

## **Supporting Information**

### **Tough, Adhesive and Self-Healing Conductive 3D Network Hydrogel of Physically Linked Functionalized-Boron Nitride/Clay/Poly(N-isopropylacrylamide)**

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## EXPERIMENTAL METHODS

**Materials.** Commercially *h*-BN Powder was purchased from ACROS ORGANICS (USA, CAS: 7782-42-5). Polyvinylpyrrolidone (PVP) was bought from STREM CHEMICALS (Fluka, CAS: 07-1815). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 30% aqueous solution was obtained from Sinopharm Chemical Reagent Co., Ltd. (China). N-isopropylacrylamide (NIPAM) monomer was received from Sigma-Aldrich, and it was used by recrystallization from a toluene/n-hexane mixture and dried in vacuum at 40°C for 48 h. Synthetic hectorite clay of Laponite-XLS (sol-forming grade, 92.32 wt% of Mg<sub>5.34</sub>Li<sub>0.66</sub>Si<sub>8</sub>O<sub>20</sub>(OH)<sub>4</sub>Na<sub>0.66</sub> and 7.68 wt% of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) was obtained from Rockwood Ltd and used after drying at 125°C for 4 h. Catalyst N,N,N',N'-tetramethylethylenediamine (TEMED) was purchased from Sinopharm Group Chemical Reagent Co., Ltd. Initiator potassium peroxydisulfate (KPS) was used after recrystallization from deionized water and dried in vacuum at room temperature. Ethanol used in all experiments was purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used without further purification since the reagent is of analytical grade. All other reagents were of analytical grade and used without further purification.

**Preparation of f-BNNS.** The process is as the following. In a typical route similar to our previous work,<sup>1-2</sup> supercritical CO<sub>2</sub> was used. Firstly, bulk *h*-BN (100 mg) and PVP (400 mg) were added to 10 mL ethanol mixture and the dispersion in the sealed flask was sonicated for 3 h to form homogeneous solutions. Then 30% H<sub>2</sub>O<sub>2</sub> solution (10 mL) was immediately put into the above mixture and was transferred into the supercritical CO<sub>2</sub> apparatus, which used in this experiment was composed mainly of a stainless steel autoclave (50 mL) with a heating jacket and a temperature controller. The autoclave was heated to 60 °C, and then CO<sub>2</sub> was charged into the reactor to the desired pressure (18 MPa) under stirring. After a reaction of 3 h, the gas was

slowly released. Then, the dispersion was sonicated in the bath for another 5 h. Finally, the dispersion was centrifuged at 3000 rpm for 15 min to remove aggregates. The resultant white color supernatant was collected by pipet. Subsequently, the supernatants was further centrifuged at 20000 rpm for 20 min and repeatedly washed with ethanol and water for three times to remove PVP and residual H<sub>2</sub>O<sub>2</sub>. Finally, the pure f-BNNS precipitate was dried at 60 °C in vacuum overnight.

**Preparation of TN Hydrogels.** The f-BNNS was first dispersed in deionized water and sonicated in the bath for about 0.5 h. The clay was loaded into the f-BNNS dispersion (1mg/ml) and sonicated for 1 h. The dyestuff (methylene blue or Rhodamine B) was also added into the suspension, if necessary. Subsequently, the NIPAM monomer was dispersed in the suspension by continuous and vigorous stirring in an ice-water bath for another 2 h, which was degassed under constant N<sub>2</sub> bubbling. Finally, KPS (20 mg/mL) and TEMED were added under stirring. The solution was quickly injected into sealed molds and left overnight for complete polymerization at 20°C to produce the f-BNNS/clay/PNIPAm TN hydrogels. The specific quantity of each component is as Table 1 shows.

**Characterization.** The morphology and structure of the samples were characterized by field-emission SEM (JEOR JSM-6700F). FTIR were recorded on TENSOR 27 FTIR spectrometer using KBr disks to explore the chemical bands of the hydrogel. X-ray diffraction (XRD) were characterized from 10° to 70° at a scanning rate of 8°/min by a D/max 2500 X-ray diffractometer (Rigaku) with Cu K $\alpha$  ( $\lambda=0.154$  nm). Raman spectra were recorded on a Renishaw microscope system RM2000 with laser wavelength of 532 nm.

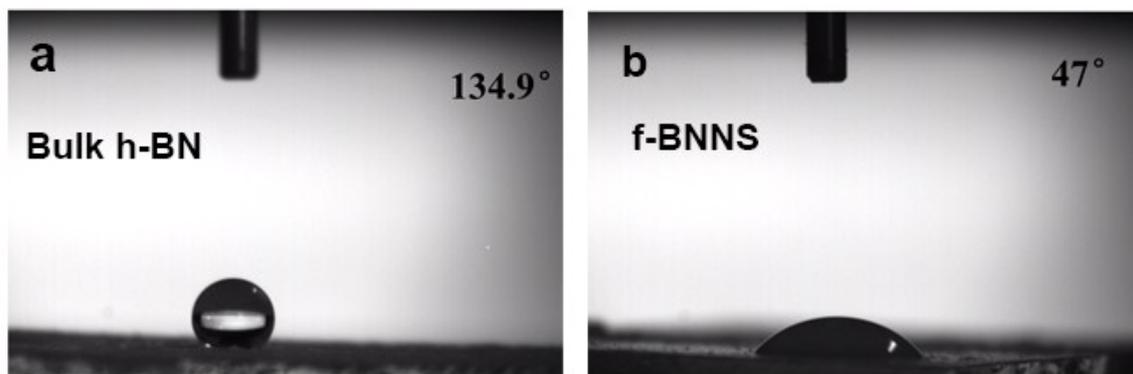
**Self-Healing.** Cylinder shaped samples, of which one added with dyestuff, were cut into two pieces, respectively. The four pieces were then brought together slightly to ensure the two

surfaces were fully contacted, and sealed (prevent water from evaporating). After a specific healing time, the hydrogels, exhibiting excellent self-healing properties, were prepared and could withstand deformation such as bending and elongation.

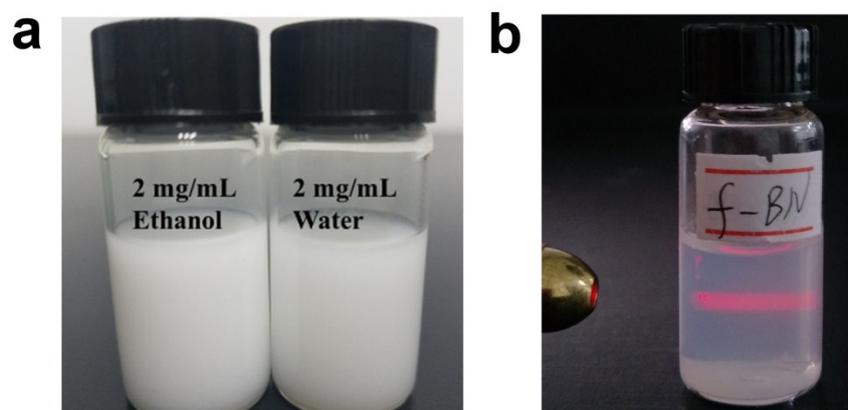
**Mechanical property measurements.** Compression test were performed at room temperature using a universal testing machine (UTM2203, Shenzhen Suns Technology Stock Co. Ltd., China). In the compression test, samples with cylinder shapes (10 mm (D) × 10 mm (H)) were placed on a metal plate coated with silicon oil to decrease the friction, at a loading speed of 40 mm/min. The tensile strength is measured by the same universal material testing machine. All the samples are made in the forms of rods with the same diameter of 6.5 mm. The initial tensile length was 15 mm. The velocity was constant at 100 mm/min.

All mechanical tests were carried out at room temperature. Measurements of each samples were repeated at least five times and were averaged for a given sample.

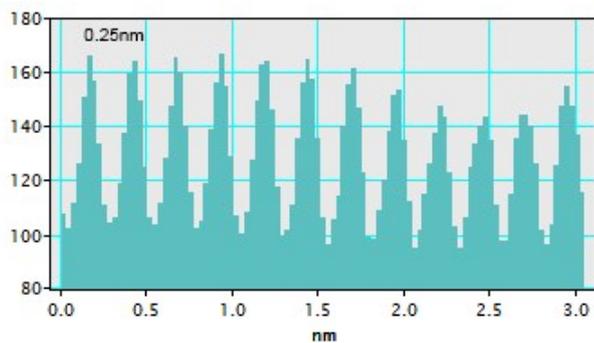
## Supplementary Figures



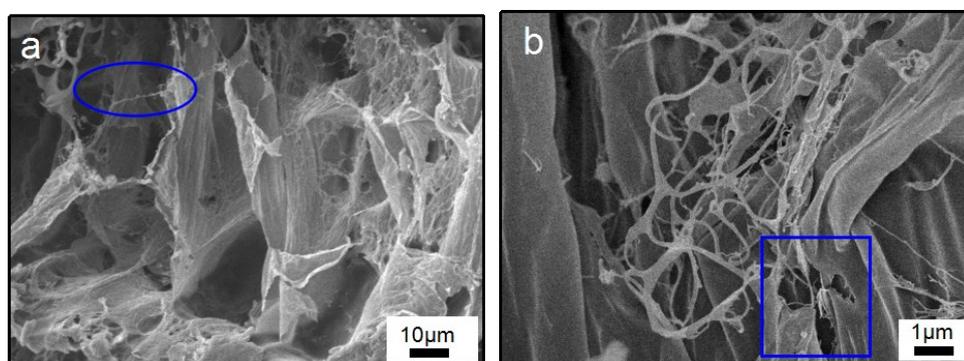
**Figure S1** Contact angle measurements. (a) Photograph of water droplet on pristine BN. (b) Photograph of water droplet on f-BNNS.



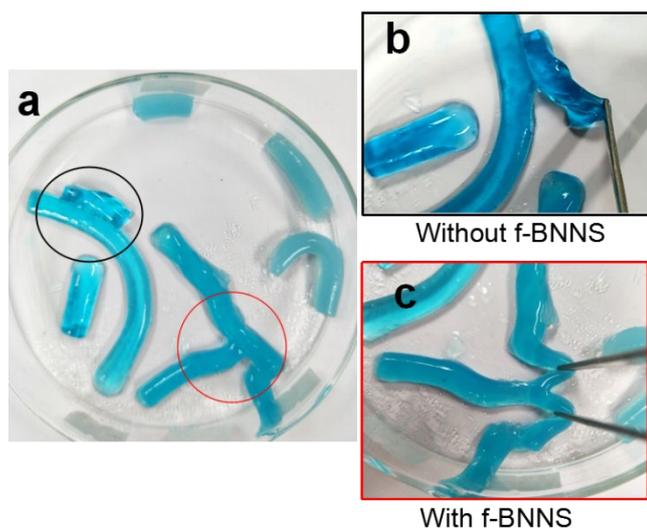
**Figure S2** (a) Photos of the as-prepared f-BNNS suspensions in ethanol and water with concentrations 2.0 mg/mL. (b) Dilute suspension in water showing a Tyndall effect upon irradiation



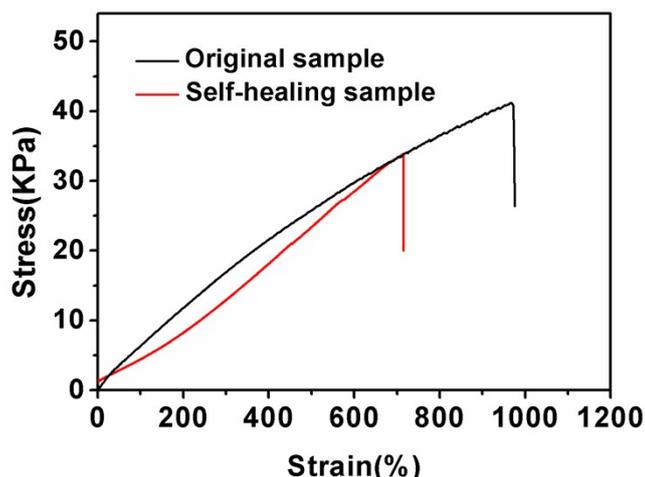
**Figure S3** TEM contrast intensity profile recorded along the marked red line, indicating that the fringe separation was  $\sim 0.25$  nm.



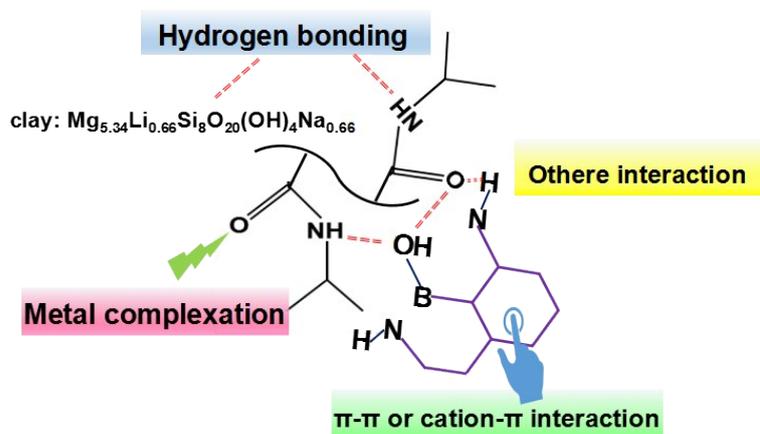
**Figure S4.** The fracture morphology of TN hydrogel after load. (a) Polymer chains were ruptured. (b) 2D nanosheets were damaged.



**Figure S5.** Self-healing behavior after tensile text with and without f-BNNS. (a) Hydrogels after tensile text. (b-c) Self-healing behavior of hydrogel with and without f-BNNS.



**Figure S6.** Typical tensile Strain-stress curves of the original and self-healed hydrogels.



**Figure S7.** Possible adhesion mechanisms including hydrogen bonding, metal complexation,  $\pi$ - $\pi$  stacking and/or cation- $\pi$  interactions, and other interactions (hydrophobic association).

**Table S1.** Compositions of hydrogel sample

NIPAM [mg]	Clay [mg]	f-BNNS (1mg ml <sup>-1</sup> ) [μl]	H <sub>2</sub> O [μl]	KPS (20 mg ml <sup>-1</sup> ) [μl]	TEMED [μl]
500	160	0 (0.00wt%)	4500	500	6
500	160	200 (0.04 wt%)	4300	500	6
500	160	400 (0.08 wt%)	4100	500	6
500	160	800 (0.16 wt%)	3700	500	6
500	160	1600 (0.32 wt%)	2900	500	6

## References

1. X. Tong, Y. Qi, J. Chen, N. Wang and Q. Xu, *ChemNanoMat*, 2017, **3**, 466-471.
2. S. Xu, Q. Xu, N. Wang, Z. Chen, Q. Tian, H. Yang and K. Wang, *Chemistry of Materials*, 2015, **27**, 3262-3272.