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## **Supporting Information**

## Highly Stretchable Supramolecular Conductive Self-Healable Gels for Injectable Adhesive and Flexible Sensor Applications

Amir Khan,<sup>a</sup> Ravinder Reddy Kisannagar,<sup>b</sup> Chinmayananda Gouda,<sup>a</sup> Dipti Gupta,<sup>b</sup> Hong-Cheu Lin<sup>\*a,c</sup>

<sup>a</sup>Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan.

<sup>b</sup>Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra 400076, India.

<sup>c</sup>Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 300, Taiwan.

\*Corresponding author: linhc@mail.nctu.edu.tw

## **Experimental Section**

**Materials:** DI-thioctic acid (TA, 98%) was purchased from TCI. 1, 2, 4, 5-benzenetetracarboxylic acid (pyromellitic acid, PA, 96%) and iron (III) chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O, 99%) were received from Acros Organics. Ammonium peroxydisulfate (APS, 98%) and aniline (ANI, 99+%) were bought from Alfa Aesar and dimethyl sulfoxide (DMSO, anhydrous, Baker Analyzed<sup>®</sup> A.C.S. Reagent) was purchased from Avantor. DI water was used to prepare for the APS aqueous solution. All materials were used as soon as received.

Synthesis of TA-PA-Fe(III)-PANI Based Conductive Self-Healable Gel: The highly stretchable selfhealable conductive gel was prepared via ring-opening polymerization of TA along with a conductive rigid network of PANI and Fe(III). Initially, 2g (9.9 mmol) of TA was added in a glass vial and heated to melt at 60 °C. After 5 min. of heating at 60 °C, a light yellow transparent liquid polythioctic acid (PTA) was obtained and then a small magnetic stirrer was used to make a complete melt at 500 rpm. After the polymerization of TA, PTA was cooled down to room temperature to acquire a yellow solid. Thereafter, 1.1 ml of DMSO was added for further supramolecular crosslinking of PTA with PANI and PA via hydrogen-bonds as well as Fe<sup>3+</sup> ion via coordination. Then, the previous solution was placed over a hot plate at 50 °C with stirring for 5 min. When a uniform yellow solution appeared, 500 mg (1.96 mmol) of PA was added into the solution with stirring at 700 rpm and heating at 40 °C. After 5 min., the solution turned into semi-transparent. Then, four different amounts (19.65 mg, 26.1 mg, 32.75 mg, and 39.29 mg) of FeCl<sub>3</sub>.6H<sub>2</sub>O (i.e., 0.75, 1.0, 1.25, and 1.5 mol% of Fe<sup>3+</sup> ion to TA) in 0.9 ml of DMSO was added with stirring at room temperature. The color was then turned to red. After 5 min. stirring, 20µl of aniline (0.2 mmol) was added inside the solution under vigorous stirring and kept in an ice bath. Meanwhile, 274 mg (1.2 mmol) of APS in 1 ml of DI water was mixed properly and kept inside an ice bath. This APS solution (1.2 mol L<sup>-1</sup>) was added slowly into the previously prepared PTA- PA-Fe(III)-ANI solution under 200 rpm. The color was turned to black to confirm the polymerization of aniline to polyaniline (PANI). Then, it was heated up to 80 °C for proper mixing under vigorous stirring for 5 min. and transferred to an ice bath for overnight stirring at 120 rpm to form conductive self-healable gels (CSGs). The molar ratio of PA to TA monomer was 1:5 and the molar ratio of aniline monomer (ANI) to PA was 1:9 in the final product of highly stretchable CSGs.

**Lap Shear Adhesion Test:** The supramolecular CSG (i.e., CSG1.0Fe) was adhered between two substrate surfaces (with a contact area of 1.0 cm× 1.0 cm and a rough thickness of 200  $\mu$ m) of different materials (rubber, paper, cotton, wood, and so on). The lap shear adhesion tests were performed by using MTS Tytron 250 instrument, where both substrates were fixed by machine holders in a parallel direction, and the strain rate was fixed at 30 mm/min.

**Sample Preparation for Mechanical & Electrical Tests:** Initially, a channel (30 mm length, 5 mm width, and 2 mm thickness) was made over a glass substrate using double-sided GLOBE TAPE as channel side supporters to maintain the thickness of the channel. The CSGs were placed inside the channel followed by heating over the hot plate at 50 °C, then the gels with a fixed channel shape were obtained after removing from the hotplate. After cooling, the well-shaped CSGs were separated using a sharp knife and proper lengths were cut for further measurements.

**Mechanical Tests:** All mechanical stress-strain tests were performed using MTS Tytron 250 tensile system with horizontally placed holders. All CSGs were shaped as 5 mm×5mm×2mm for tensile testing keeping a constant tensile speed of 30mm/min. The tensile stress ( $\delta$ ) is calculated by  $\delta$ =F/A, where F represents the tensile load value whereas A represents a cross-sectional area of the rectangular-shaped gel. The strain ( $\epsilon$ ) is calculated by  $\epsilon = (\Delta L/L_0) \times 100 \%$ ,  $L_0$  denotes the initial length and  $\Delta L$  denotes the change in length after stretching.

**Electrical Tests of Strain & Pressure Sensing Performance:** Electromechanical tests were measured at ambient atmosphere using Mark 10 Force Torque Measurement Products (USA) & a digital source meter (keithley 2450, Tektronix Inc., USA) at a constant bias of 1V. The authors were involved in real time motion detection experiments and are well aware of the experiment.

**Other Performed Characterizations:** The chemical structures of the CSGs were characterized by <sup>1</sup>H NMR spectroscopy using Bruker DRX-300 Avance series (300 MHz) at room temperature, where chemical shifts were referenced to DMSO-d<sub>6</sub>  $\delta$ =2.52 ppm. The morphological characteristics were studied by Field Emission Scanning Electron Microscope (JEOL JSM-6700F). Before measurements, the CSGs were freeze-dried over glass using liquid nitrogen and then coated with a thin layer of gold for 100 sec. The FTIR data were recorded over the range of 400-4000 cm<sup>-1</sup> for CSGs and monomeric powder by using the PerkinElmer spectrum 100 FTIR (with a resolution of 4 cm<sup>-1</sup>), where KBr was used as a powder reference. The Raman spectrum was obtained by using Horiba Jobin Yvon Labram HR 800 Raman spectroscopy with 514.5 nm Ar laser. The Olympus BX51 microscope & EOS200 camera was used to show the mechanical self-healing process. The thermal decomposition properties were recorded by the Q500 thermogravimetric analysis (TGA) instrument (heating rate 10 °C/min) and the thermal properties were measured using the Pyris<sup>™</sup> Diamond DSC-PerkinElmer (heating/cooling rate=10 °C/min). The high-resolution XRD data were obtained from beamline BL17A at National Synchrotron Radiation Research Center (NSRRC), Taiwan ( $\lambda$ =1.02108 Å).



**Figure S1.** Photographs of each step during the CSG-forming process: (a) TA monomer powder (b) PTA (transparent yellow) after polymerization by heating TA to melt at 60 °C for 5 min (c) After the addition of  $Fe^{3+}$  ion inside PTA (reddish color) (d) After the formation of conductive PANI inside CSG product (black color).

**Table S1.** Concentration Effects of  $Fe^{3+}$  ion on Gel Properties of CSGs with Fixed Amounts of TA, PA, and APS (20µl aniline was added as a conductive component).

Name	TA (g)	PA (g)	FeCl <sub>3</sub> .6H <sub>2</sub> O/TA (mol %)	APS (mg)	Gel property	Optical image
Without Fecl <sub>3</sub> .6H <sub>2</sub> O	2	0.5	0.0	274	No gelation	
CSG0.75Fe	2	0.5	0.75	274	Mechanically Weak structure	
CSG1.0Fe	2	0.5	1.00	274	Mechanically stable structure	
CSG1.25Fe	2	0.5	1.25	274	Poor structure	

CSG1.5Fe	2	0.5	1.5	274	weak structure	
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**Table S2.** Comparative Study of Conductive Self-healable Sensors. (Auto: autonomous; Non: Non-autonomous)

Ref.	Classifi	Self-healing	Combinations	Healing	Mechanical	Electrical	Toughness	Strain	Year
	-cation	mechanism	combinations	conditions	healing	healing	(MJ/m³)	(%)	
1	Auto	H-bonding	Silicon microparticle- conductive carbon black nanoparticles	RT	90 % 3 hr	1 min	-	300	2013
2	Non	Host-guest interaction	β-Cyclodextrin decorated single- walled carbon nanotubes and adamantine acetic modified polyethyleneimine oligomer complex	Water	90 % 5 min	90 %	-	7	2015
3	Auto	Hydrogen and disulfide bond	Hyperbranched poly(amidoamines) and carbon nanotubes	RT	50 % 1 min	100 % 18 min	-	-	2015
4	Auto	lonic bond and chemical bond	PAA, PPy, chitosan, MBAA, Fe <sup>3+</sup>	RT	100 % 2 min	96 % 1 min	-	1500	2016
5	Auto	H-bonding	CNT, Borax, PVA	RT	60 s	(98±0.8) % 3.2 s	-	1000	2017
6	Auto	lonic bonding	PAA, CNC-TA, Al <sup>3+</sup>	placed in a sealed vessel to minimize the effect of water evaporatio n at 25°C	92 % 30 min	97.1 % 3 s	5.6	2952	2018
7	Auto	Reversible physical crosslinking	Zwitterionic nanocomposite	RT	74 % 24 hr	11 s	2.45	2000	2018
8	Auto	Metal- coordinated bonding, tetrahedral borate interactions	PAA, PVA, Fe <sup>3+</sup> , CNT, PEDOT:PSS	Heat needed for mechanica I healing & Ambient condition for electrical healing (no external stimulus needed)	90.4 % 6 hr	125 ms	-	550	2019
9	Auto	H-bonding and	PANI/PSS-UPy	RT	30 s	30 s	-	300	2019

		electrostatic interaction							
10	Auto	H-bonding	TA, SA, PAM	RT	96 % 2 hr	-	1.1	4000	2019
This work	Auto	Hydrogen bonding & ionic bonding	Thioctic acid, pyromellitic acid, Fe <sup>3+</sup> , polyaniline	RT	100 % 90 s	95 % 0.7 s	5.795	5000	2020



**Figure S2.** <sup>1</sup>H NMR spectrum (300 MHz, 298K, DMSO- $d_6$ ) of CSG1.0Fe. DMSO- $d_6$  solvent was taken in a very little amount so that the degree of polymerization of the supramolecular polymer network had the least impact by solvent.



**Figure S3.** SEM images of (a) CSG in the presence of PANI network (porous) at different magnifications and (b) CSG without PANI network (uniform mixing without any porosity) at different magnifications.



Figure S4. Schematic representation of the effect of Fe<sup>3+</sup> inside the CSG network with (a) less Fe<sup>3+</sup> ions and

(b) more Fe<sup>3+</sup> ions.



**Figure S5.** Effects of physical crosslinker PA in conductive self-healing gels (CSGs with 1 mol% Fe<sup>3+</sup> ion) on (a) stress-strain curves and (b) XRD spectra with different weight ratios (0, 15, 25, and 35 wt%).

Increasing the amount of physical crosslinker PA in Figure S5a, the mechanical strengths and stiffnesses of CSGs were enhanced, but the stretchabilities were decreased due to more crosslinking sites. Without crosslinker PA, the gel structure has a weak mechanical strength with very high stretchability and the calculated toughness is 2.2 MJ/m<sup>3</sup>. However, the addition of crosslinker PA with 15 wt% (1.18 mmol; 300 mg), 25 wt% (1.96 mmol; 500 mg), and 35 wt% (2.76 mmol; 700 mg) will increase the toughness of CSGs to 4.2, 5.79, and 5.35 MJ/m<sup>3</sup>, respectively, where all values of PA wt% were calculated with respect to TA weights. With the increase of crosslinker PA in Figure S5b, the XRD peak is enhanced to have higher crystallinities and shifted towards wider angles ( $2\theta = 17.2^{\circ}$  to  $18.4^{\circ}$  with respective d spacing values of 3.4 Å and 3.2Å obtained at beamline TLS-17A1, NSRRC with the incident beam of =1.02108 Å) due to the higher amounts of PA and the reduced inter-chain distances.



Figure S6. Stress-strain curve of ultrafast self-healable CSG1.0Fe at different healing time.



**Figure S7.** Demonstration of ultrafast self-healability of CSGs: (a) During the cutting process, (b) After cutting into two pieces, (c) Two separate pieces brought together to connect with each other, and (d) Showing self-healable property to join together after immediate contact.



**Figure S8.** SEM photo-images of the top views for CSG1.0Fe (a) after cut, (b) after healing and the cross-sectional views for CSG1.0Fe (c) after cut, (d) after healing.



**Figure S9.** XRD spectra of CSG1.0Fe at different heating and cooling processing conditions: (a) During gradual heating at different temperatures, (b) During gradual cooling at different temperatures, (c) At 50 °C during gradual heating and cooling, (d) At room temperature before heating and after cooling.

We observed that upon heating the full width half maxima (FWHM) (5.74 at RT, 5.86 at 50 °C, and 5.95 at 150 °C) of Figure S9 (a) increased for CSG1.0Fe which gradually decreased again accordingly during cooling in Figure S9 (b). At particular temperatures of 50 °C and room temperature during heating and cooling cycles CSG1.0Fe almost revealed the same FWHM values in Figures S9 (c) and S9 (d), which support its reversible crystalline properties with non-covalent crosslinks by different thermal treatments.



**Figure S10.** FT-IR spectra of TA monomer powder (black), PA powder (red), and CSG1.0Fe (blue) in different ranges of (a) broader and (b) narrower wavenumbers, where KBr pellets were used as a reference in powder samples.

FTIR spectra in Figure S10 are used to characterize the formation of featuring bonds or the presence of functional groups through stretching vibrations in CSGs. The presence of a large FTIR band around 3500 cm<sup>-1</sup> region is because the stretching vibrations of several –OH groups in CSG1.0Fe are overlapped with the stretching vibrations of N-H in polyaniline. The peak at 817 cm<sup>-1</sup> appears because the tetra-substituted C-H bending confirms the presence of pyromellitic acid inside the gel. The small peak around 707 cm<sup>-1</sup> is observed due to the presence of benzene derivatives. The stretching peak at 1413 cm<sup>-1</sup> appears in pyromellitic acid owing to the presence of –OH bending in carboxylic acid, which shifted to 1408 cm<sup>-1</sup> in gel due to the formation of hydrogen bonding. The presence of emeraldine PANI salt is observed by the presence of characteristic 1498 cm<sup>-1</sup> peak which is because of benzenoid ring deformation.



**Figure S11**. Raman spectrum of the gel (CSG1.0Fe): Peaks appearing around 900 cm<sup>-1</sup> for aromatic ring vibrations, 1220 cm<sup>-1</sup> for C-N, 1320 cm<sup>-1</sup> for C-H, and 1490 cm<sup>-1</sup> for N-H band. (Silicon substrate was used as a reference and the characterization was performed using Argon laser.)



Figure S12. DSC thermograms of (a) TA monomer, (b) PA cross linker, and (c) CSG1.0Fe.

A melting peak at 55.5 °C for TA monomer was observed during heating, whereas for the DSC curve of CSG1.0Fe no such a characteristic melting peak at 55.5 °C was found to confirm the complete polymerization of TA monomer.



**Figure S13.** TGA curves of (a) CSG1.0Fe and (b) TA monomer, FeCl<sub>3</sub>.6H<sub>2</sub>O, and CSG1.0Fe.



**Figure S14.** Temperature dependent frequency sweep rheology curves of CSG1.0Fe: (a) Storage (G') and loss (G'') moduli at different temperatures and (b) Viscosity changes at different temperatures (showing shear thinning behavior).



**Figure S15.** Shear adhesion curves of conductive gel CSG1.0Fe (a) adhered to different substrates with a displacement rate of 30 mm/min (b) repetitive adhesion tests of CSG1.0Fe for 3 cycles at 4 different substrates (steel, glass, PDMS, and Teflon).



Figure S16. Peeling off adhesive CSGs from skin surface without any residue.



**Figure S17.** Gauge factor comparison of our best CSG work (CSG1.0Fe) with reported conductive gel-based strain sensors.<sup>5,7–9,11–17</sup>



**Figure S18.** Comparison of our CSG1.0Fe-based pressure sensor sensitivity with recently reported pressure sensor works.<sup>8,18–25</sup>



**Figure S19.** Representative photo-images of piezoresistive processes of CSGs through a white LED bulb. The light intensity enhances significantly with gradually increased pressure from (a), (b), (c), to (d).



**Figure S20.** Electro-mechanical responses of CSG1.0Fe-based sensor during (a) index finger bending, (b) elbow movement, and (c) knee bending.



**Figure S21.** Photo-images of injectable CSG writing through different sizes of needles: (a) 18 gauge and (b) 22 gauge. Inset: Photo images of LED lighting showing conductivity through injectable CSGs.

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