Supporting Information

Natural Polyphenolic Nanodots-Knotted Conductive Hydrogels for Flexible Wearable Sensors

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Materials

Gallic acid (GA, 98%), Acrylamide (Aam, 98%), and Methylene-Bis-Acrylamide (MBA, 99%) were purchased from Energy Chemical (Shanghai, China). $FeCl_3 \cdot 6H_2O$ (99%), acrylic acid (99%, containing 180-200 ppm MEHQ), and poly (ethylene glycol) diacrylate (Mw ~1000, containing 100ppm MEHQ and 300ppm BHT) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Epicatechin (98%), epigallocatechin gallate (EGCG, 98%), and chlorogenic acid (98%) were obtained from Dasf biotechnology Co., Ltd. (Nanjing, China). Pyrogallol was purchased from J&K Chemical Ltd (Beijing, China). Ammonium persulfate (APS, AR), tertiary butanol (AR), and potassium iodide (AR) were purchased from Chengdu Kelong Chemical Reagent Co. Ltd.

All reagents are freshly used as received.

Characterization

Transmission electron microscopy (TEM) images were performed on FEI transmission electron microscope (F20). A Zetasizer NanoZS (Nano ZS ZEN 3690) was applied to measure zeta potentials and size distribution. The UV-Vis absorption spectra were detected on a micro-spectrophotometer with a 1 cm quartz cell (PerkinElmer, Lambda 650). ICP-OES results were determined by Agilent ICP-OES 5100 SVDV. The samples were dipped in concentrated nitric acid overnight, which was diluted to tested solution with ~1% nitric acid. The elemental composition of the sample surfaces was examined by X-ray photoelectron spectroscopy (PHI Quantera SXM spectrometer) using Al Kα X-ray radiation. Cyclic voltammogram (CV) measurements were performed on a CHI760E electrochemical workstation using indium tin oxide (ITO) coated with sample as the working electrode. Pt wire was as the counter electrode, and Ag/AgCl was as the reference electrode in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. Electron Paramagnetic Resonance (EPR) spectrum was performed on Bruker EPR EMX_Plus. The dynamic rheological experiment was carried out on AntonPaar MCR 302e.

Synthesis of natural polyphenolic nanodots

Five natural water-soluble polyphenols (gallic acid, epicatechin, EGCG, chlorogenic acid, and pyrogallol) were selected. 12.5 mg polyphenols were solved in 9 mL deionized water. 25 mg $FeCl_3 \cdot 6H_2O$ was solved in another 1 mL. Then, the $FeCl_3$ solution was dropwise added into the polyphenol solution. The mixture was stirred for 2 hours at room temperature. Afterwards, the solution was filtered through a 0.22 μm membrane filters (Beijing Balb Technology Co. Ltd.), then dialyzed against water through a dialysis bag (molecular weight cut-off 3500 Da) for 48 h. Finally, the obtained purified polyphenol/metal nanodots were freeze-drying and stored for further use.

Synthesis of hydrogels based on GA/Fe^{3+} NDs

First, 1 mg/mL GA/Fe^{3+} NDs solution, 10 mg/mL MBA solution, and 10 mg/mL APS solution were prepared. GA/Fe^{3+} NDs solution, MBA solution, and water were mixed.

Then the APS solution was injected into the mixed solution. The components of hydrogels for the experiences are listed in Table S1-2.

Radical quenched tests

Taken GA/Fe^{3+}-0.4 (Table S1) formulation as example. Before adding APS, 10 mg tertiary butanol (or 4 mg KI) was added. After mixing, the APS solution was injected. The final solution was observed after 3 min.

Free GA and Fe^{3+} for gelation

According to the ICP results, GA/Fe^{3+} NDs was replaced with equal GA and Fe^{3+}. The components of hydrogels for the experiences are listed in Table S3.

Mechanical tests

The mechanical tests were performed on a texture analyzer (TA.XTC-20, Bosintech, China) equipped with a 50 N sensor at room temperature. For tensile tests, the hydrogel was prepared in a dumbbell shaped mold (PTFE) with a gauge length of 25 mm, width of 2.5 mm, and thickness of 2 mm. The stretch rate was at 1 mm/s for normal tensile tests and cyclic tensile tests. The tensile stress was determined as the loading force divided by the cross-sectional area of the original sample. The elongation ratio was defined as the ratio of the elongation at break to the initial length. Young' modulus was calculated based on the initial linear slope of the stress-stain curve (5-20% stain). Toughness was got by integrating the area underneath the stress-stain curve. Strength and ductility product was the product of tensile strength and elongation ratio. For compressive tests, the hydrogel was prepared in a cylindrical shaped mold (PTFE) with a height of 10 mm and diameter of 10 mm. The loading rate was at 0.5 mm/s for normal tensile tests and cyclic tensile tests. The stain was fixed at 70%. Dissipated energy was estimated from integrating the area between the stress-stain curve. A little silicone oil was covered on hydrogel to avoid the bias from adhesion.

Adhesion tests

The hydrogel was cut to a size of 10 mm × 20 mm. Two pieces of thin substrates were pasted on the surfaces of hydrogel with a junction area of 10 mm × 20 mm. The sandwich-like samples were wrapped with preservative film and compressed with a weight of 100 g for 6 h. The adhesion tests were performed on a texture analyzer (TA.XTC-20, Bosintech, China) equipped with a 50 N sensor at room temperature. The stretch rate was at 0.1 mm/s until the split of the junction. The adhesion strength was determined as the loading force divided by the contact area.

Conductivity tests

The conductivity of the hydrogel was tested by CHI760E electrochemical workstation. Stripe hydrogels were sandwiched by copper tapes. Different fixed electric current was applied (0.0002 A, 0.0004 A, 0.0006 A, 0.0008 A, 0.0010 A) for 30 s. Then, the potential was recorded. The conductivity of the hydrogel was determined by the followed equation

$$\sigma = \frac{I * l}{V * d * h}$$

where I was the electric current, V is the potential, l, d, and h were the length, width, and thickness of hydrogel.

Preparation and tests of stain sensor

The sensor was fabricated by fixing two Pt wires in two ends of the hydrogel (dumbbell shape with a gauge length of 25 mm, width of 2.5 mm, and thickness of 2 mm). During the test, the stain was recorded by a texture analyzer (TA.XTC-20, Bosintech, China) and the electric current was recorded by CHI760E electrochemical workstation (fixed potential: 10 V. ΔR/R was calculated to evaluated the sensor property according to the followed equation

$$\Delta R/R_0 = (R - R_0)/R_0$$

where R and R_0 were the real-time resistances with and without stain during the test, respectively. The gauge factor (GF) was defined and calculated by the followed equation

$$GF = \frac{(R - R_0)/R_0}{\varepsilon}$$

where R and R_0 were the real-time resistances with and without stain during the test, respectively. ε was the stain of the hydrogel.

For monitoring human activities, the sensor was directly adhered on the skin.

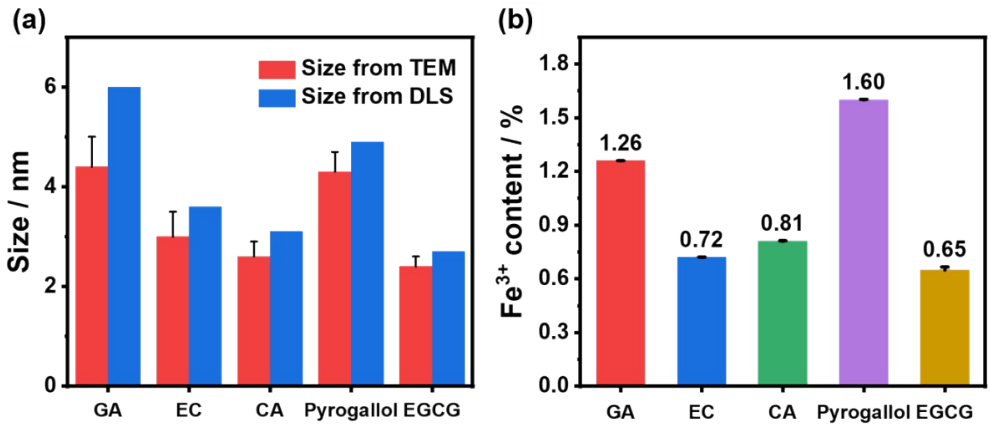

Figure S1. (a) Size of different nanodot from five kinds of polyphenols. (b) Fe^{3+} content of different nanodot from five kinds of polyphenols.

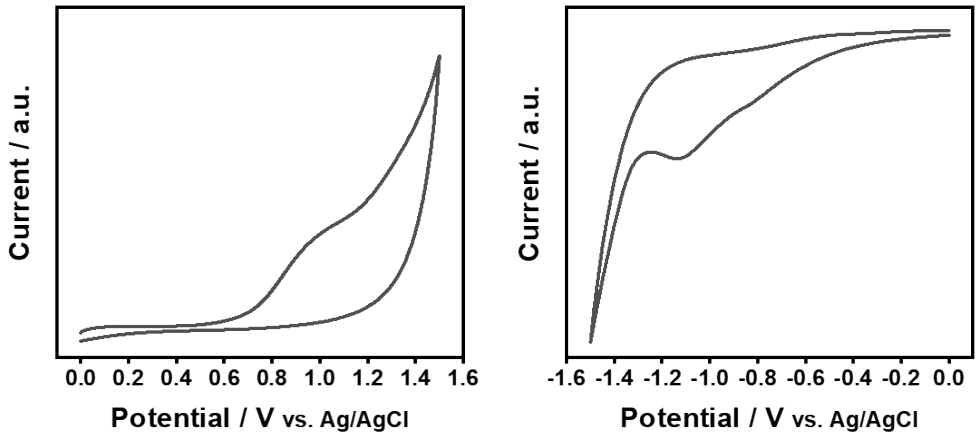

Figure S2. CV curves of GA/Fe^{3+} NDs.

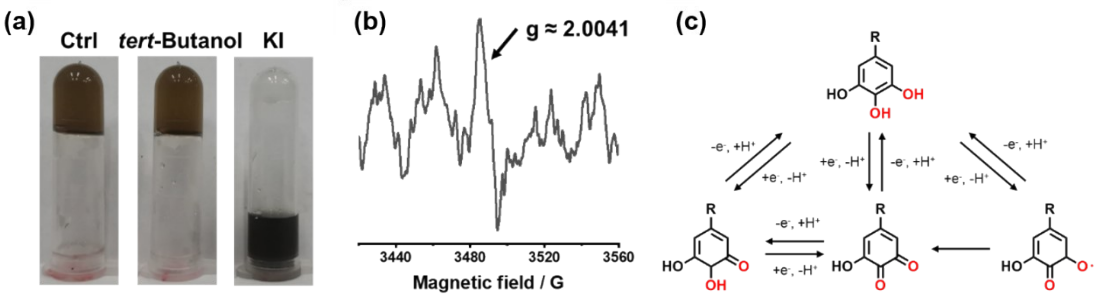

Figure S3. (a) Optical photos of hydrogel formation in the present of tert-butanol and KI. (b) EPR spectrum of GA/Fe^{3+}. (c) The proposed semiquinone radicals' formation process in GA/Fe^{3+} NDs.

Table S1. The content of different components of the different type hydrogels

	GA/Fe^{3+} NDs solution / mL	Monomers	MBA solution / mL	H_2O/mL	APS solution / mL
PAA	0.2	2.7 mL	0.425	7.375	2
PAAm	0.2	2.6 g	0.39	7.61	2
Poly(PEGDA)	0.2	1.2 g	—	7.8	2

Table S2. The content of different components of the GA/Fe^{3+} hydrogels (AAm: 0.5 g/mL, MBA: 0.75 mg/mL, APS: 2.5 mg/mL)

	GA/Fe^{3+} NDs solution / mL	AAm / mg	MBA solution / mL	H_2O / mL	APS solution / mL
GA/Fe^{3+}-0.1	0.1	400	0.06	0.64	0.2
GA/Fe^{3+}-0.2	0.2	400	0.06	0.54	0.2

GA/Fe^{3+}-0.4	0.4	400	0.06	0.34	0.2
GA/Fe^{3+}-0.6	0.6	400	0.06	0.14	0.2

Table S3. The content of different components for gelation

		AAm	MBA	H_2O	APS
Nanodot	GA/Fe^{3+} NDs 0.1 mg	0.5 g	0.75 mg	1 mL	1 mg
Free monomer	Gallic acid 0.0987 mg $FeCl_3 \cdot 6H_2O$ 0.0063 mg	0.5 g	0.75 mg	1 mL	1 mg

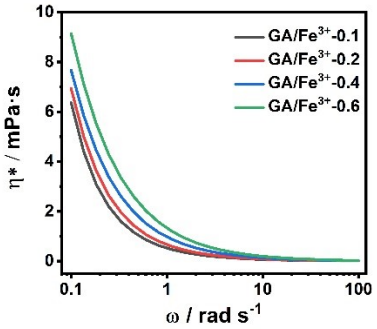

Figure S4. Elongation ratio of different GA/Fe^{3+} hydrogels.

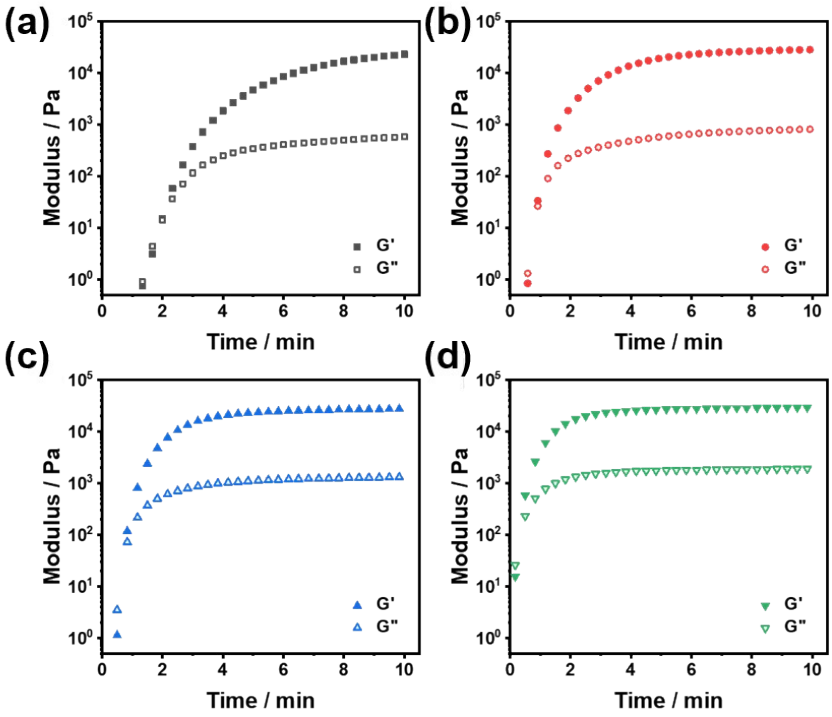

Figure S5. Dynamic storage modulus (G′) and loss modulus (G″) at different time points of different GA/Fe^{3+} hydrogels (a) GA/Fe^{3+}-0.1, (b) GA/Fe^{3+}-0.2, (c) GA/Fe^{3+}-0.4, and (d) GA/Fe^{3+}-0.6.

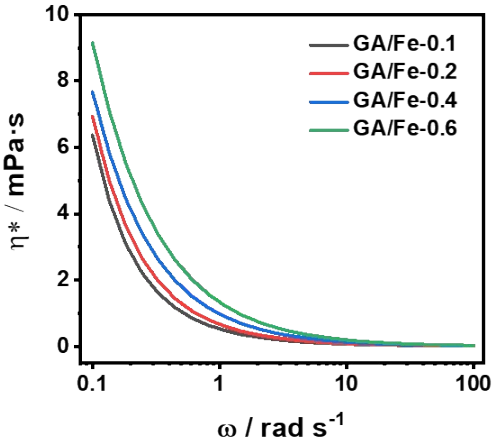

Figure S6. Shear-thinning of different GA/Fe^{3+} hydrogels.

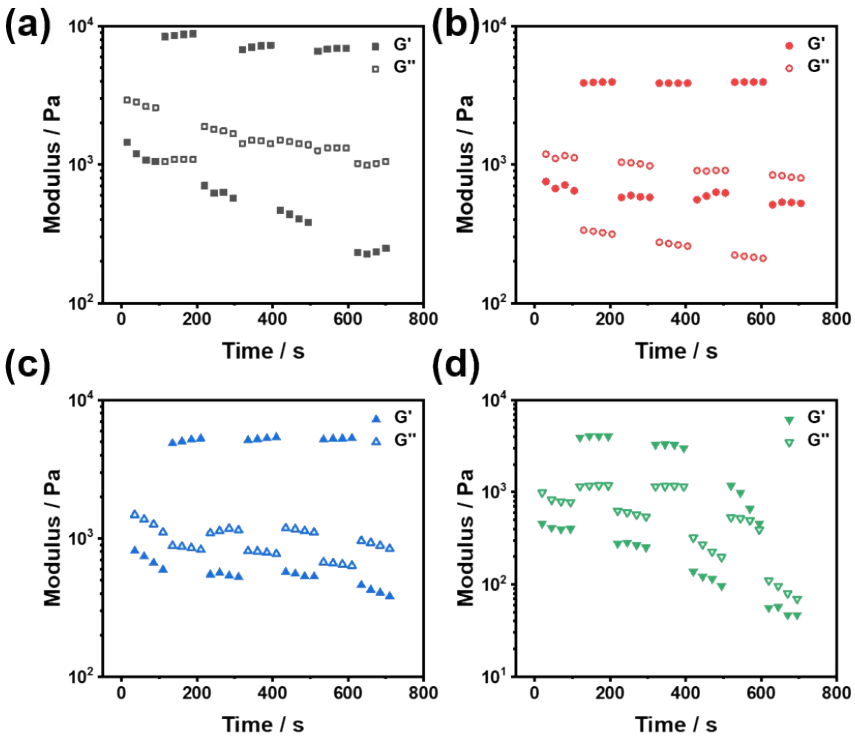

Figure S7. Thixotropic test by continuous step strain measurement of the model hydrogel. (alternating strain: 2 and 120%, angular frequency 10 rad/s)

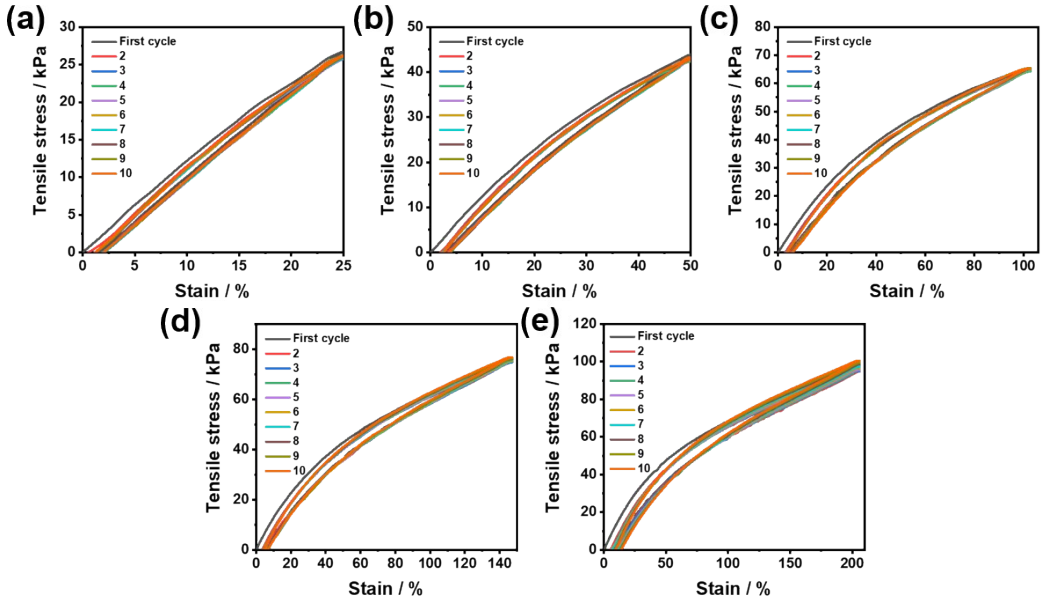

Figure S8. Successive tensile loading–unloading curves of GA/Fe^{3+}-0.4 as stretching to different strains (a) 25%, (b) 50%, (c) 100%, (d) 150%, and (e) 200%.

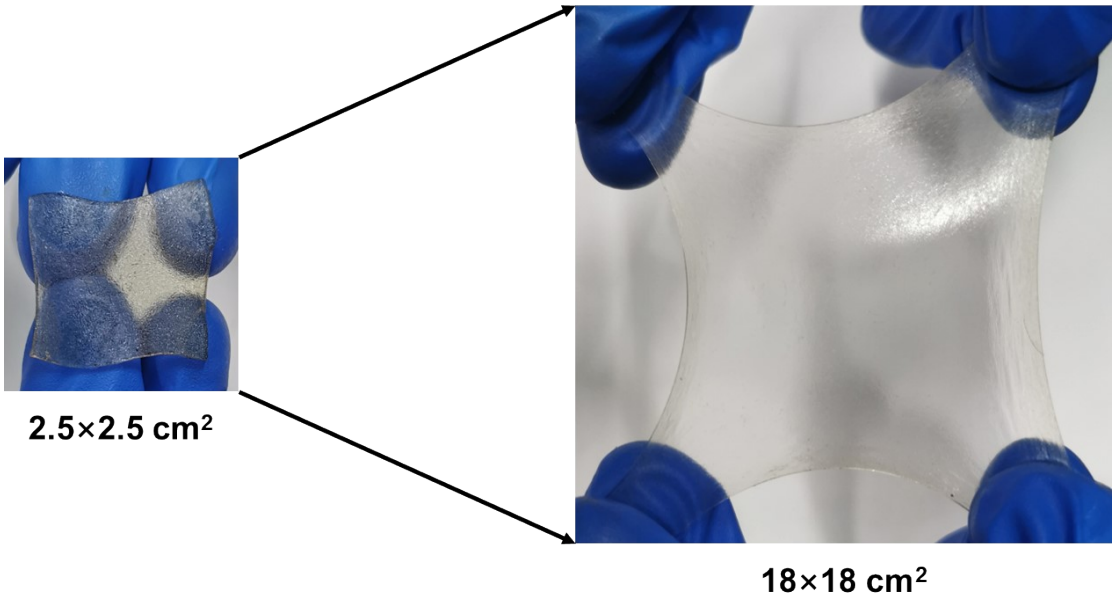

Figure S9. Biaxial tension of a square GA/Fe^{3+}-0.4.

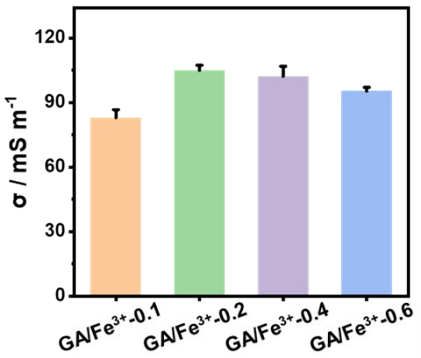

Figure S10. Conductivity of different GA/Fe^{3+} hydrogels.

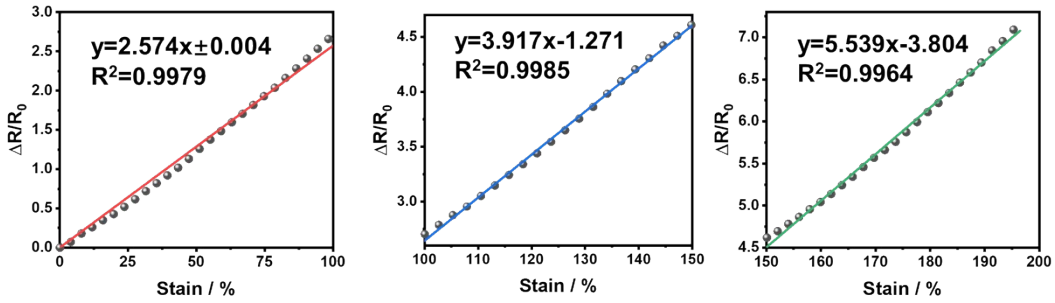

Figure S11. The relationships between relative resistance change and applied strain when applied different stain.