

Supporting Information

A Super-Stretchable and Tough Functionalized Boron Nitride/PEDOT:PSS/Poly(*N*-isopropylacrylamide) Hydrogel with Self-healing, Adhesion, Conductive and Photothermal_{al}ie Activity

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Experimental Section

Materials and Reagents: *N*-Isopropyl acrylamide (Aladdin, 98%), PEDOT:PSS suspension (13 mg mL⁻¹, Clevios, PH1000), h-BN powder (Acros Organics), synthetic hectorite clay of Laponite-XLS (Rockwood Ltd, sol-forming grade, 92.32 wt% of Mg_{5.34}Li_{0.66}Si₈O₂₀(OH)₄Na_{0.66} and 7.68 wt% of Na₄P₂O₇), polyvinylpyrrolidone (PVP) (Strem Chemicals) were all commercially supplied. Hydrogen peroxide (H₂O₂, 30% aqueous solution), initiator potassium persulfate (KPS), catalyst *N,N,N',N'*-tetramethylethylenediamine (TEMED), catalyst, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NIPAM and KPS were used after recrystallization. All other reagents were of analytical grade and used without further purification.

Preparation of Hydrogels: The f-BNNS nanosheets were prepared via a SC CO₂ treatment according to our previous work.¹ The hydrogels were prepared as follows: Firstly, the NIPAM monomer was dispersed into the PEDOT:PSS suspension by continuous and vigorous stirring in an ice-water bath for 1 h under nitrogen atmosphere. Subsequently, the f-BNNS and clay (including Rhodamine B, if necessary) were ultrasonicated and stirred for two hours, and then were added into the aforementioned suspension. After the suspension was entirely dissolved, KPS (32 mg/mL) and TEMED were added under stirring. Finally, the obtained mixture was quickly poured into the sealed mold for complete free-radical polymerization, which proceeded at 20 °C to generate hydrogels with desired 3D geometries. The specific quantity of contents of each component is shown in Table S2 in Supporting Information.

Mechanical property measurements: All of the mechanical properties of the conductive hydrogels were tested on a universal tensile-compressive tester (UTM_2203, Shenzhen Suns Technology Stock Co., Ltd., China) equipped with an electrically contactable jig for in-situ resistance measurements. In the compression test, samples with cylinder shapes (10 mm (D) \times 10 mm (H)) were placed on a metal plate coated with silicon oil to decrease the friction and were tested at a loading speed of 40 mm/min. For the tensile test, conductive hydrogels were made into rods (10 mm in initial tensile length and 6.5 mm in diameter) and tested at the test velocity of 100 mm/min. All the stresses measured were engineering stresses or nominal stresses ~~which that were~~ calculated by the following formula:

$$\sigma = \frac{F}{A_0}$$

Where F is the applied load, and A_0 is the initial cross-sectional area.

The engineering strain (ε) was calculated as follows:

$$\varepsilon = \frac{\Delta L}{L_0}$$

Where L_0 is the original specimen height and ΔL is the measured extension.

All the tests were performed at the room temperature, and the average value was ~~taken~~obtained at least three times.

Rheological mMeasurements: The rheological behaviors of the hydrogels were analyzed with a modular compact rheometer (Anton Paar, MCR 302). Samples were prepared in the shape of a cylinder with a diameter of 25 mm and a thickness of 2 mm. The frequency (ω) sweep test was conducted at $\omega = 1-100$ rad/s and strain (γ) = 0.5% of f-BNNS and PEDOT:PSS hydrogels at 25 °C.

Self-healing: The cylindrical samples (~~(dyed and undyed)~~) were cut into two pieces with a razor blade. Then, the separated gel surfaces were re-contacted slightly and sealed quickly to avoid the evaporation of water. The self-healing was completed after an appropriate time. The healed hydrogel maintained its conductive property and could endure deformation, such as bending and stretching.

Characterization: Surface images and structure of the PEDOT:PSS hydrogels were characterized using scanning electron microscopy (SEM, JEOR JSM-6700F). Fourier transform infrared (FT-IR) spectroscopy measurements were recorded on a TENSOR 27 FTIR spectrometer (Bruker) in the absorption mode. Ultraviolet (UV) spectra were collected by using a Lambda 35 UV-vis spectrometer (Perkin Elmer, USA). The Raman spectra of the samples were recorded using ~~in~~ a Renishaw microscope system RM2000 with a 532 nm laser as the excitation source. The XRD patterns from 5° to 80° were obtained using a D/max 2500 X-ray diffractometer (Rigaku) at a scanning ~~rate~~ of 8°/min with Cu K α (λ = 0.154 nm).

Supplementary Figures

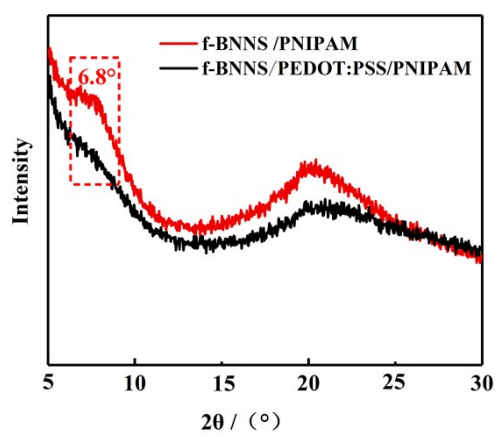


Figure S1. XRD patterns of f-BNNS/PEDOT:PSS/PNIPAM hydrogels and f-BNNS/PNIPAM hydrogels.

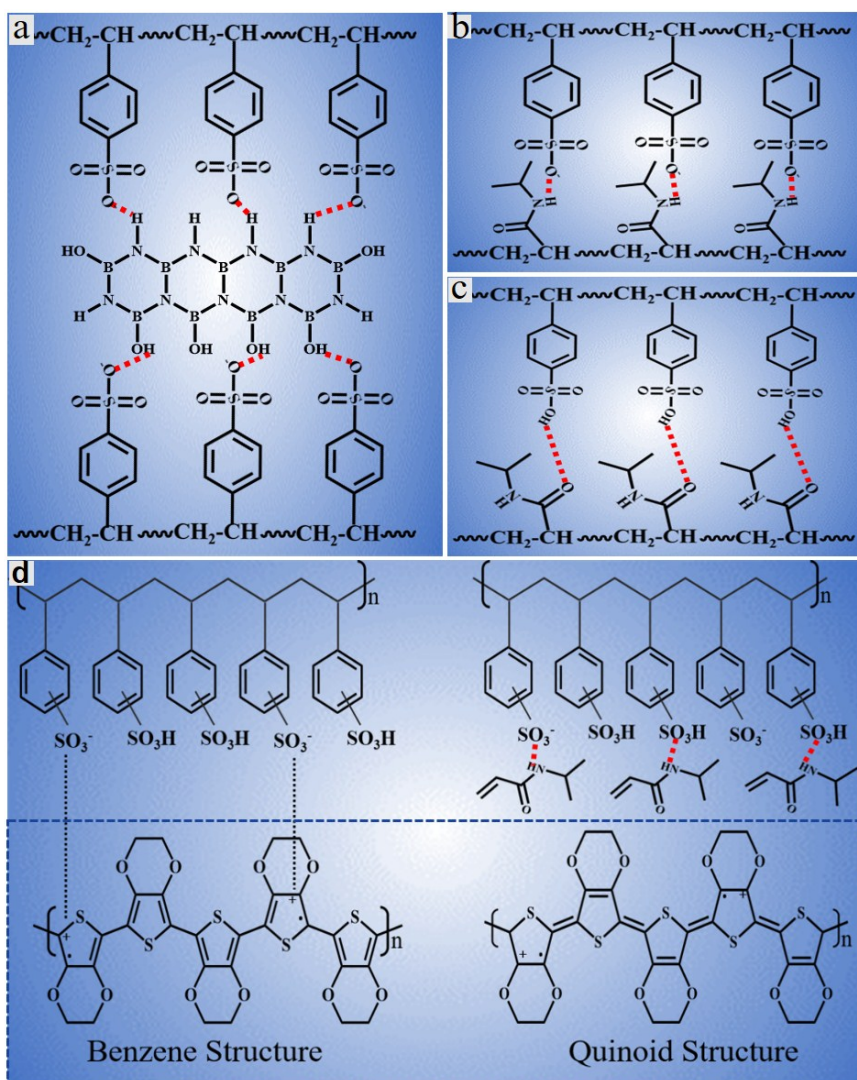


Figure S2. Possible (a and b) and impossible (c) forms of hydrogen bonding; (d) PEDOT molecular chain conformation changed from benzene structure to quinoid structure.

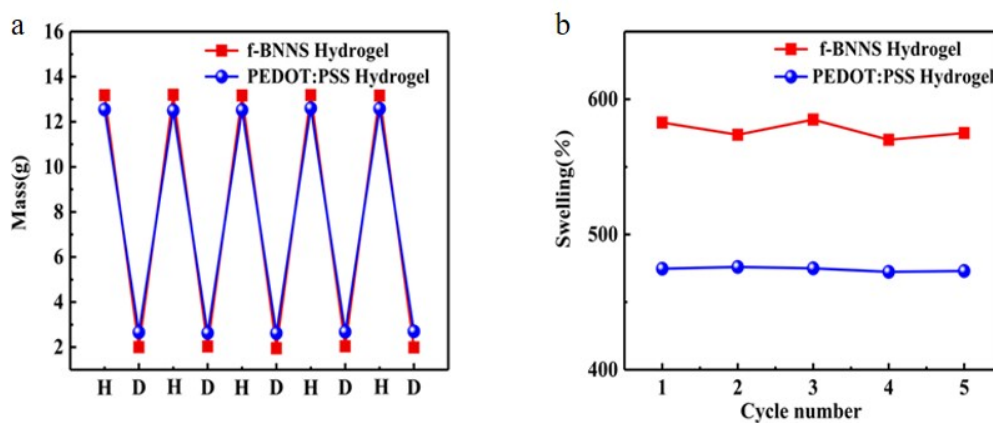


Figure S3. (a) The mass of dried (D) and hydrated (H) states of the f-BNNS/PEDOT:PSS/PNIPAM hydrogel and f-BNNS/PNIPAM hydrogel; and (b) Calculated swelling ratio upon the dimension of mass.

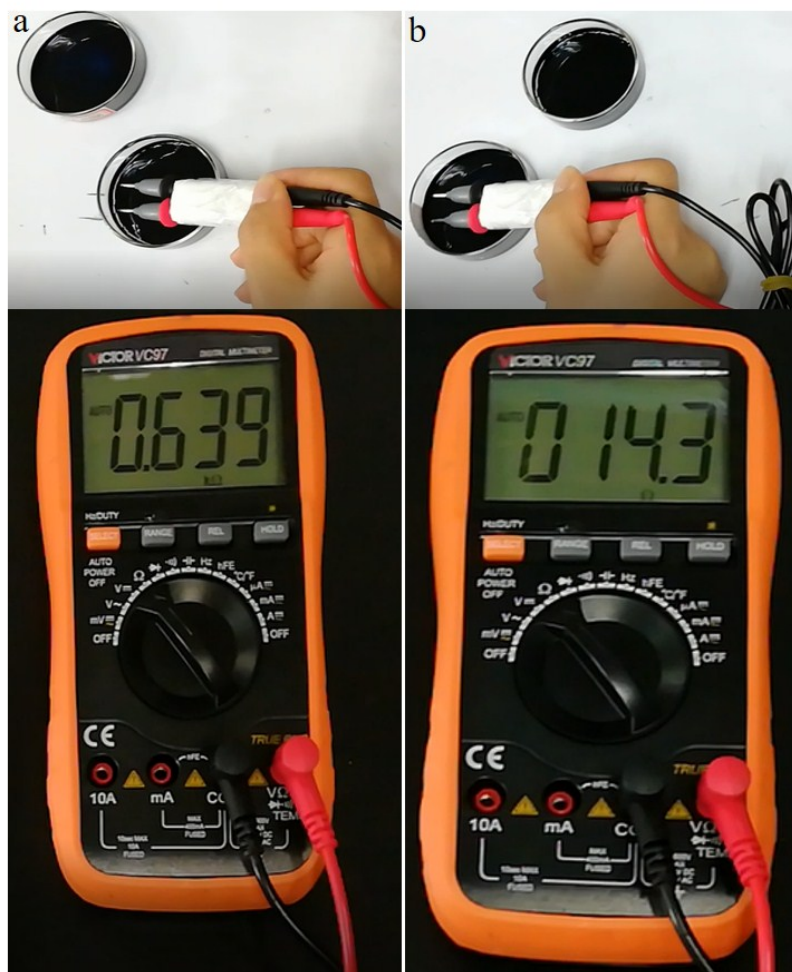


Figure S4 Evaluation of conductivity using a multimeter with a constant distance between the electrodes. The results demonstrated that PEDOT:-PSS&NIPAM (b) has higher conductivity than PEDOT:-PSS (a).

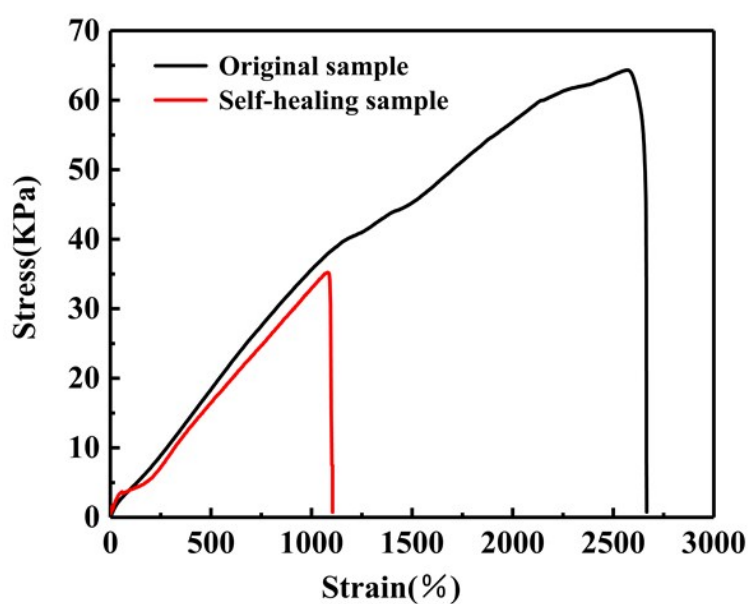


Figure S5 Typical tensile sStrain—stress curves of the original and self-healed hydrogels.

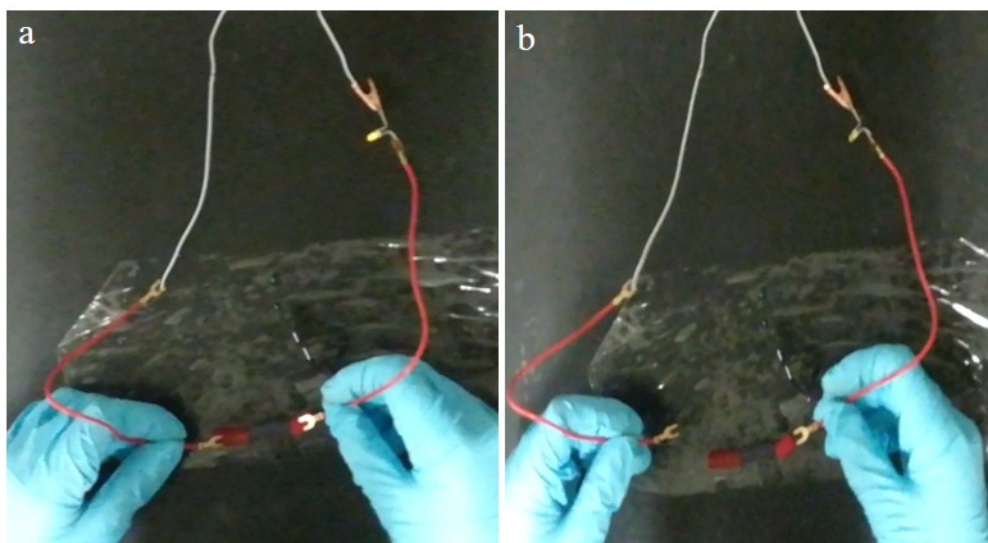


Figure S6: (a) Conductive after adding self-healing f-BNNS/PEDOT:PSS/PNIPAM hydrogels and; (b) nNo conductivity when the circuit is disconnectedd.

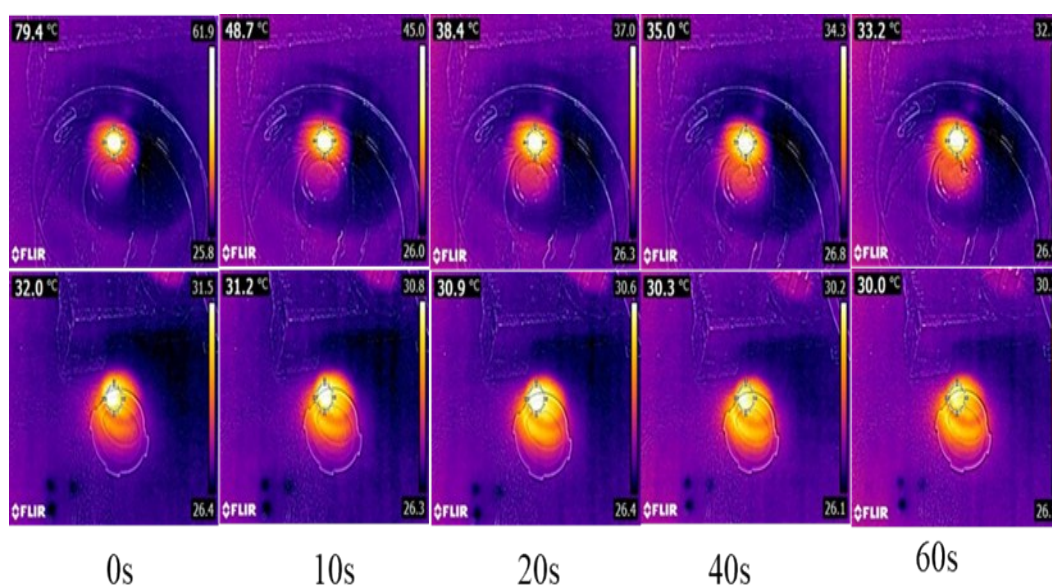


Figure S7 Digital photographs of temperature change of f-BNNS/PEDOT:PSS/PNIPAM hydrogels (overheadabove) and pure water (below) after the removal of light source.

| NIPAM (mg) | PEDOT:PSS (PH1000) (13 mg mL ⁻¹) (μL) | Clay (mg) | f-BNNS (1 mg mL ⁻¹) (μL) | H ₂ O (μL) | KPS (20 mg mL ⁻¹) (μL) | TEMED (μL) |
|---------------|---|--------------|--|--------------------------|--|---------------|
| 500 | 0 (0.00 wt%) | 160 | 800 | 4500 | 500 | 6 |
| 500 | 120 (0.03 wt%) | 160 | 800 | 4380 | 500 | 6 |
| 500 | 200 (0.05 wt%) | 160 | 800 | 4300 | 500 | 6 |
| 500 | 280 (0.07 wt%) | 160 | 800 | 4220 | 500 | 6 |
| 500 | 500 (0.11 wt%) | 160 | 800 | 4000 | 500 | 6 |

Table S1. Performance comparison chart of hydrogels.

Table S2. Compositions of f-BNNS/PEDOT:PSS/PNIPAM sample.

1. X. Tong, L. N. Du and Q. Xu, *J. Mater. Chem. A*, 2018, **6**, 3091-3099.

| Materials | Elongation at break (%) | Compressive strength (KPa) | Self-healing | Conductivity | Adhesion | Optical-thermal performance | Reference |
|--|-------------------------|----------------------------|--------------|--------------|----------|-----------------------------|---|
| f-BNNS/PNIPAM | 960% | 200 | 6 h | × | ✓ | × | <i>J. Mater. Chem. A</i> , 2018,6,3091-309 |
| AuNPS/BACA/PNIPAM | 2300% | 160 | 1_min | × | × | ✓ | <i>Chem.</i> ,2017,3, 691–705, |
| PPY/CNT/PNIPAM | 561% | × | × | 0.40 S/cm | × | ✓ | <i>Chem. Mater.</i> , 2018,30,1729–1742 |
| PEDOT:PSS(6.83%) /PAAm/MBAAm | 530% | × | × | 0.01 S/cm | × | × | <i>Adv. Mater.</i> , 2016, 28, 1636–1643 |
| PEDOT:PSS hydrogel (treated with concentrated H ₂ SO ₄) | × | × | × | 8.80 S/cm | × | × | <i>Adv. Mater.</i> , 2017, 1700974 |
| PEDOT:PSS/aAcrylicacid-/PAAc | > 100% | 8–374 | × | > 0.29 S/cm | × | × | <i>Nat. Commun.</i> , 2018, 2740 |
| EG/PVA /PEDOT:PSS | 962% | 448 | 20 | 0.009 S/cm | × | × | <i>Angew. Chem. Int. Ed.</i> , 2017, 56, 1–6 |
| CNT/PEDOT:PSS/PNIPAM | × | × | × | ✓ | ✓ | ✓ | <i>ACS Appl. Mater. Interfaces</i> , 2018,10, 7263–7270 |
| f-BNNS/ PEDOT:PSS (0.03-0.11%) /PNIPAM | 2666% | 700 | 6 h | 0.0004 S/cm | ✓ | ✓ | Our <u>n</u>Work |