Supporting Information for

Facile Fabrication of a Printable Conductive Self-Healing Hydrogel for Human Motion and Electrocardiogram Monitoring

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Additional Supporting Information may be found in the online version of this article.

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Experimental Section

Graphene Oxide Preparation: Graphene oxide (GO) was produced using modified Hummer's method from pure graphite powder. Briefly, 0.225 g graphite (99.95% 325 Mesh, Aladdin, Shanghai, China) was added into a mixing solution of 27 mL sulfuric acid (H_2SO_4) and 3 mL phosphoric acid (H_3PO_4, Real & Lead Chemical, Tianjin, China), followed by slowly addition of 1.32 g potassium permanganate ($KMnO_4$, Jiangtian Chemical, Tianjin, China) under vigorous stirring. This solution was kept stirring at room temperature for 6 h until it turned dark green. Then 0.675 mL hydrogen peroxide solution was dropwise added and the whole reactionware was set in an ice bath. Subsequently, 10 mL hydrochloric acid (HCl, Real & Lead Chemical, Tianjin, China) and 30ml of deionized water (DIW) was added and then the solution was centrifuged and washed with DIW until the PH of supernatant reach 7.0±0.2. The washed GO solution was then freeze-dried to obtain GO powders.

PVA/Agar-rGO-Gly Hydrogel Preparation: To synthesis PVA/Agar-rGO-Gly hydrogel, GO suspension was first prepared by dissolving certain amount of GO powders in DIW/glycerol and then sonicated for 30 min using a tip sonicator (180 W, Scientz-IID, Scientzbio, China). Then 0.25 g polyvinyl alcohol (PVA, type 1799, Aladdin, Shanghai, China) and certain amount of agarose (Transition Temperature 40 °C, Aladdin, Shanghai, China) was added into 5 mL above GO suspension. The pH of whole solution was adjusted to 10.0±0.1 by 1 M sodium hydroxide (NaOH) solution. Then the solution was heated up to 95 °C for 2 h under mechanical stirring. Afterwards, 1.25 mL of 4 wt% borax solution was added for crosslinking. A black hydrogel was

obtained and submerged in DIW for 12 h to equilibrate, then stored at 4 °C fridge before further use.

PVA/Agar-rGO-Gly Hydrogel Printing: PVA/Agar-rGO-Gly hydrogel was printed by a homemade 3D printer, which consisted of a computer controlled 3-axis movement platform, a screw-driven fluid dispenser, and a nozzle (18 Gauge). The hydrogel was loaded in a 5 mL syringe and heated up to 85 °C using a silicone rubber heat jacket. The as-prepared hydrogel was printed into a square pattern (speed was set as 3 mm/s.

Rheology Test: Dynamic rheological measurements were carried out using a DHR-2 rheometer (Waters, China). Test samples were made by molding the prepared hydrogel at 85 °C in a shape of cylinder (25 mm×25mm×1mm). For the frequency sweep test, frequency was varied from 0.01 to 10 Hz while strain was kept at 1%. For Temperature sweep test, frequency and strain were fixed at 10 Hz and 1% with temperature varied from room temperature to 80 °C. For the thixotropic test, shear rate was varied from 1 to 20 s^{-1} while the strain was fixed at 10%. In addition, applied strain amplitude was controlled at 1 % for 60 s and then 100% for 180 s, this procedure was repeated several circles.

Tensile experiment: The tensile tests were performed on a universal test machine (Instron, 5567, USA). The loading rate was 100 mm/min. The specimens were prepared using a standard dog-bone-shaped mold which had the width of 13 mm and the thickness of 3.2 mm. The gauge length between the clamps was 50 mm. The nominal stress (σ) was calculated by the following equation:

$$\sigma = \frac{F}{A} \#S1$$

where F is the tensile load and A is the cross-sectional area.

Morphology Characterization: The morphology of PVA/Agar-rGO-Gly hydrogel was observed using scanning electron microscopy (SEM, S-4800, Hitachi, Japan). Hydrogel samples were first lyophilized (starting temp. -196 °C) and then coated with platinum before test. Morphology of the *in situ* alkaline reduced graphene was observed by transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The sample was prepared using the same condition as described above without borax crosslinking, and the resultant solution was diluted for 100 times before test.

Spectrum Characterization: Spectrum characterization tests were performed using the lyophilized samples without any further treatments.

ECG Signal Measurement: ECG signals were collected by a portable ECG monitor (PC-80B, Healforce, China) using three electrodes in Einthoven's triangle. The test electrodes were prepared through the following steps: First, hydrogel layer of the commercial Ag/AgCl electrodes (CH50RB, Healforce, China) were peeled off and then scraped using a scraper to remove the Ag/Cl layer; subsequently, polished using 800#, 1000#, 1200#, and 1500# abrasive paper respectively; finally, scrubbed with 1M HCl and acetone and dried at ambient before use.

Electrical Experiments: Electrical experiments were performed on an electrochemical workstation (CHI660E, CH Instruments, China). For the shape changing resistance measurement, amperometric i-t curve mode was used with a constant potential of 3 V. For the AC impedance measurement, electrochemical impedance spectroscopy mode was applied.

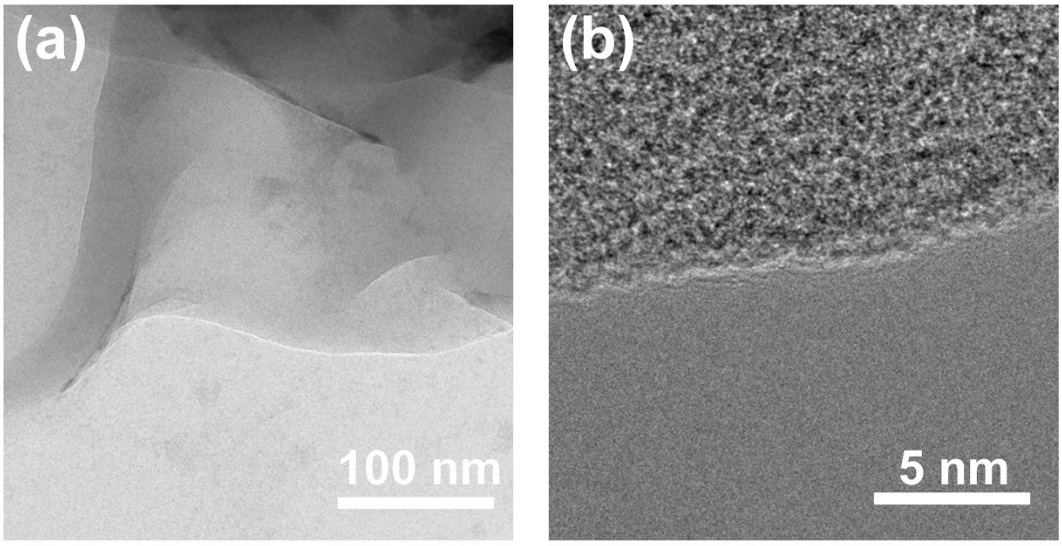

Figure S1. TEM images of rGO by alkaline heating reduction method in PVA/Agarose reaction solution.

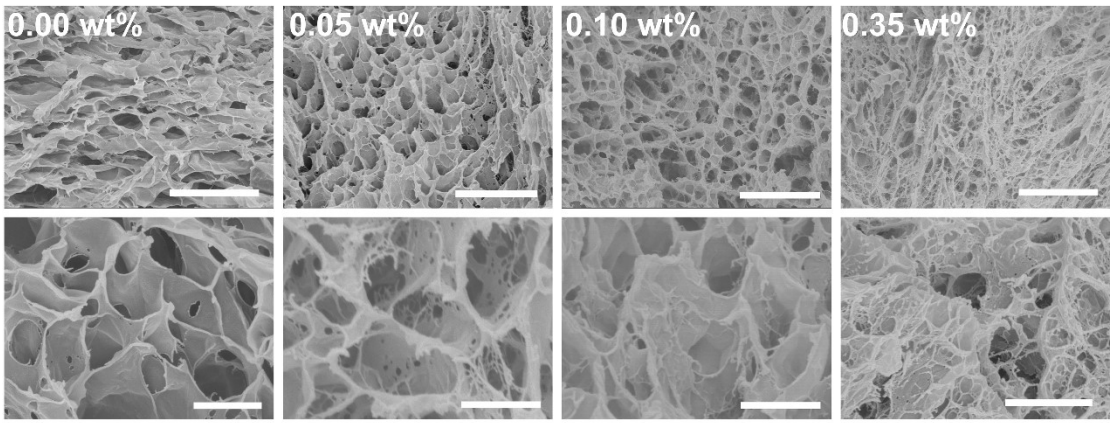

Figure S2. SEM images of as-prepared PVA/Agar-rGO-Gly hydrogel at different agarose addition. Scale bar: 5 μm and 1μm respectively.

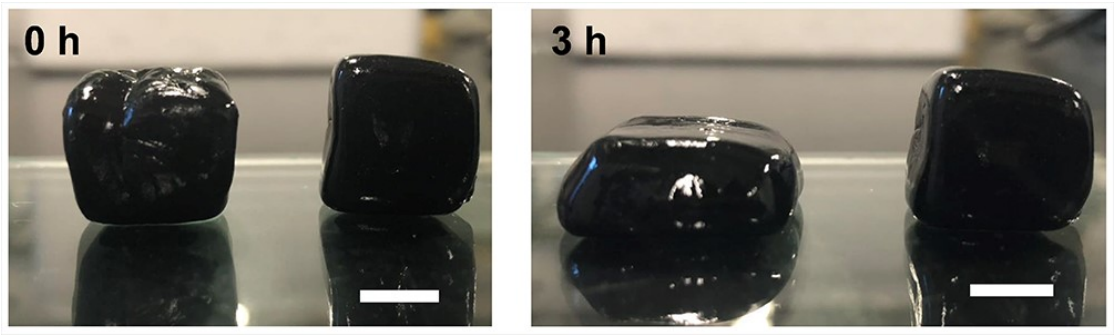

Figure S3. Free-standing property of the as-prepared hydrogel with (right) and without (left) addition of agarose. Scale bar is 5 mm. Samples were set still for 3 hours at 25 °C 80% R.H. in a Temp & RH Controlled Incubator.

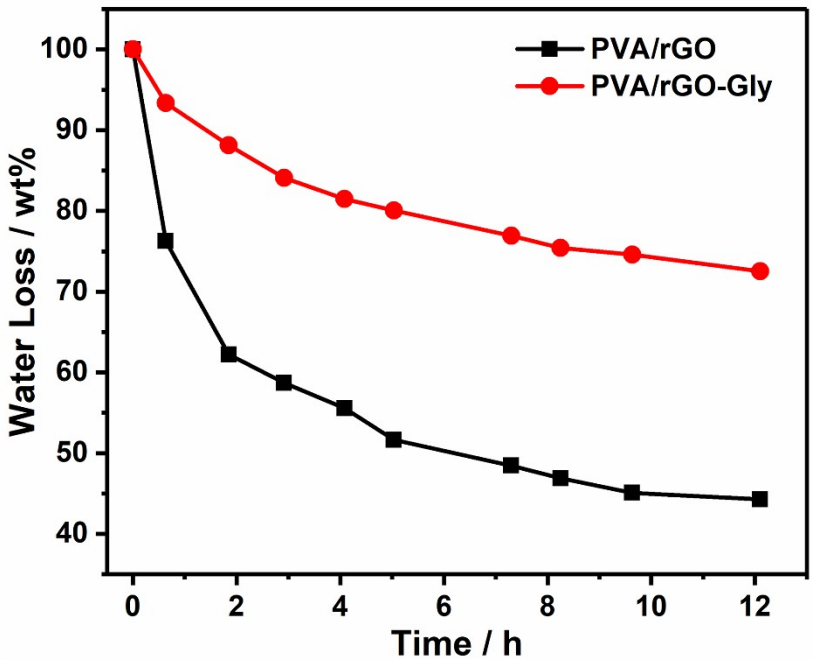

Figure S4. Water loss rate of as-prepared rGO hydrogel with and without glycerol.

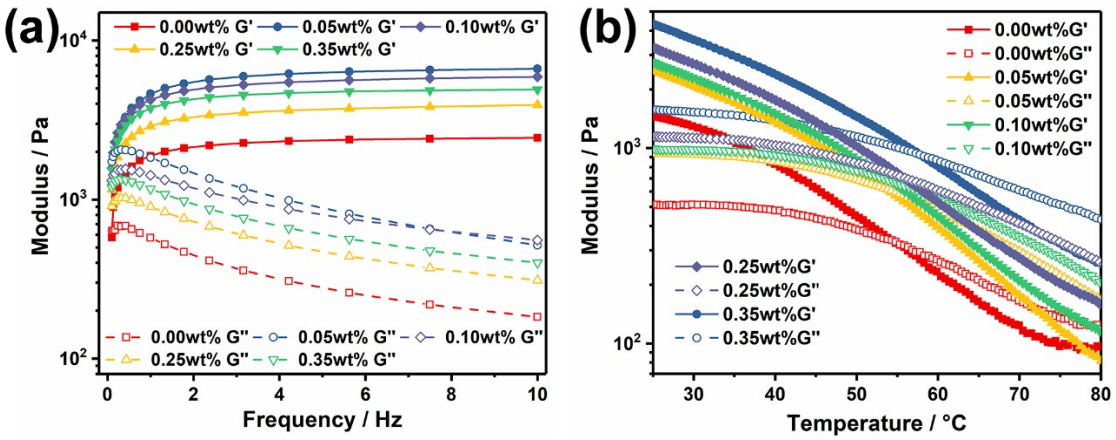

Figure S5. (a) Frequency-dependent (strain of 1%) oscillatory rheology and (b) temperature sweep of oscillatory rheology test at different agarose addition.

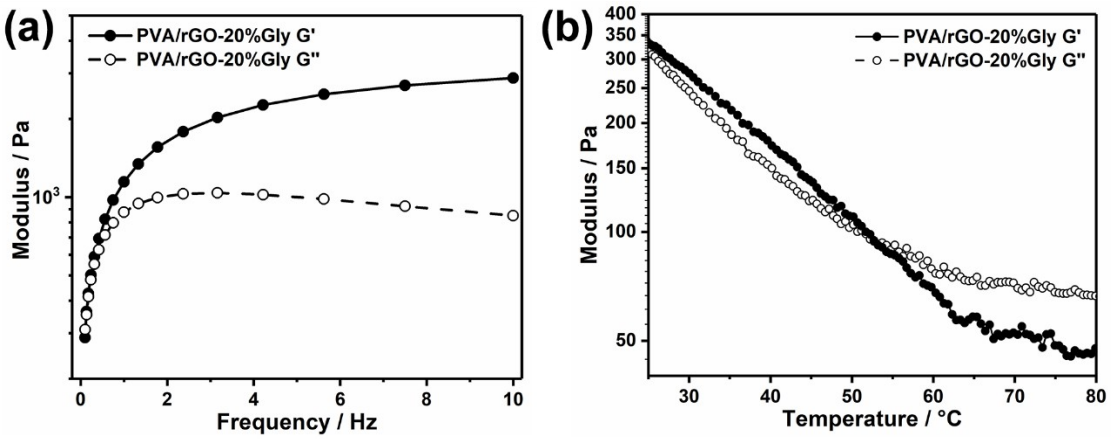

Figure S6. (a) Frequency-dependent (strain of 1%) oscillatory rheology and (b) temperature sweep of oscillatory rheology test for PVA/Agar-rGO hydrogel with 20 wt% glycerol.

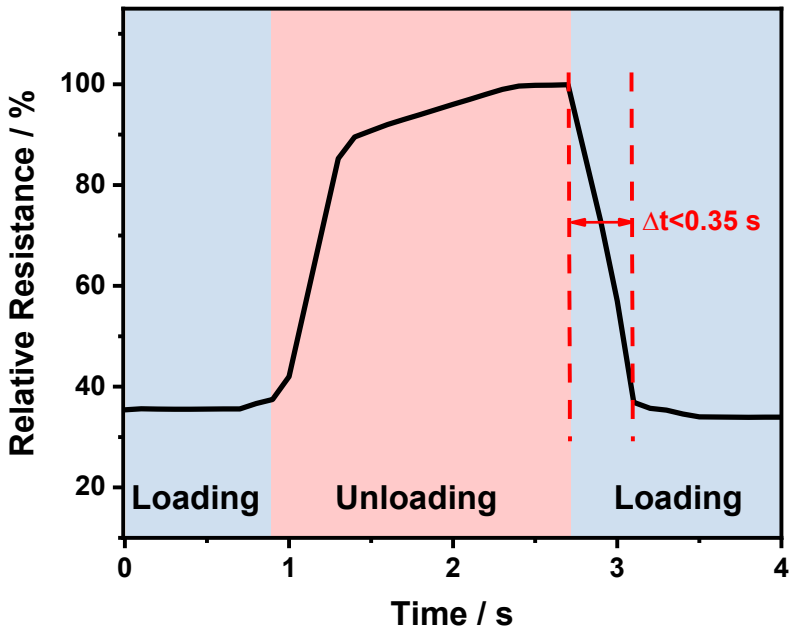

Figure S7. Response time of as-prepared PVA/Agarose-rGO hydrogel sensor.

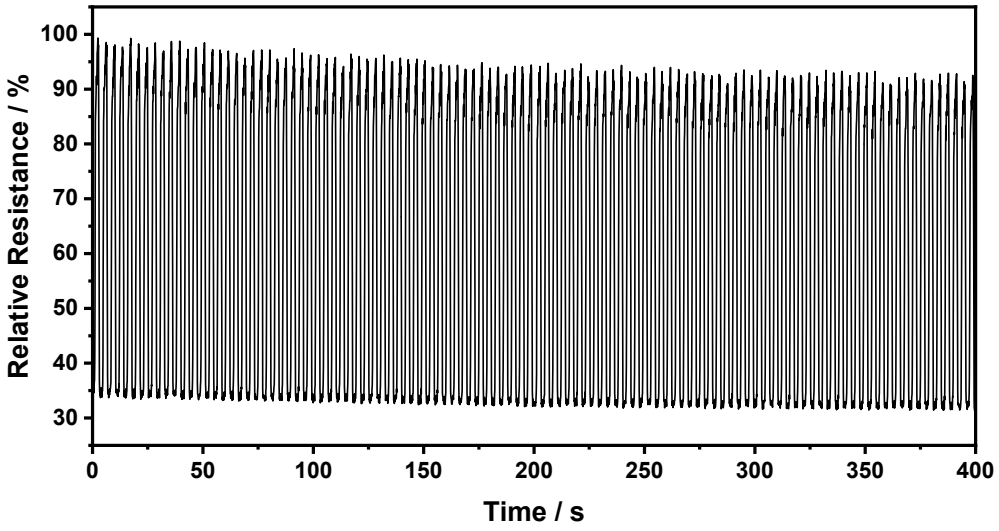

Figure S8. Relative resistance change of PVA/Agar-rGO-Gly sensor for up to 100 cycles with repetitive 4 kPa loading.

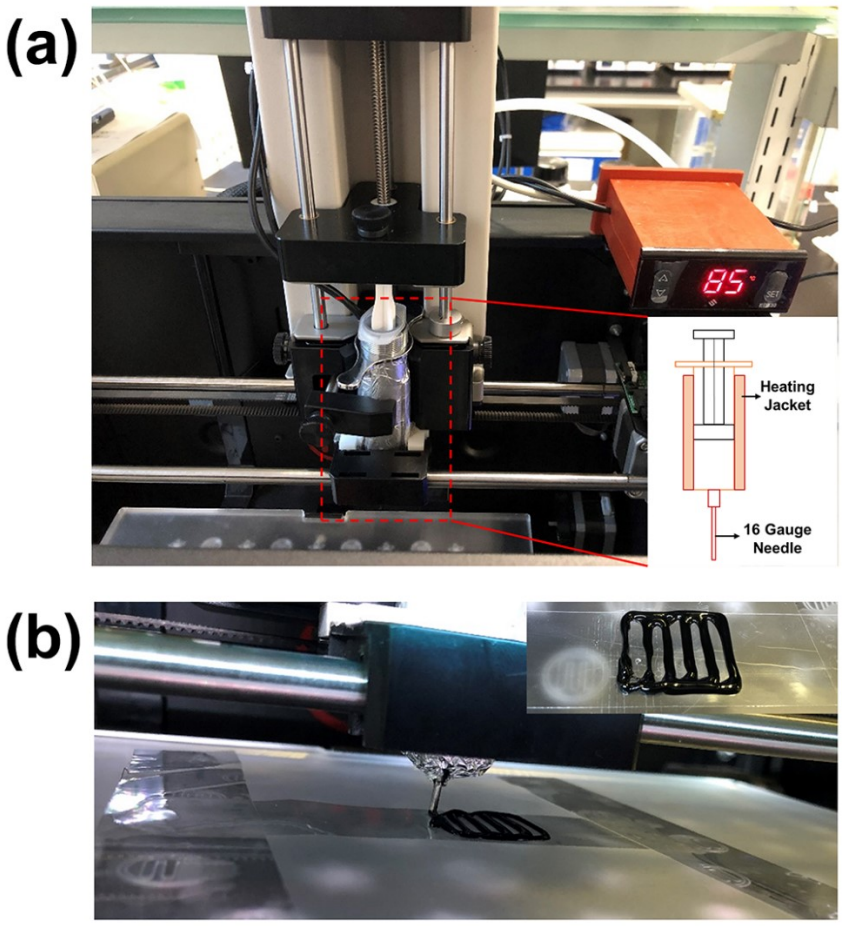

Figure S9. (a) 3D printing setup and (b) printing process.

Table S1 Performance comparison of PVA hydrogel with difference compositions.

Sample	Conductivity ($S \cdot cm^{-1}$)	Self-Healing Time (s)	Self-Standing Time (min)	Stretchability	Reshapability at 85 °C
Ag0Gly10rGO5	1.23×10^{-3}	2	2	2000%	good
Ag5Gly10rGO5	1.19×10^{-3}	5	5	1100%	good
Ag10Gly10rGO5	1.15×10^{-3}	12	20	350%	good
Ag25Gly10rGO5	1.28×10^{-2}	30	＞180	250%	good
Ag35Gly10rGO5	9.45×10^{-3}	50	＞180	130%	good
Ag0Gly0rGO5		5	5	1300%	good
Ag5Gly0rGO5		10	30	800%	good
Ag10Gly0rGO5		60	60	180%	good
Ag25Gly0rGO5		120	＞180	150%	good
Ag35Gly0rGO5		200	＞180	110%	good
Ag5Gly20rGO5		＜2	1.5	1200%	good
Ag25Gly20rGO5		5	5	500%	good
Ag25Gly10rGO1	3.6×10^{-3}	30	＞180	250%	good
Ag25Gly10rGO2	5.59×10^{-3}	30	＞180	250%	good
Ag25Gly10rGO3	9.26×10^{-3}	30	＞180	250%	good
Ag25Gly10rGO4	1.01×10^{-2}	30	＞180	250%	good
Ag25Gly10rGO6	1.33×10^{-2}	30	＞180	260%	good

[a] Ag: agarose, wt‰. Gly: glycerol, wt%. rGO: mg/mL. PVA content was fixed at 5 wt%.