Supporting Information

Bio-Inspired Design of Strong, Tough and Highly Conductive Polyol-Polypyrrole Composites for Flexible Electronics

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Experimental Section

Chemicals and materials. All chemicals were purchased from Sigma-Aldrich. Pyrrole and boron trifluoride diethyl etherate (BFEE) were distilled under reduced pressure prior to use. All the other chemicals were used without further purification. Microscopy glass slides (2.5 cm × 7.5 cm) were washed by acetone, isopropanol and water, then dried at 70 °C. A 10-nm Ti layer and then a 25-nm Pt layer were deposited onto the glass slides by vacuum sputtering.

Synthesis of polyol-PPy composites. Polyol-PPy composite films were synthesized using an electrochemical method.[22] The synthesis was performed in a one-compartment electrochemical cell consisting of a Pt-coated glass electrode (2.5 cm × 4 cm) as the working electrode, a 10 cm × 10 cm stainless steel sheet (0.5 mm thick, Type 304) as the counter electrode, and a 2.0 mm diameter Ag/AgCl wire (immersed directly in the solution) as the quasi-reference. The experiments were controlled by using a 660E electrochemical workstation (CHI). The typical electrolyte was 0.05 M pyrrole in a mixture of isopropanol (IPA) and boron trifluoride diethyl etherate (BFEE) at volume ratio V_{IPA}:V_{BFEE} = 7:3, with or without 5% polyols by volume. All the polyols used in this study except for PEG 1000 and PEG 2000 are liquid at room temperature, which were facilely dissolved in IPA. Regarding PEG 1000 and PEG2000 that are solid at room temperature, they were firstly dissolved in warm isopropanol under stirring. Then, the solution was cooled in an ice-water bath, and mixed with BFEE. Pyrrole was added to the solution at the last. The solution was degassed on a rotavap at 100 kPa for 5 min. The electro-polymerization was carried out at a constant current density of 0.8-1.0 mA/cm^2 at 0 °C for 2 hours. After synthesis, the working electrode was rinsed by isopropanol. Then the polymer film was readily peeled off the electrode, immersed in isopropanol for 5 min and left in the ambient air for overnight. The PPy film thickness was measured by using a micrometer caliper. Multiple sites on

one film were measured and the results were averaged to give the average thickness of the film. By controlling the duration of polymerization reaction, all the PPy films' thickness were controlled around 18-20 μm.

Material characterization. The infrared spectra of polyol-PPy samples were recorded on Thermo Scientific Nicolet iS5 with ATR diamond sensor. Polyol-PPy samples were firmly pressed on the diamond sensor and the spectra were recorded at room temperature with relative humidity 30%. The Raman spectra of polyol-PPy samples were recorded on Olympas Optical Raman Microscope employing a 514 nm laser beam, by using a 50× objective at a low power (0.5 mW) and accumulated two times for 60 s each. The morphology of polyol-PPy films was examined by field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F). The X-ray diffraction of PEE-PPy films before and after tensile test was performed at Shanghai synchrotron radiation center.

Conductivity and mechanical properties. The electrical conductivity of polyol-PPy composite films was measured by standard four-probe method at room temperature. Mechanical property analysis of polyol-PPy composite films was performed on Instron 3340 universal testing instrument at 25 °C and under the relative humidity of 30%. For mechanical test, the typical sample size was 0.4 cm wide, 2 cm long and 18-20 μm thick. The distance between the two clamps on the Instron machine was 7 mm. The elongation rate was 1 mm/min.

Demonstration of PEE-PPy samples as flexible conductors. PEE-PPy film was cut into a stripe (0.46 cm × 5 cm × 26 μm) and made into different shapes such as spiral stripe and knots, which can be stretched repeatedly. The PEE-PPy stripe was used as a flexible conductor in a circuit for lighting up a blue LED by using a 3 V battery. The deformation of PEE-PPy stripe did not affect the brightness of the LED.

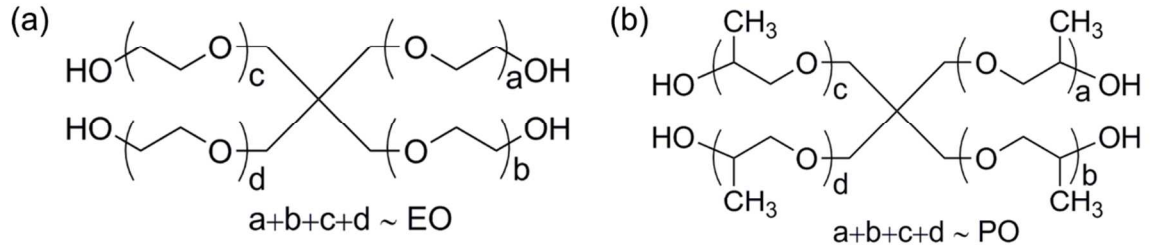

Figure S1. The tetra-armed structure of PEE 800 (a) and PEP 600 (b). EO and PO represented the structural unit respectively.

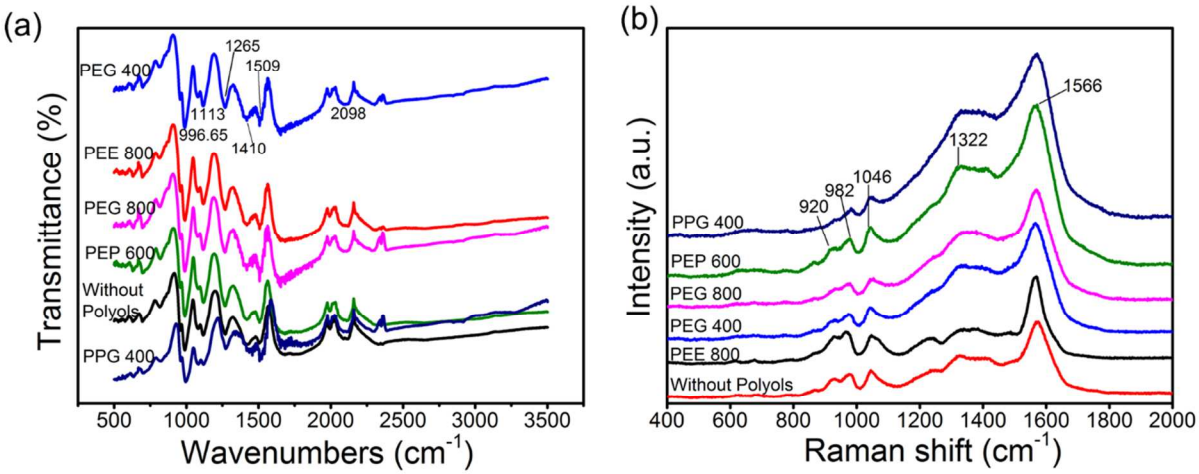

Figure S2. The FTIR spectra (a) and Raman spectrum (b) of several typical polyol-PPy composites and PPy without polyols.

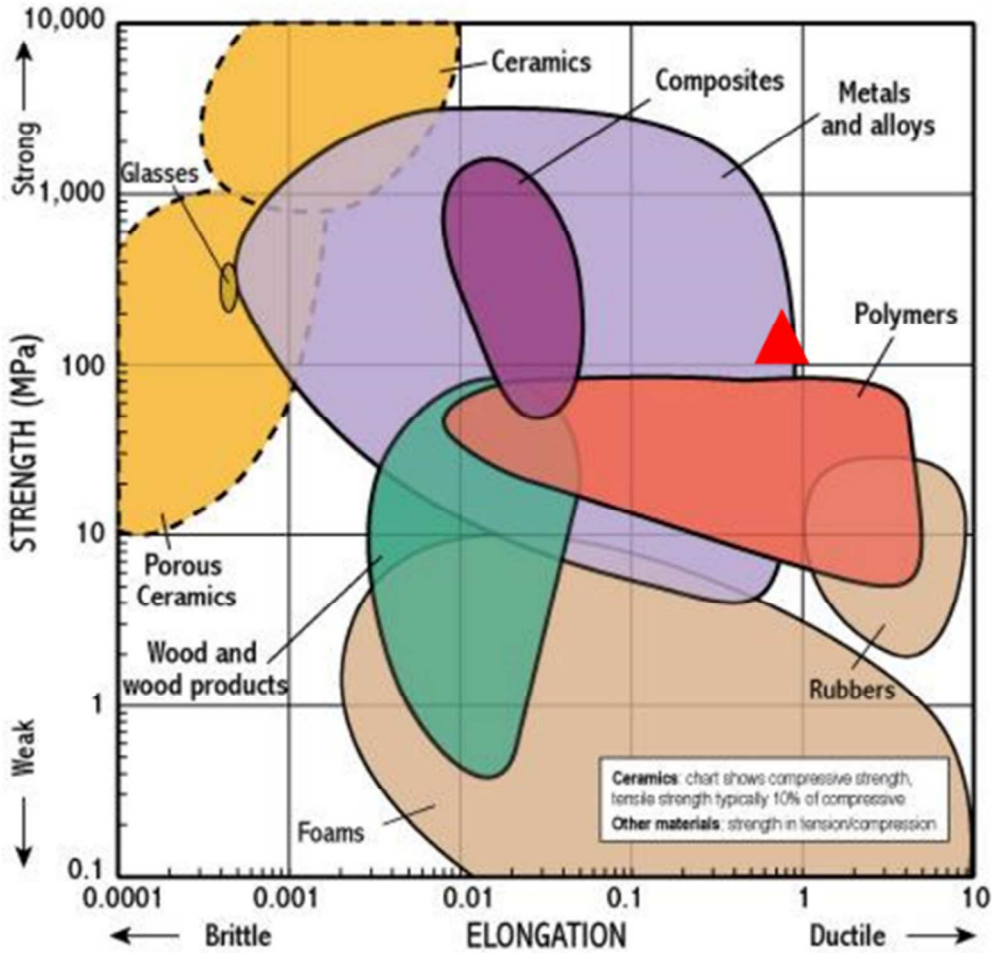

Figure S3. The comparison between PEE-PPy composite and several typical materials on mechanical performance. The red triangle indicates the PEE-PPy film's corresponding strength-elongation value. The strength-elongation distribution of different materials were adapted from http://www-materials.eng.cam.ac.uk/mpsite/interactive_charts/strength-ductility/basic.html

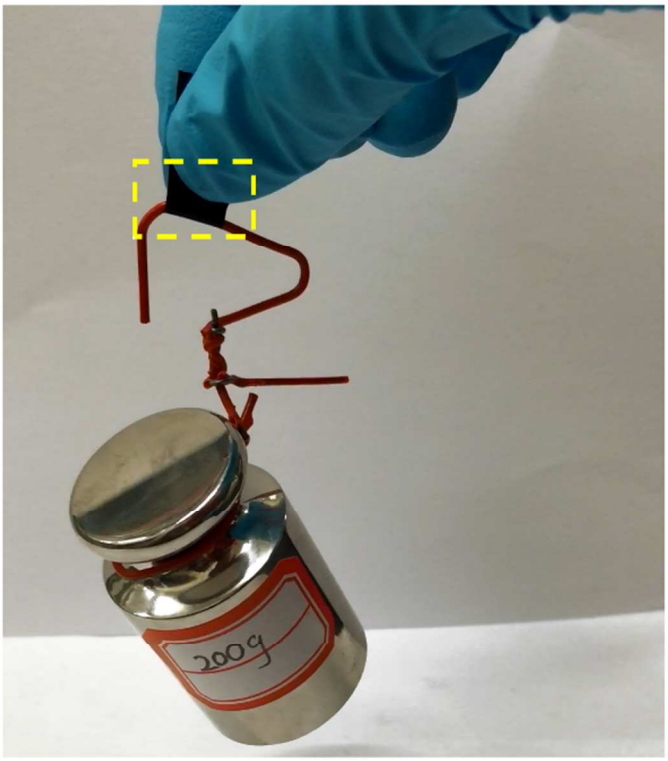

Figure S4. A small piece of PEE-PPy film (width of 7 mm and thickness of 30 μm) can be used as a rope to hold a 200-g weight. The yellow dotted area indicates PEE-PPy sample.

Table S1. Conductivity, density and mechanical properties of polyol-PPy composites and PPy without polyols.

Polyol	Conductivity (S/cm)	Density (g/cm^3)	Tensile Strength (MPa)	Elongation at break (%)
PEE 800	115 (±10)	1.911	125	75
PEG 2000	110 (±9)	1.703	85	65
PEG 1000	93 (±7)	1.748	104	62
PEG 800	105 (±7)	1.696	109	58
PEG 600	113 (±4)	1.659	112	60
PEG 400	102 (±12)	1.75	116	50
PEG 200	110 (±11)	1.716	123	31
PEP 600	85 (±10)	1.793	122	37
PPG 400	87 (±2)	1.671	113	29
Without Polyols	89 (±5)	1.516	115	17

Movie S1. A 200-g weight can be easily pulled up by using a small piece of PEE-PPy as rope (width of 7 mm and thickness of 30 μm).

Movie S2. A PEE-PPy stripe can be twisted into a spiral shape, which can be repeatedly stretched and released.

Movie S3. A long PEE-PPy stripe (0.46 cm × 5 cm × 26 μm) was used as a flexible conductor in a circuit. A blue LED in this circuit can be steadily lighted when the PEE-PPy conductor was deformed.