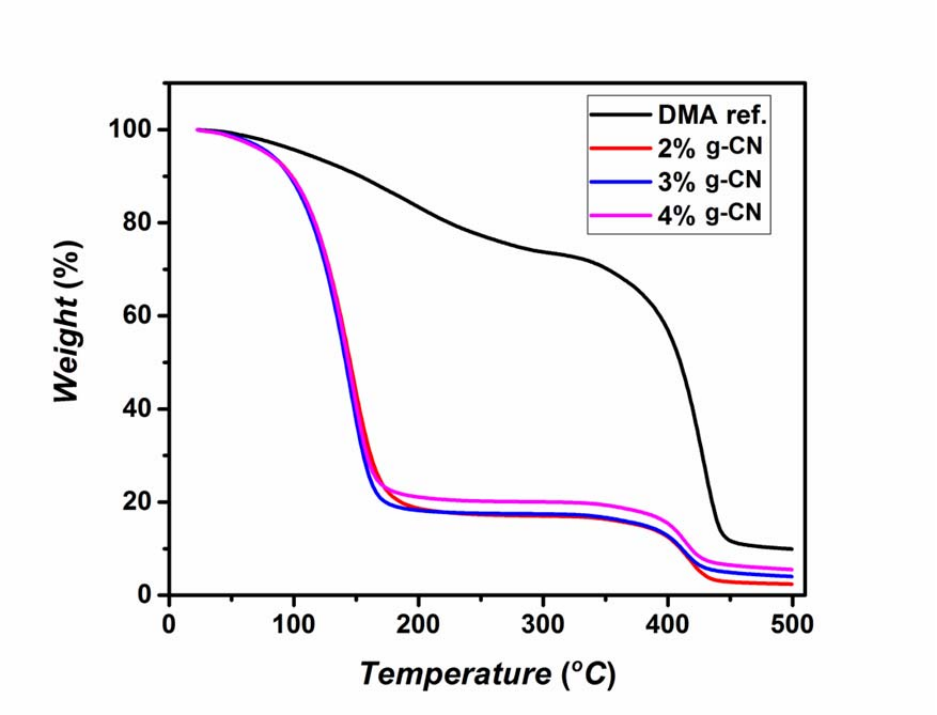


Figure S25. TGA diagrams of freeze dried g-CN EG gels.

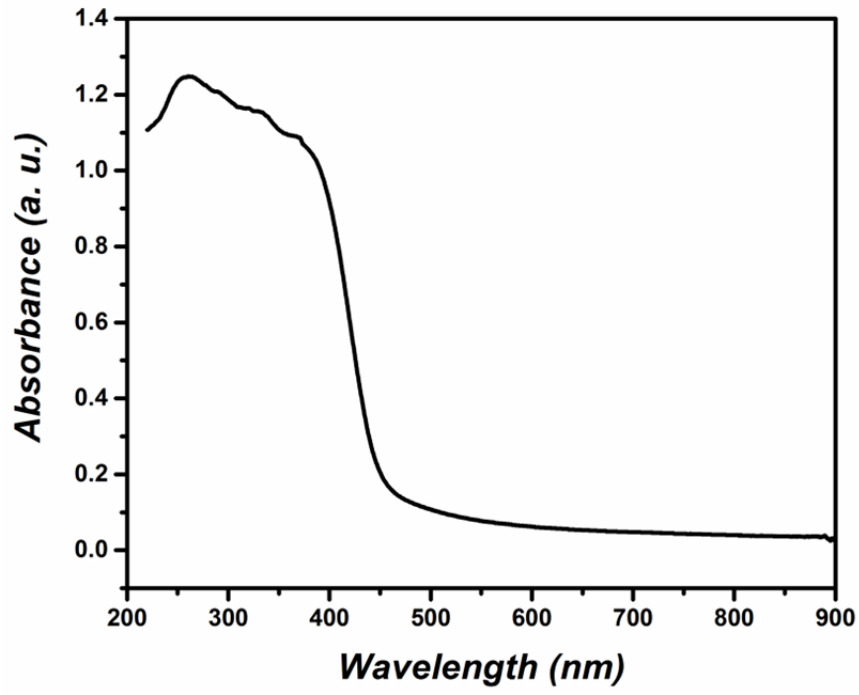


Figure S26. UV-Vis spectra of g-CN.

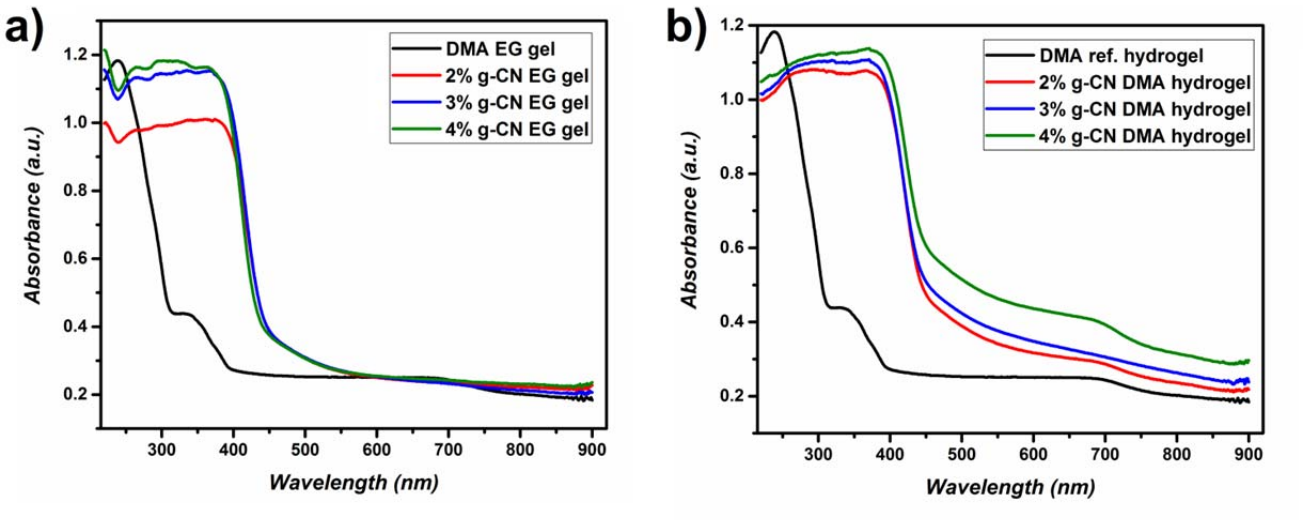


Figure S27. UV spectra of a) EG gels and b) hydrogels.

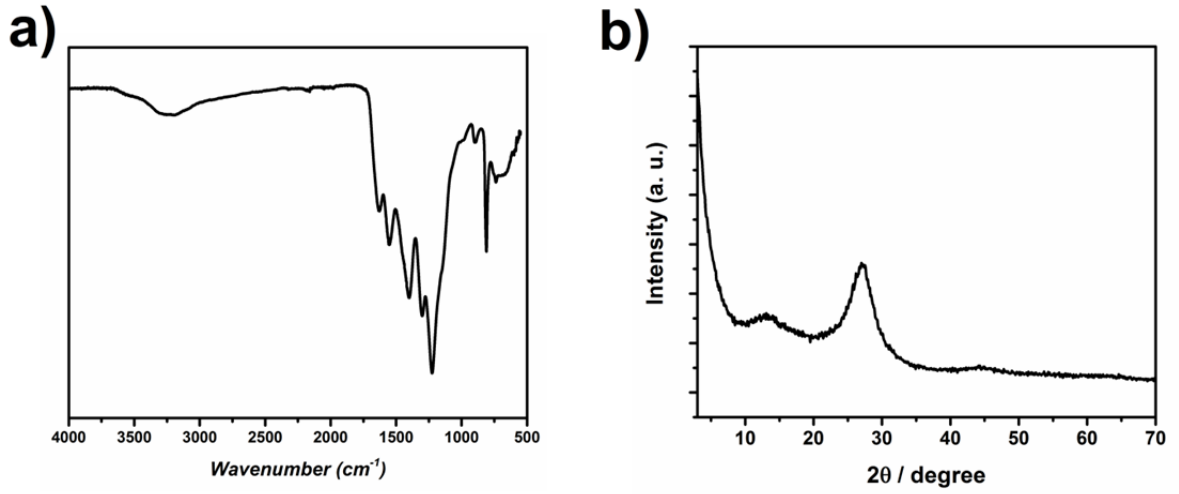


Figure S28. FT-IR and XRD profiles of g-CN.

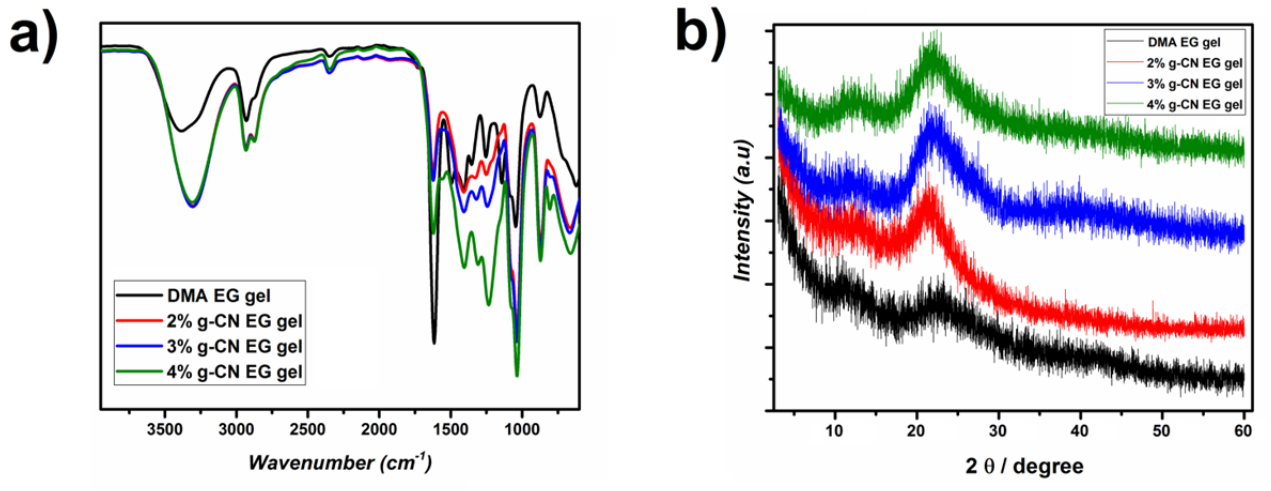


Figure S29. FT-IR and XRD profiles of g-CN EG gel samples.

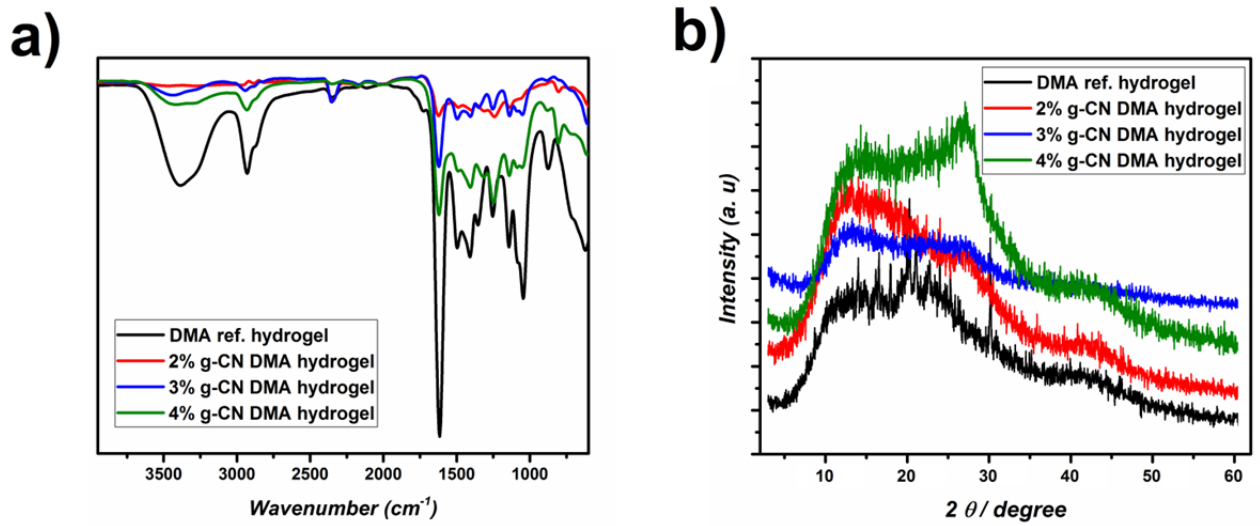


Figure S30. FT-IR and XRD profiles of g-CN hydrogels.

Figure S31. Symbols from deck of cards (spade, heart and diamond) gels synthesized via photopatterning (after rinsing with water).

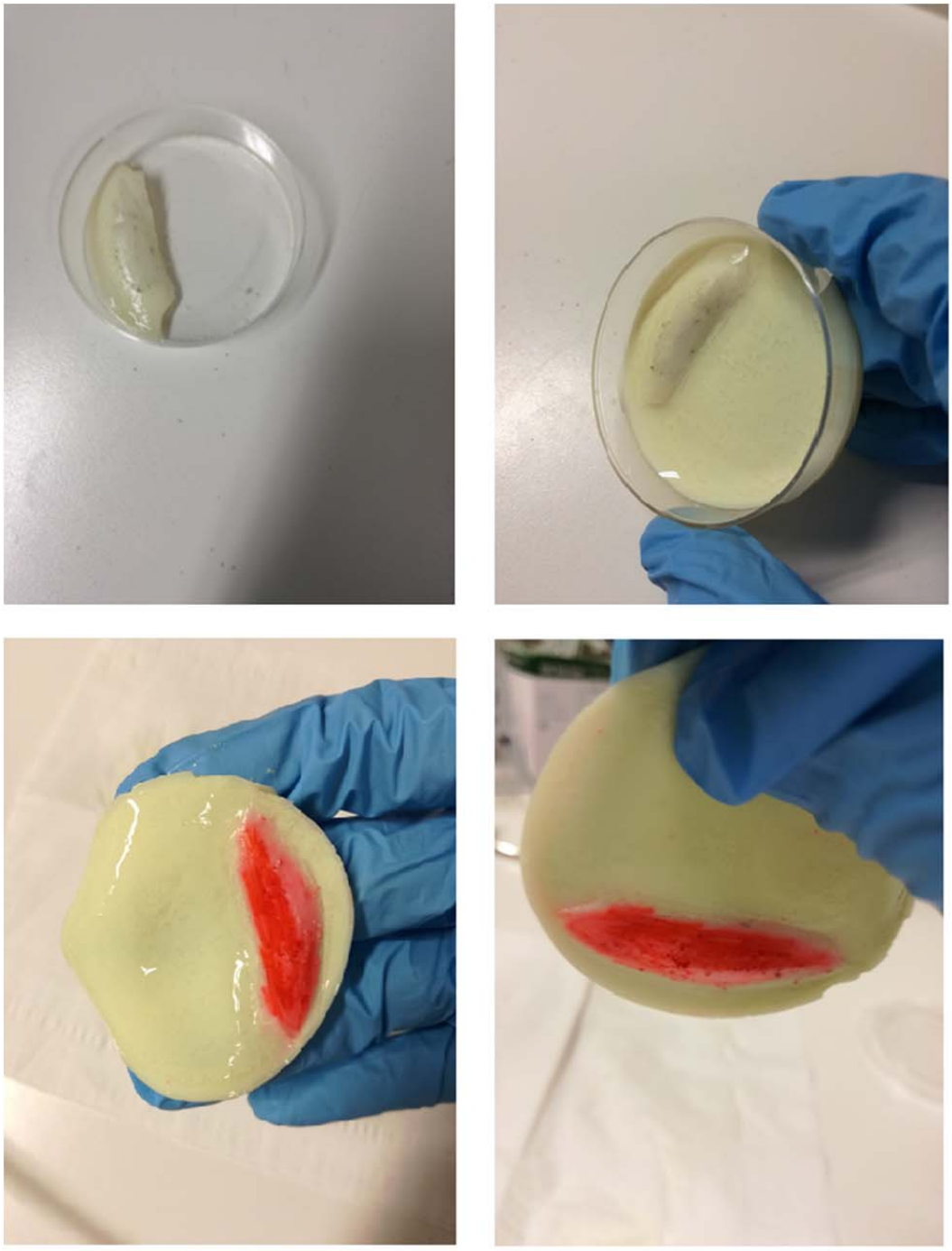


Figure S32. Formation of an initial gel network and subsequent gelation around initial gel. The initial gel was colored for visualization.

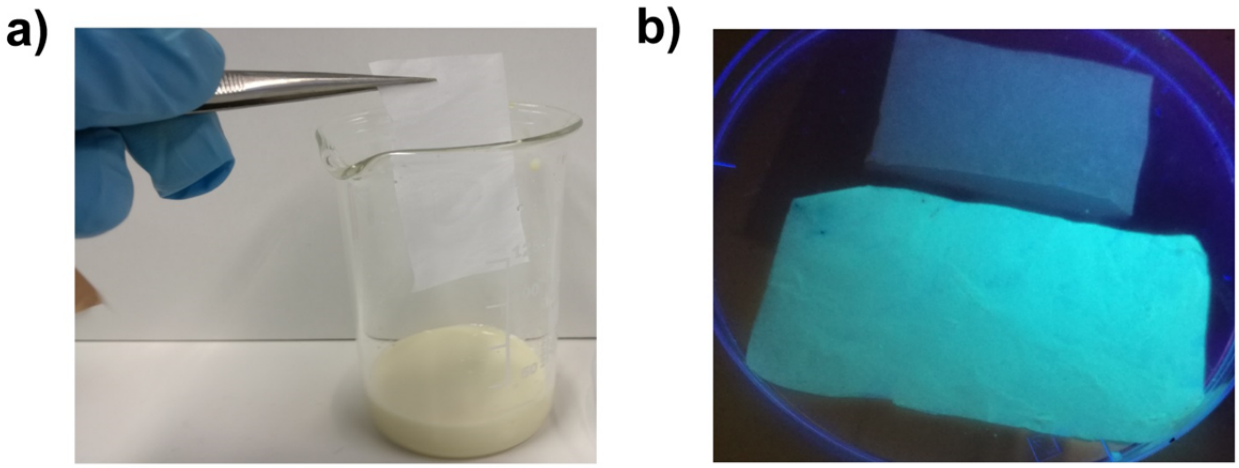


Figure S33. a) Soaking thin tissue paper into EG-based CM dispersion, b) after polymerization and washing, tissue glows under UV light due to g-CN incorporation whereas reference tissue remains dark.

References

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