Supplementary Information

Stretchable, environmentally stable, and mechanically robust nanocomposite polyurethane organohydrogel with anti-freezing, anti-dehydration, and electromagnetic shielding properties for strain sensors and magnetic actuators

Yang Liu [a, b], Zetian Zhang [a, b], Xiaohan Yang [a, b], Fufen Li [a, b], Ze Liang [a, b], Yong Yong [a, b], Songbo Dai [a, b], Zhengjun Li [a, b, *]

[a]*National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University, Chengdu, 610065, China*

[b]*Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu, 610065, China*

* Corresponding author: lizhengjun@scu.edu.cn (Z. J. Li)

Materials and methods

Materials

Fe$_3$O$_4$ NPs (~200 nm) were purchased from Shanghai Macklin Biochemical Co., Ltd. Tannic acid (TA, 98%, Mw = 1701.2) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Isophorone diisocyanate (IPDI) was provided by Chengdu Huaxia Chemical Reagent Co., Ltd. Poly(propylene glycol) (PPG, Mn = 1000), polyethylene glycol (PEG, Mn = 4000), 1, 4-butanediol (BDO), N, N-dimethylformamide (DMF), dibutyltin dilaurate (DBTDL), glycerol, calcium chloride anhydrous (CaCl$_2$), ammonium persulfate, ethanol, and 4 Å molecular sieves were obtained from Chengdu Kelong Chemical Reagent Co., Ltd. Phytic acid was supplied by Shanghai Titan Scientific Co., Ltd. Aniline was obtained from Chengdu Jinshan Chemical Reagent Co., Ltd. PEG and PPG were dehydrated under reduced pressure at 120 °C for 2 h before use. BDO and DMF were dried by using 4 Å molecular sieves before use. All of the reagents above except IPDI were analytical grade.

Preparation of tannic acid functionalized magnetic nanoparticles (Fe$_3$O$_4$@TA)

Fe$_3$O$_4$@TA nanoparticles were prepared via a simple surface modification of commercial Fe$_3$O$_4$ nanoparticles with tannic acid (TA) molecules. Briefly, 1 g of Fe$_3$O$_4$ nanoparticles were dispersed in mixed solution containing 80 mL of deionized water

and 20 mL of ethanol, followed by ultrasonic treatment for 1.5 h. Subsequently, 13 g of TA (dissolved in 50 mL of deionized water) was added into the above mixed solution and stirred at room temperature for 3 h. Afterward, the suspension was further treated by ultrasonic treatment for 3 h. Finally, after being washed with deionized water for three times, the Fe_3O_4@TA nanoparticles were collected, and then dried in vacuum at 60 °C for 6 h.

Preparation of tannic acid-based magnetic polyurethane nanocomposites (TAPU/Fe$_3$O$_4$@TA)

The TAPU/Fe$_3$O$_4$@TA polyurethane nanocomposites were prepared by using an in situ polymerization method. Briefly, a certain amount of IPDI (4.44 g, 20.00 mmol), PEG (6.00 g, 1.50 mmol), PPG (7.00 g, 7 mmol), Fe$_3$O$_4$@TA, and one drop of DBTDL were first added into a four-neck flask (250 ml) and stirred at 85 °C for 2 h under N_2 atmosphere. Afterward, BDO (0.32 g, 3.55 mmol) was dropped into the above oligomer, and the system was allowed to react for 1 h. Subsequently, a defined amount of TA (2.20 g, 1.29 mmol) dissolved in DMF was introduced to the above solution. After reacting at 85 °C for extra 3 h, the tannic acid-based magnetic polyurethane nanocomposites (TAPU/Fe$_3$O$_4$@TA) were obtained. The TAPU/Fe$_3$O$_4$@TA nanocomposites containing 5 wt%, 10 wt%, and 15 wt% of Fe$_3$O$_4$@TA nanoparticles were coded as TAPU/Fe$_3$O$_4$@TA-1, TAPU/Fe$_3$O$_4$@TA-2, and TAPU/Fe$_3$O$_4$@TA-3, respectively. For comparison, TAPU polymer without Fe$_3$O$_4$@TA nanoparticles was prepared by the same procedures. Besides, the physical blending nanocomposite was fabricated based on TAPU polymer and pure Fe$_3$O$_4$ nanoparticles.

Preparation of the interpenetrating polyurethane and polyaniline (TAPU/Fe$_3$O$_4$@TA-PANI)

The dual interpenetrating and synergistic networks of polyurethane and polyaniline were constructed according to a previously reported method. [1] Firstly, aniline (1.86 g, 20 mmol) and phytic acid (6.6 g, 10 mmol) were dissolved into 100 mL deionized water. Subsequently, the prepared TAPU/Fe$_3$O$_4$@TA films were immersed in the above solution to absorb the aniline for 2 h. Afterward, ammonium persulfate (4.56 g, 20 mmol) was dissolved in 5 mL deionized water and then added into the mixture to initiate the in situ polymerization of aniline within TAPU/Fe$_3$O$_4$@TA networks at 5 °C. After the reaction was allowed to proceed for 12 h, the TAPU/Fe$_3$O$_4$@TA-PANI hydrogels were taken out and washed with deionized water to remove impurities. TAPU/Fe$_3$O$_4$@TA-PANI-X (X=I, II, and III) hydrogel was prepared from the aqueous solution containing aniline monomers of 0.1, 0.2, and 0.3

mol/L, respectively. Besides, the contrast sample TAPU/Fe$_3$O$_4$@TA hydrogel was prepared by immersing TAPU/Fe$_3$O$_4$@TA film in deionized water for 12 h.

Preparation of magnetic polyurethane organohydrogel

To obtain good conductivity, freezing resistance and anti-dehydration properties, the prepared TAPU/Fe$_3$O$_4$@TA-PANI hydrogel was further immersed in a mixed solution of CaCl$_2$/glycerol/water for predetermined time (0, 1, 5, 10, 30, and 60 min) at room temperature to construct TAPU/Fe$_3$O$_4$@TA-PANI organohydrogel, the mass ratio of glycerin to water in a CaCl$_2$/glycerin/water solution was 2:5. To further evaluate the influence of CaCl$_2$ on conductivity of TAPU/Fe$_3$O$_4$@TA-PANI organohydrogel, the TAPU/Fe$_3$O$_4$@TA-PANI hydrogel was immersed in the mixed solution containing glycerol and different CaCl$_2$ concentrations (0, 0.5, 1, 2, and 3 mol/L) for 60 min.

Characterizations

X-ray diffraction (XRD) analysis was carried out on an X′ Pert Pro MPD DY129 diffractometer (Panalytical, Holland) from 2θ angle of 20° to 70° using CuKα radiation (λ=1.541 Å) at a scanning speed of 10°/min. Fourier transform infrared (FT-IR) spectra were collected on a Spectrum 3 instrument (PerkinElmer, USA). The magnetic properties of all samples were tested by a vibrating sample magnetometer (VSM, LakeShore-7404, USA) at room temperature. Scanning electron microscopy (SEM) image was observed under the field emission scanning electron microscopy (FE-SEM) (Apreo S HiVac FEI, Thermo Scientific, USA). Mechanical tests of the prepared samples with a dumb-bell shape (~50 mm × 4 mm × 0.8 mm) were performed using a UTM 6203 universal material testing machine (Suns, China) according to ASTM D-638 standard at a stretch speed of 100 mm/min under room temperature. The cyclic tensile tests were carried out for 20 loading-unloading cycles at 100 mm/min and strain of 50% without intervals between consecutive cycles. Swelling behavior of the prepared samples was determined by a gravimetric process. The dry films were immersed in deionized water at room temperature, and the samples were weighed at stipulated time points after removing any excess water on the surface. Five measurements were carried out for each sample, and the swelling ratio of the samples was calculated by using the equation (1).

$$\text{Swelling ratio (\%)} = (W_s - W_d)/W_d \times 100\% \qquad (1)$$

where W_s and W_d are the mass of swollen and dried hydrogels, respectively.

Differential scanning calorimetry (DSC) was carried out on a DSC 204 F1 (Netzsch, Germany). The obtained organohydrogels were scanned from -80 to 25 °C at

the rate of 5 °C/min under nitrogen atmosphere. For frost resistance test, the prepared organohydrogel sensor was placed in a self-made temperature box equipped with a thermometer to maintain the test temperature. Water retention capacity of the prepared organohydrogels was reflected by the mass changes. The samples were placed at different temperature and humidity conditions ((60 °C, 37% RH) and (25 °C, 67% RH)) for different storage time. The water retention rate was calculated by the following formula:

$$\text{Relative weight (\%)} = (W_t/W_0) \times 100\% \qquad (2)$$

where W_0 is the initial weight of the sample, and W_t is the weight of the sample at the corresponding time.

The electrical signals of the prepared samples were collected by an electrochemical workstation (CHI760E, China). The conductivity (δ, mS/cm) of the samples was calculated according to the following equation (3).

$$\delta = L/(R \times S) \qquad (3)$$

where L is the length between two adjacent probes (cm), R is the resistance of the hydrogel (Ω), and S represents the cross-sectional area of the sample (cm^2). The real time resistance changes of the samples were recorded by the electrochemical workstation at 1 V voltage. The strain sensitivity of the tensile testing was defined as the following equation (4).

$$GF = ((R-R_0)/R_0)/\varepsilon \qquad (4)$$

where R_0 and R are the instantaneous resistance values without and with applied strain, ε is the strain of the sample. The prepared organhydrogel sensor was fixed on the volunteer's forefinger, wrist, throat, and knee to monitor the human motions, and the real time electrical signals caused by various motions were collected by electrochemical workstation at 1 V voltage.

The electromagnetic interference shielding performance of the samples were tested by a vector network analyzer (Agilent N5247A, USA) in the frequency range of 8.2-12.4 GHz. TAPU organohydrogel was prepared based on the same preparation procedure of TAPU/Fe_3O_4@TA-PANI-II organohydrogel except that by substituting TAPU/Fe_3O_4@TA-PANI-II hydrogel with TAPU hydrogel. The thickness of all of the tested samples was 2 mm. The total shielding effectiveness (SE_T) is the summary of reflection effectiveness (SE_R), absorption effectiveness (SE_A) and multiple reflection effectiveness (SE_M). SE_M could be neglected if SE_T is greater than 15 dB. Scattering parameters (S11, S21, S21 and S22) were used to calculate SE_T, SE_A, SE_R from the following equations[2]:

$$SE_T = -10\log(|S21|^2) \tag{5}$$
$$SE_R = -10\log(1-|S11|^2) \tag{6}$$
$$SE_A = -10\log(|S21|^2/(1-|S11|^2)) \tag{7}$$

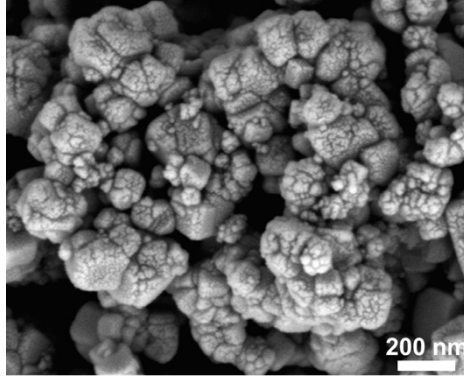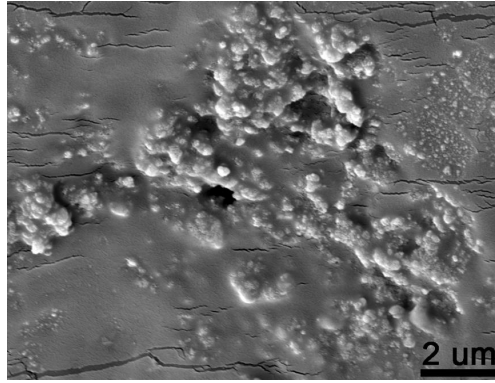**Fig. S1.** SEM image of Fe_3O_4@TA nanoparticles.

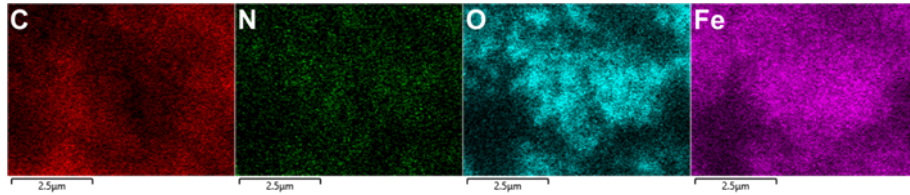**Fig. S2.** SEM image of fracture morphology of TAPU/Fe_3O_4 nanocomposites prepared by physical blending.

Fig. S3. SEM-EDS mapping results of the cross-section of the TAPU/Fe_3O_4@TA-2 film.
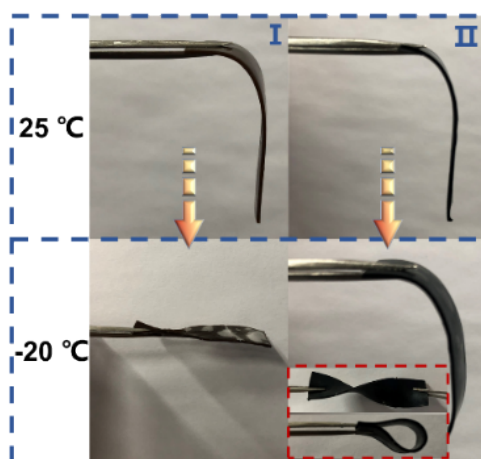
Fig. S4. Photograph of the pristine hydrogel (I) and the organohydrogel (II) at 25 °C and -20 °C.
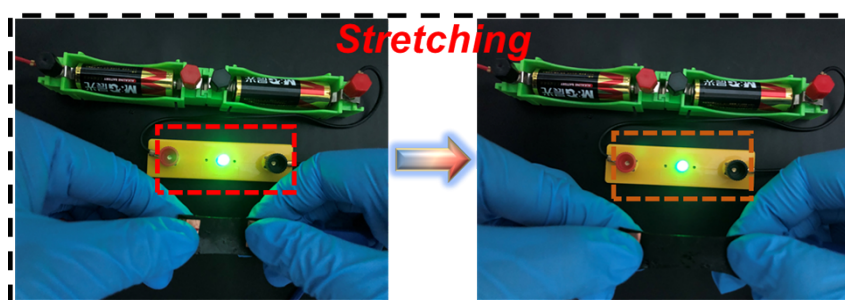

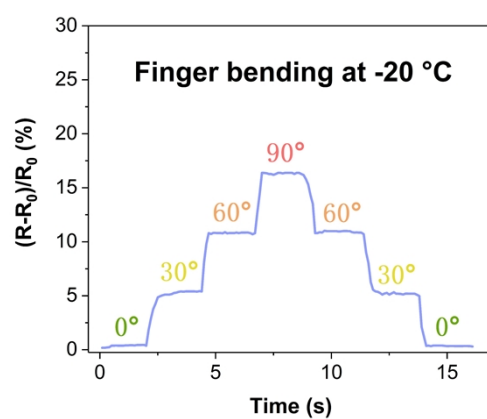**Fig. S5.** Demonstration of the conductivity of the organohydrogel by lighting the bulb.

Figure S6. Relative resistance change of finger bending at -20 °C.

References

1. Y. Fang, J. Xu, F. Gao, X. Du, Z. Du, X. Cheng and H. Wang, *Compos. B Eng.*, 2021, **219**, 108965.
2. Y. Yu, P. Yi, W. Xu, X. Sun, G. Deng, X. Liu, J. Shui and R. Yu, *Nano-Micro Lett.*, 2022, **14**, 77.