Supplementary Information (SI) for Journal of Materials Chemistry C.

Direct-Ink-Writing of Multi-functional Dynamic Polymer-Carbon Nanotube Hydrogel Composites – Supporting Information

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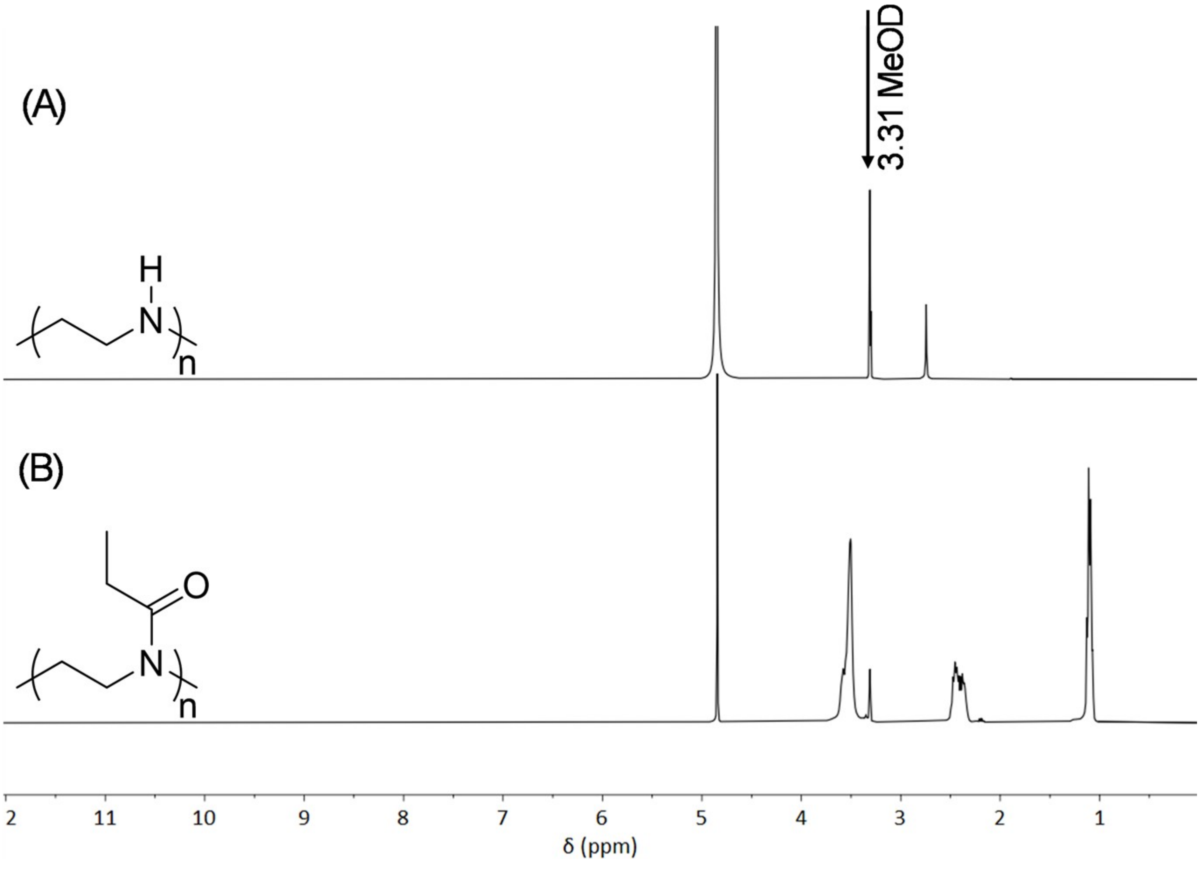


Figure S1. (A) ^{1}H-NMR spectrum of lab synthesized L-PEI (20 KDa) using MeOD as the solvent, with one proton environment observed at 2.74 ppm (2H, backbone methylene), showing successful hydrolysis and good purity, (B) Reference ^{1}H-NMR spectrum of the starting material PEtOx (50 KDa) purchased from Sigma-Aldrich using MeOD as the solvent, with three proton environments apparent:

Backbone methylene, 3.50 ppm, 2H+2H; end chain methylene, 2.45 ppm, 2H; end chain methyl, 1.10 ppm, 3H).

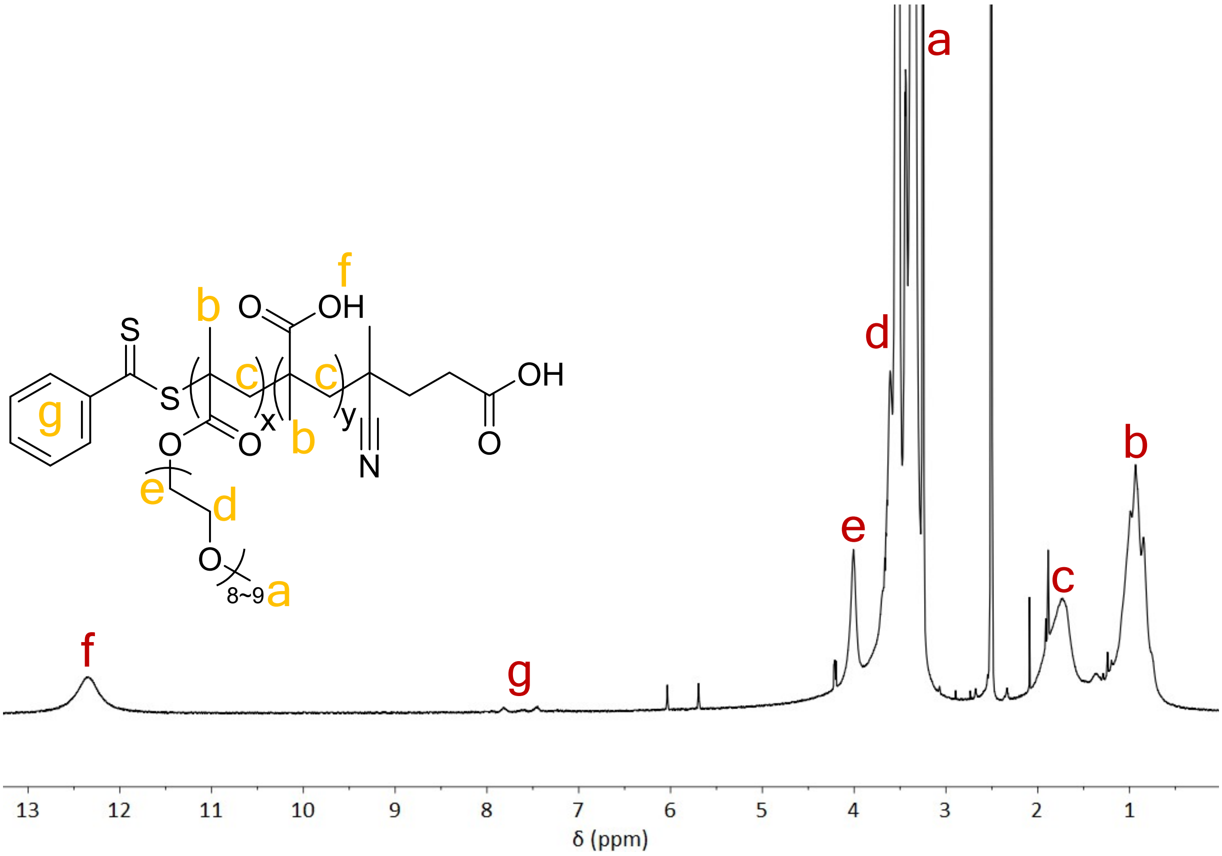


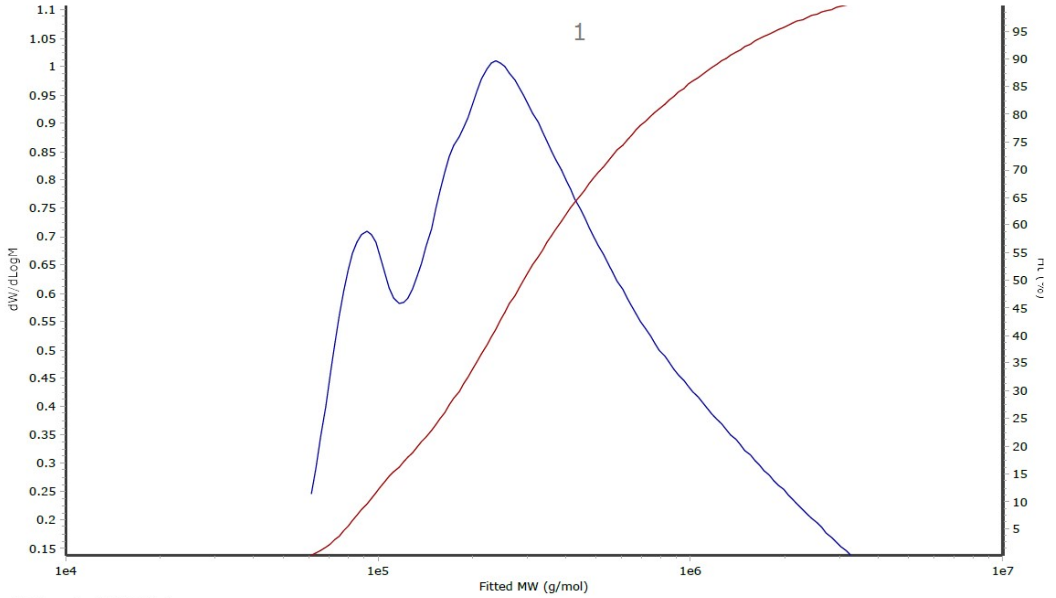
Figure S2. ^{1}H-NMR spectrum of the parent polymer with relative chemical shift of protons using DMSO-d_6 as the solvent.

Sample name	Mn of L-PEI (kDa)	Aldehyde:Diamine Ratio	Water swelling ratio
P1	-	1:0	Fully dissolved
Hydrogel-1	2	1:1	1020%
Hydrogel-2	10	1:1	609%
Hydrogel-3	20	1:0.25	Fully dissolved
Hydrogel-4	20	1:0.5	831%
Hydrogel-5	20	1:0.75	612%
Hydrogel-6	20	1:1	523%

Chart S1. Hydrogel compositions with water swelling ratios varying molar feed ratios of aldehyde:diamine and increasing L-PEI chain length.

Sample name	**Mn of L-PEI (kDa)**	**Aldehyde:Diamine Ratio**	**MWCNTs:P1 mass ratio**	**Water Swelling Ratio**
Hydrogel composite-1	2	1:1	1%	Fully dissolved
Hydrogel composite-2	10	1:1	1%	530%
Hydrogel composite-3	20	1:1	1%	341%
Hydrogel composite-4	20	1:0.5	1%	624%
Hydrogel composite-5	20	1:0.75	1%	387%
Hydrogel composite-6	20	1:1	3%	316%
Hydrogel composite-7	20	1:1	5%	286%

Chart S2. Hydrogel composite library prepared using polymer and surfactant, with water swelling ratio as a function of L-PEI length, feed aldehyde-to-diamine ratio and MWCNT loading.



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	238225	219261	517807	1169837	1817154	1069546	2.362

Figure S3. Size-exclusion chromatography data of parent copolymer synthesized from RAFT process.

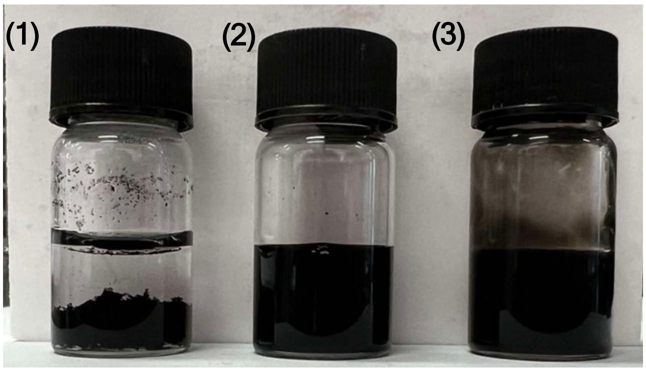


Figure S4. Condition of aqueous based MWCNTs (0.5 *wt*%) in different stage of treatments: (1) MWCNTs suspended in water, (2) MWCNT aqueous suspension treated with SDS, (3) gelled crosslinked polymer-CNT composite hydrogel.

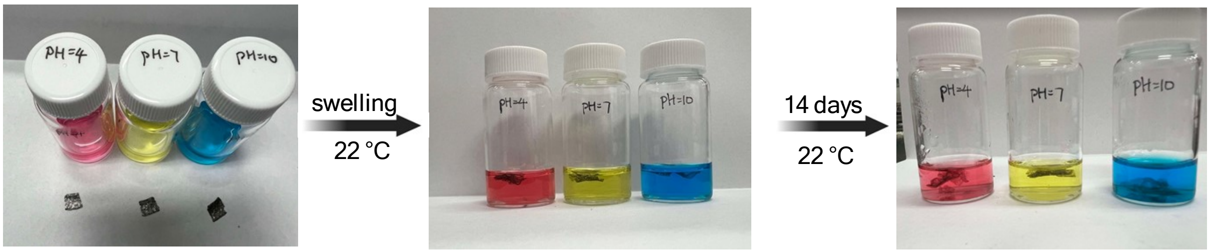


Figure S5. Hydrogel composite HC1-20K-100-1% stability tests in different pH aqueous environments at room temperature.

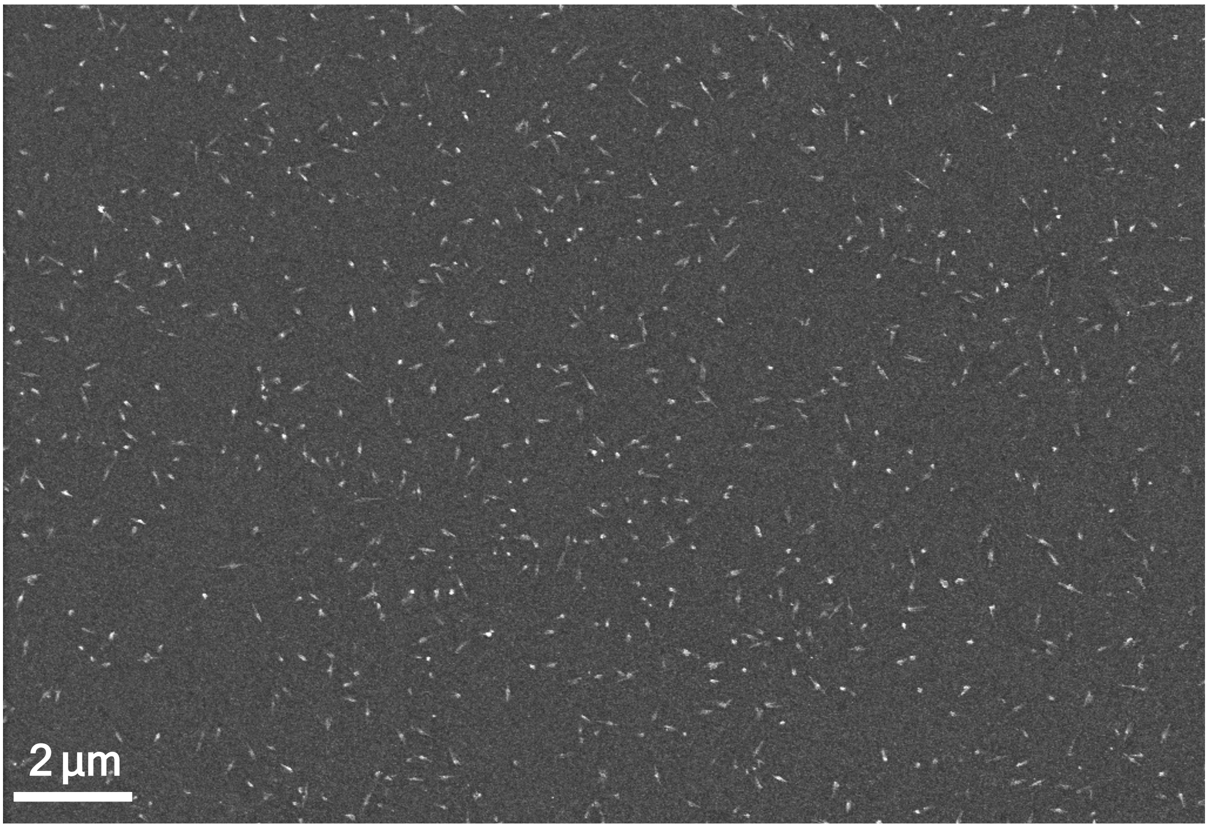


Figure S6A. SEM observation of the printed surface after DIW using hydrogel-composite ink with 1 *wt*% MWCNTs incorporation. No nanotube agglomeration was observed. The head and tail of the nanotubes were highlighted under SEM due to their high electric conductivity.

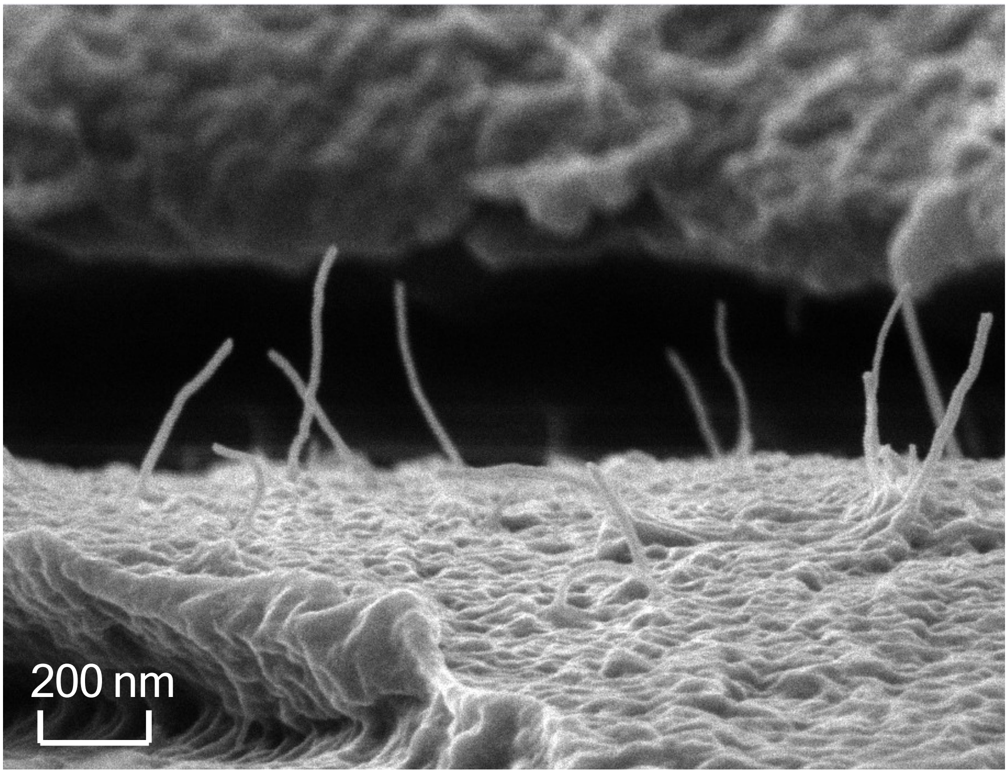


Figure S6B. SEM image of the cross-section area of the printed object after DIW using hydrogel-composite ink with 1 *wt*% MWCNTs incorporation. Zoomed image clearly showed individual carbon nanotubes "buried" within the hydrogel matrix without agglomeration, exhibiting good dispersion.

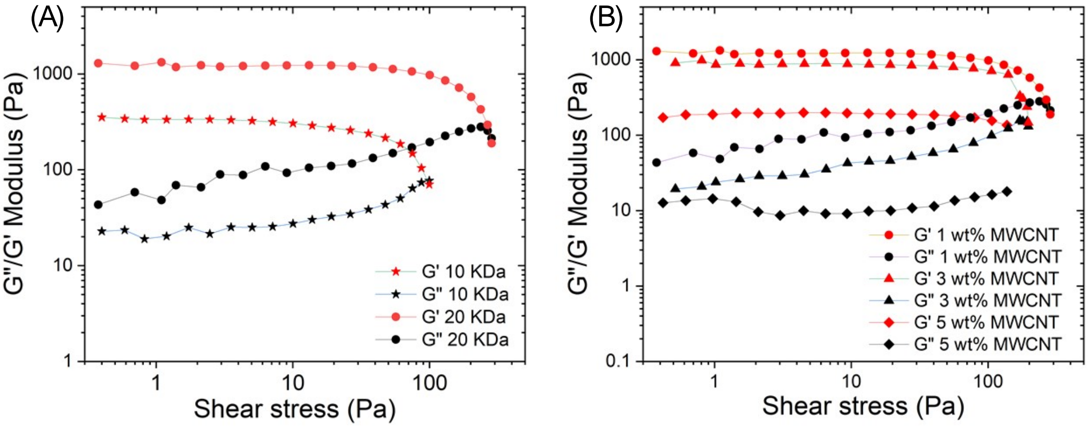


Figure S7. Storage and loss modulus with respect to shear stress of hydrogel composites, with different L-PEI molecular weight (A) and MWCNTs loadings (B).

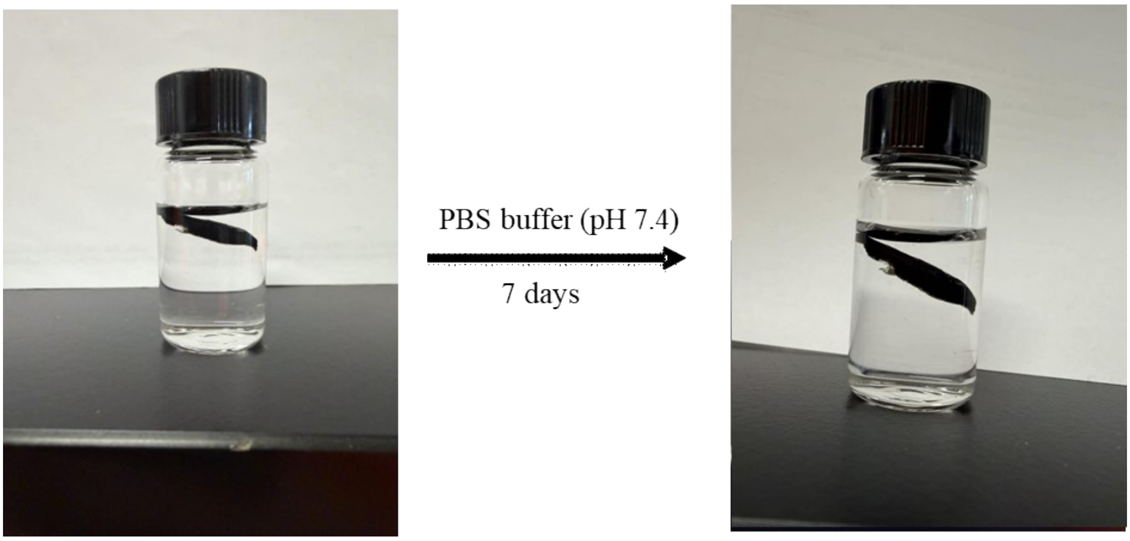


Figure S8. Physiological testing of hydrogel-composite ink with 1 *wt*% MWCNTs incorporation in PBS buffer for 36 hours. After the treatment, no carbon nanotube leakage was found visually and there was 17.6% increasing of water swelling and 35.4% increasing of electrical conductivity of the film was recorded.

Methods and characterisation

Materials and characterizations:

All the materials were purchased from Sigma-Aldrich unless stated otherwise. The ^{1}H-NMR measurements were conducted on Bruker Ascend 400 instrument. Compression tests were performed on Imada EMX Exceed series, with a fixed compression rate of 10 mm/min. DIW process were performed on a commercial 3D printer Zmorph VX 2038. Rheological studies were conducted on Anton Paar MCR 702 Dynamic Mechanical Analyzer at 25 °C. Amplitude sweeps were performed at a fixed angular frequency of 25 rad s^{-1} over a strain range of 0.1% to 100%. Viscosity was evaluated through shear rate sweeps ranging from 0.01 to 100 s^{-1}. Frequency sweeps were carried out from 0.01 Hz to 100 Hz under a constant strain of 0.5%.

Synthesis of parent polymer P_{RAFT}.

All chemicals used were purchased from Sigma-Aldrich unless otherwise specified. To a round bottom flask, methacrylic acid (1.37 mL, 15 mmol), oligo ethylene glycol methacrylate 500 (2.68 mL, 5.00 mmol), 2,2'-azobis(isobutyronitrile) (6.56 mg, 0.04 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (14.05 mg, 0.1 mmol) and 5.00 mL of anhydrous DMF were added, followed by degassing with nitrogen for 30 minutes at 0 °C. The mixture was then submerged in an oil bath maintained at 70 °C and heated with gentle stirring for 22 h. The resultant mixture was then precipitated into chilled diethyl ether (1:20 v/v ratio of reaction solution: ether) to generate a pale pink precipitate, which was then re-dissolve into 10 mL of RO water, dialysed for 48 hours, and the resulting solution dried at 50 °C to afford the purified parent polymer, P_{RAFT}.

Post-functionalization of P_{RAFT}.

To a conical flask, P_{RAFT} (3.50 g, containing 13.84 mmol of carboxylic acid groups), 4-hydroxyl benzaldehyde (1.69 g, 13.82 mmol), *N,N'*-dicyclohexylcarbodiimide (3.15 g, 16.40 mmol), 4-dimethylaminopyridine (278.72 mg, 2.31 mmol) and 6 mL of anhydrous DMF were added. The reaction was started at 0 °C in an ice bath with gentle stirring, then, after 24 hours, the mixture was filtered through a sintered funnel to remove DCU. The viscous, orange solution obtained was then precipitated into chilled diethyl ether (1:20 v/v ratio of reaction solution: ether), subsequently re-dissolved into 25 mL of de-ionized water and dialysed for 48 hours, the solution was then dried at 50 °C for 22 h followed by freeze-drying at -57.3 °C for 24 hours to offer the esterified polymer.

Synthesis of linear polyethylene imine.

Poly(2-ethyl-2-oxazoline) (Mn = 50 kDa, PDI < 1.3, 5.00 g, 0.1 mmol), 15 mL of deionized water, and concentrated hydrochloric acid (36.5 %, 45 mL) were added to a round bottom flask with gentle stirring. When the polymer was fully dissolved, the mixture was fitted with a condenser heated to reflux in an oil bath for 12 h. After the reaction was completed, the mixture was cooled to room temperature before being neutralised with 25% ammonia solution (50 mL). The solution afforded was then concentrated down to a volume of 30 mL under reduced pressure before dialysis in RO water for 48 h followed by dialysis in 10% aqueous ammonia for 24 hours. The white powder in the dialysis tubing was then collected, washed with 10% aqueous ammonia (3 × 10 mL) and RO water (5 × 10 mL), freeze-dried at -57.3 °C for 48 hours, after which we obtained purified L-PEI (0.61 g, 27% yield).

Preparation of printing ink for DIW process.

In this research inks with different composition were prepared, hence a model hydrogel composite-3 ink was typically chosen as an example. 2 mg of MWCNTs (O.D 6~13 nm x 2.5~20 µm) was suspended into 2 mL of Reverse Osmosis (RO) water with gentle ultrasonication (48 W, 35 kHz) for 30 minutes, then the suspension was added to sodium dodecyl sulphate (SDS) aqueous solution (1 mL containing 8 mg SDS) drop wisely, the mixture was then sent to high power ultrasonication (240 W, 40 kHz) for 20 minutes. Subsequently, 40 mg of L-PEI (20 kDa, PDI < 1.3) dissolved in 100 µL of methanol was added to the mixture to obtain a pre-gelled MWCNTs suspension, which was then added to the P1 solution (200 mg in 2 mL of water) followed by 20 minutes of high power ultrasonication, offering a solidified, black and uniform hydrogel ready for printing. After printing process, the shaped structure should be sent to dialysis (RO water, 48 h) to remove unbounded L-PEI residue before handling.

PBS buffer formulation and hydrogel physiological stability testing.

PBS buffer was formulated by 137 mmol of NaCl, 2.7 mmol of KCl, 10 nmol of Na_2HPO_4, and 1.8 mmol of KH_2PO_4, with a pH of 7.4.

A pre-weighed, small piece of hydrogel composite-3 (crosslinked with L-PEI 20kDa, feed aldehyde:L-PEI = 1;1 crosslinking ratio, loaded with 1 *wt*% of MWCNTs) was soaked in RO water for overnight and reached maximum swelling equilibrium; On the next day, weighed the mass of the hydrogel as well as the surface conductivity, and immerse the hydrogel into PBS buffer for 7 days. After 7 days, carefully take out the hydrogel composite sample and weigh the mass, measure the electrical conductivity.