Supplementary Information

Polymer in-situ imbedding for highly flexible, stretchable and water stable PEDOT:PSS composite conductor

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Experimental

Materials

3, 4-Ethylenedioxythiophene (EDOT, 126213-50-1, 97%,) was obtained from TCI. Poly(sodium 4- styrenesulfonate) (NaPSS, Mw 70,000, 25704-18-1) was purchased from Sigma-Aldrich. $Fe(NO_3)_3 \cdot 9H_2O$ was analytical grade obtained from Beijing Chemical Reagent Co. Int. PDMS base and curing agent (SYLGARD®184) were from Dow Chemical Co. Int. Other chemical reagents with analytical grade were used as received.

Synthesis of PEDOT:PSS Hydrogel

PEDOT:PSS hydrogel was synthesized via a method from a reported literature.[1] The typical procedure for synthesis PEDOT:PSS: 600 μL (5.4 mmol) of the EDOT monomer was diluted with 2 mL ethanol. And then 0.84 g NaPSS powder was dispersed in 9 mL deionized water by sonication. The NaPSS aqueous solution was mixed with EDOT ethanol solution. Then the $Fe(NO3)_3$ aqueous solution (8.15 g (20.17 mmol) of $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 2.0 mL of deionized water) was added to the above dispersion with vigorous magnetic stirring. PEDOT:PSS were formed in a designed reaction cell when the mixed reaction solution was kept at the room temperature without agitation for 24 h. The purified process of PEDOT:PSS was referred by ref 1.

The PEDOT:PSS aerogels were prepared by a freeze-dried way until the water was removed completely.

Preparation of PEDOT:PSS@PDMS Conductor

The PDMS oligomer liquid (Sylgard 184, Dow Corning, Midland, MI) was firstly mixed with the curing agent (10:1 by weight) in a beaker. Then n-hexane was added to beaker with weight ratio 15:11 of PDMS precursor mixed liquid in order to reduce the viscosity of solution. After that, PEDOT:PSS aerogel was completely immersed into the PMDS precursor n-hexane solution. After 72 h, the beaker was put in a vacuum oven under the temperature of 80 °C. After this had been cured at 80 °C for about 6 h, the PEDOT:PSS@PDMS conductor was obtained.

Characterization

SEM studies were done with Hitachi S-4800 microscope at an accelerating voltage of 10 kV. The digital photos were taken by Panasonic LUMIX GF2 cameras. Compression measurements and tensile stress-strain, using a Model 3365 Table Mounted Materials Testing System (Instron Co. USA), were obtained under the following conditions: d=11.00 mm, h=12.38 mm; compression speed, 10 mm min $^{-1}$; compression distance, 7.5 mm; T = 25 °C. Tensile measurements were performed under the following conditions: size, 11.27 mm×10 mm×0.82 mm; gauge length, 20 mm; speed, 50 mm min $^{-1}$; T = 25 °C. Current-voltage (I–V) curves were measured using a KEITHLEY 4200.The dependent temperature of conductivity was measured via four probe method using a physical property measurement system. The dependent temperature of conductivity was measured via four probe method using a Quantum Design Physics Property Measurement System (PPMS-9) under the following conditions: sample size, 13.6 mm × 2.73 mm × 0.74 mm; current, 1 mA; temperature rising rate, 3 K/min; temperature range, 2-300 K, wait times, 0 S; four silver silks (Φ=100 μm) fixed parallel by high purity silver paint on the surface of sample at interval of 2.73 mm were connected with the four probes of PPMS-9, separately. Bending cycles were performed on home-made bending station with Multimeter UT803 connecting two sides of samples. The specimen for electromechanical test was made into rectangular blocks with a dimension of 15 mm (length) × 8 mm (width) × 0.8 mm (thickness). Tensile cycle test was carried out on Instron 5843 equipped with a 1 kN load cell with a period of 60 s. Electrical properties of the composites were characterized by a standard two-probe method using a source meter (Keithley 2400). Roman spectra were recorded on a Jobin Yvon (Laboratory RAM HR800) confocal micro-Raman spectrometer backscattered geometry through a 10×(NA = 0.25) microscope objective. Ar+ laser emitting at a wavelength of 514.5 nm was used as a source of excitation. The Fourier transform infrared (FTIR) spectroscopy was taken on a Bruker EQUINOX55 FT-IR spectrometer under ambient conditions. CAs were measured on an OCA20 machine (DataPhysics, Germany) contact angle system at ambient temperature.

Roman Spectra of PEDOT:PSS and PEDOT:PSS@PDMS

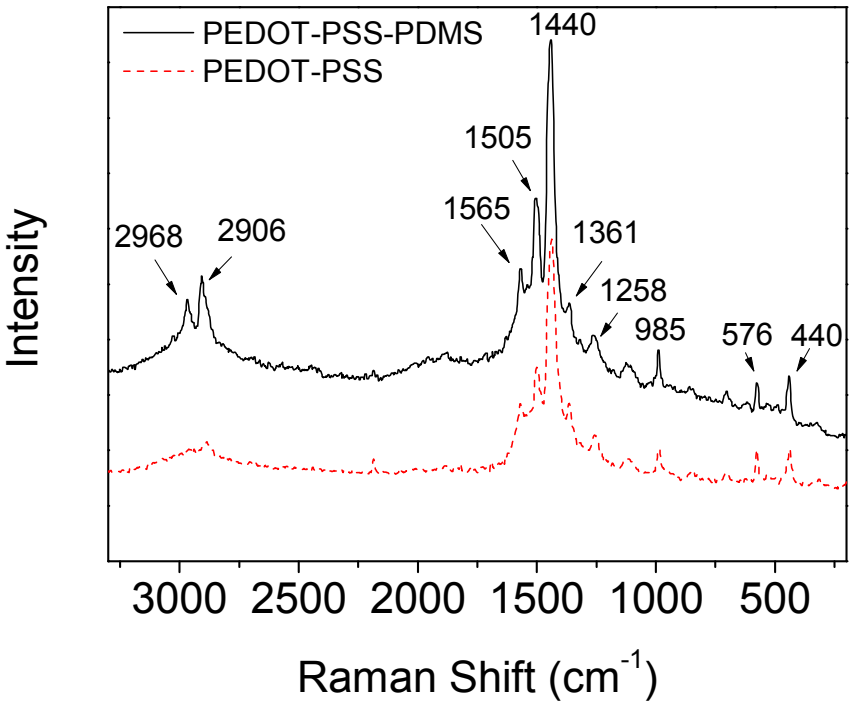

Fig. S1 Raman spectra of the as-prepared PEDOT:PSS aerogel (red line) and PEDOT:PSS@PDMS IPN conducting polymer composites (black line).

In order to determine the molecular structure of the resulting of frangible PEDOT:PSS aerogel belt and the flexible PEDOT:PSS@PDMS belt, Roman spectra were well performed. Fig. S1 show the Roman spectra of above-mentioned samples. In the Raman spectra, both samples exhibit the characteristic of PEDOT. A strong vibrational Raman band centered at 1440 cm^{-1} contributed to the symmetric stretching mod of the aromatic C=C band which had about 15 cm^{-1} red shift compared with the reported results.[2] This red shift might be related to the much larger size of macropores in our aerogel. Three important bands located at 1565, 1361 and 1258 cm^{-1} are related to the antisymmetric C_α- C_α, C_β- C_β stretching deformations and C_α- C_α inter-ring stretching vibrations, respectively. The bands located at 985 and 576 cm^{-1} could be ascribed to the oxyethylene ring deformation. It was also be found that the band for SO_2 bending from PSS was located at 440 cm^{-1}.[2] Compared with the Raman spectra of two samples, intense stretching vibrations of the methyl group appeared at 2968 and 2906 cm^{-1} were related to PDMS which demonstrated that PDMS had been

successfully embedded into the 3D network of PEDOT:PSS aerogel.[3]

3 D Structures of PDMS in PEDOT:PSS@PDMS

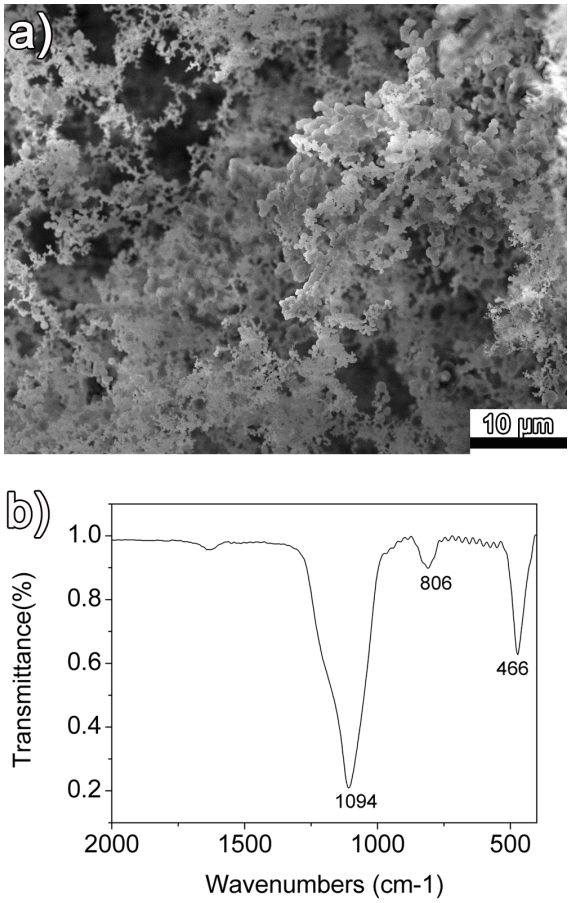

Figure S2 a) SEM image and b) IR spectra of sample obtained from PEDOT:PSS@PDMS heating under 600 ^{o}C

3 D structures of PDMS in PEDOT:PSS@PDMS composited polymer conductors were well examined. In oxygen atmosphere, PEDOT: PSS lost all its weight under 600 ^{o}C within 30 minutes. However, PDMS could not decompose completely due to formation of SiO_2 in the presence of oxygen. 3D structure of as-prepared film by heating PEDOT:PSS@PDMS, as shown in Figure S2 a) , indicates that PDMS has 3D structures in PEDOT:PSS@PDMS. Figure S2 (b) shows the FTIR spectroscopy analysis to obtained film. The spectra present three important bands identifying the SiO_2.[4] A peak at 1094 cm^{-1} was contributed to stretch antisymmetric mode of Si-O-Si group. 806 cm^{-1} corresponds to the bending vibration mode of Si-O group. It is also found that rocking mode of the Si-O group was located at 466 cm^{-1} .

Temperature dependence of the conductivity of PEDOT:PSS and PEDOT:PSS@PDMS

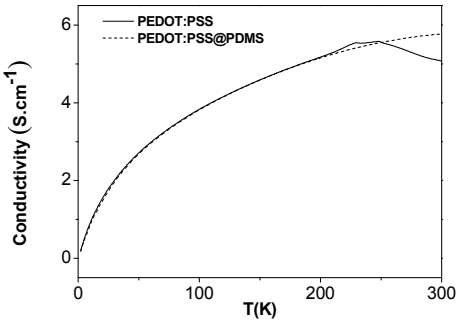

Figure S3 Temperature dependence of the conductivity of PEDOT:PSS and PEDOT:PSS@PDMS

The conductivity of PEDOT:PSS@PDMS increases monotonically from 0.2056 $S \cdot cm^{-1}$at 2 K to 5.0747 $S \cdot cm^{-1}$ at 300 K shown in Figure S3, indicating a semiconducting behavior.[5] The conductivity of PEDOT:PSS could not obey the linear relationship above the 245 K. The moisture/water content in PEDOT:PSS might result in the completely anomalous behavior of PEDOT:PSS aerogel above the temperature of 245 K.

Wettability of PEDOT:PSS and PEDOT:PSS@PDMS

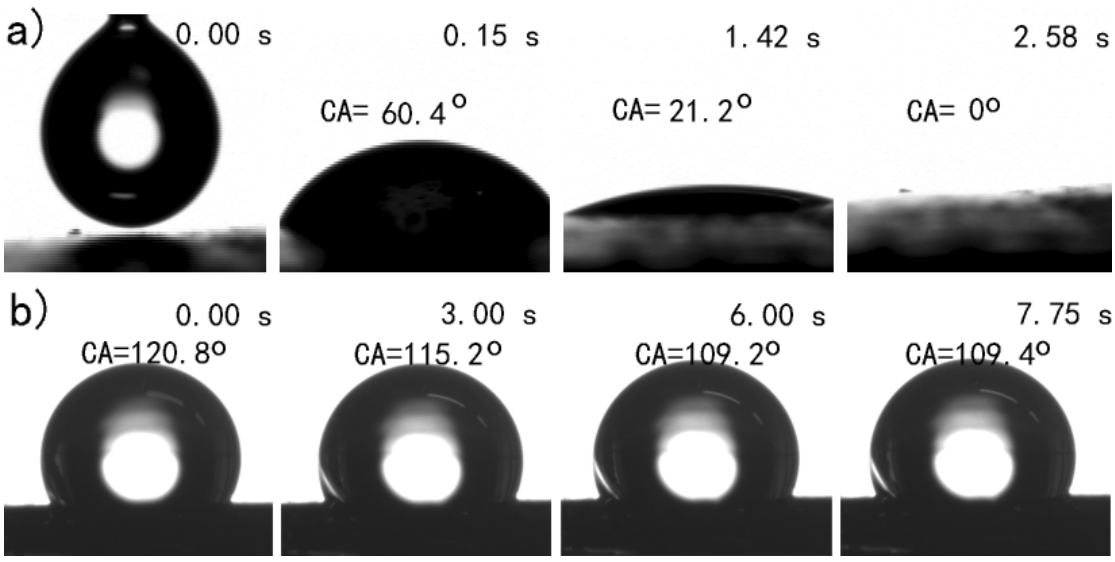

Fig. S4 a) Shapes of a water drop versus time placed on PEDOT:PSS film; b) Shapes of a water drop versus time placed on PEDOT:PSS@PDMS film.

When a water drop was placed on the PEDOT:PSS aerogel film, the CA of water drop became 0 within 2.58 s. This phenomena was from hydrophilic PSS segments and 3D macropores of PEDOT:PSS aerogel. The PEDOT:PSS@PDMS composite conductors could remain relative stable hydrophobic properties within long time.

References

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