

## Supporting Information

### A highly temperature- and pressure-sensitive soft sensor self-powered by a galvanic cell design

Chenghao Dai<sup>a,b</sup>, Huan Chen<sup>a,b</sup>, Lei Wang<sup>a,b</sup>, Yongqi Liu<sup>a,b</sup>, Qiyang Yin<sup>a,b</sup>, Jintao Jiang<sup>a</sup>, Qiyang Zhou<sup>a</sup> and Gengsheng Weng<sup>a,b,\*</sup>

<sup>a</sup> *School of Materials Science and Chemical Engineering, Ningbo University, Ningbo, 315211, China*

<sup>b</sup> *Ningbo Key Laboratory of Specialty Polymers, State Key Laboratory Base of Novel Functional Materials and Preparation Science, Ningbo University, Ningbo, 315211, China*

#### 1. Materials

Carboxylated nitrile butadiene rubber (XNBR, NANCAR 1072, Mooney viscosity of 48, carboxylic acid content of 7 wt%) was kindly supplied by NANTEX. The 2,2'-azobis (isobutyronitrile) (AIBN) and N, N-Dimethylacrylamide (DMA) were provided by TCI. The glycidyl methacrylate (GMA), Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2-hydroxy-2-methylpropiophenone (photo initiator) and ethylene glycol dimethacrylate (EGDMA) were purchased from Macklin. NiCl<sub>2</sub>·6H<sub>2</sub>O was supplied by Adamas Reagent. Anthracene-9-carboxylic acid (Anca) was purchased from Aladdin. Benzyltriethylammonium chloride (BTAC) was purchased from Energy Chemical. Multi-walled carbon nanotubes (CNTs, diameter of 30~50 nm, length of 10-20 μm and purity > 95 wt%) was purchased from TIME NANO. The CNTs were stirred in a mixture of sulfuric acid (98 wt%) and nitric acid (68 wt%) with a volume ratio of 3:1 at 40 °C for 48 h, and washed several times with deionized water until the filtrate showed neutral pH to remove the amorphous carbon and metallic nanoparticles (used as a catalyst during synthesis). GMA was passed through a basic aluminum oxide column prior to use. AIBN was recrystallized from ethanol. Deionized water (High-Q, Inc. 103S Stills) with a resistivity of > 10.0 MΩ was used throughout the preparation of soft sensors.

#### 2. Preparation of the self-powered elastomeric sensors

##### 2.1 Preparation of Ni<sup>2+</sup>-and Zn<sup>2+</sup>-elastomers

The XNBR was first dissolved in dioxane under room temperature to obtain the XNBR solution (10 w/v%). Typically, to prepare the IPN elastomer with a Ni-to-COOH ratio of 0.086:1, 2 mL of XNBR solution (0.3 mmol COOH), 0.4 g of DMA (4 mmol), 20 μL of EGDMA (0.021g, 0.1mmol), 15 μL of photo initiator (0.1 mmol), 0.006 g of CNTs and 10 μL of NiCl<sub>2</sub>·6H<sub>2</sub>O methanol solution (50 w/v%, 0.026 mmol) were first mixed

and sonicated (power of 180 W) for 30 min. Then, the mixture was poured into a Polytetrafluoroethylene (PTFE) mold ( $40 \times 40 \times 7 \text{ mm}^3$ ). After exposed to UV light ( $1 \text{ mW/cm}^2$ , 365 nm) for 20 min, an organogel with interpenetrated networks was obtained. Through subsequent drying of the as-prepared organogel, a  $\text{Ni}^{2+}$ -elastomer film was obtained. Using  $18 \mu\text{L}$  of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  methanol solution (50 w/v%, 0.026 mmol) instead of the  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  methanol solution, a  $\text{Zn}^{2+}$ -elastomer film was prepared.

## **2.2 Fabrication of the self-powered soft sensor**

The as-prepared  $\text{Zn}^{2+}$ - and  $\text{Ni}^{2+}$ -elastomer films were first subjected to saturated water vapor for 3h. Then, using a Cu foil electrode as the cathode and a Zn foil electrode as the anode, the galvanic-cell-based soft sensor was fabricated by sandwiching the  $\text{Ni}^{2+}$ - and  $\text{Zn}^{2+}$ -elastomers between the Cu and Zn electrodes.

## **3. Preparation of the fluorescent probe containing $\text{Zn}^{2+}$ -elastomer film**

The anthracene-9-carboxylic acid (Anca) modified P(DMA-*co*-GMA) was used as a blue-emissive fluorescent probe to observe the distribution of the PDMA in the  $\text{Zn}^{2+}$ -elastomer matrix by confocal laser scanning microscopic (CLSM) imaging. First, a P(DMA-*co*-GMA) was prepared with a DMA-to-GMA mole ratio of 15/1. Typically, DMA (2g, 20.2mmol), GMA (0.192g, 1.35mmol) and AIBN (7 mg, 0.0431 mmol) were dissolved in 4mL of anisole in a 25 mL flask. After degassed under vacuum and filled with nitrogen for 10min, the mixture was then sealed and placed in a pre-heated oil bath at  $65^\circ\text{C}$  for 8 h. After reaction, the mixture was cooled down to room temperature and precipitated in hexane and dried under vacuum for 24 h to obtain the P(DMA-*co*-GMA).

The grafting of Anthracene-9-carboxylic acid (Anca) to the copolymer was carried out via the ring-opening reaction of epoxide moieties. The P(DMA-*co*-GMA) (0.5 g, 0.307 mmol in terms of GMA units) was firstly dissolved in 5 mL methanol. The 4 mL Anca and benzyltriethylammonium chloride (BTAC) methanol solution (0.206 g Anca and 0.211 g BTAC) was then added into the P(DMA-*co*-GMA) solution dropwise and refluxed at  $65^\circ\text{C}$  for 12 h. After reaction, the mixture was then precipitated in mixed solvent of hexane/diethyl ether (1/1, v/v) for three times and dried under vacuum for 24 h to obtain Anca-modified P(DMA-*co*-GMA).

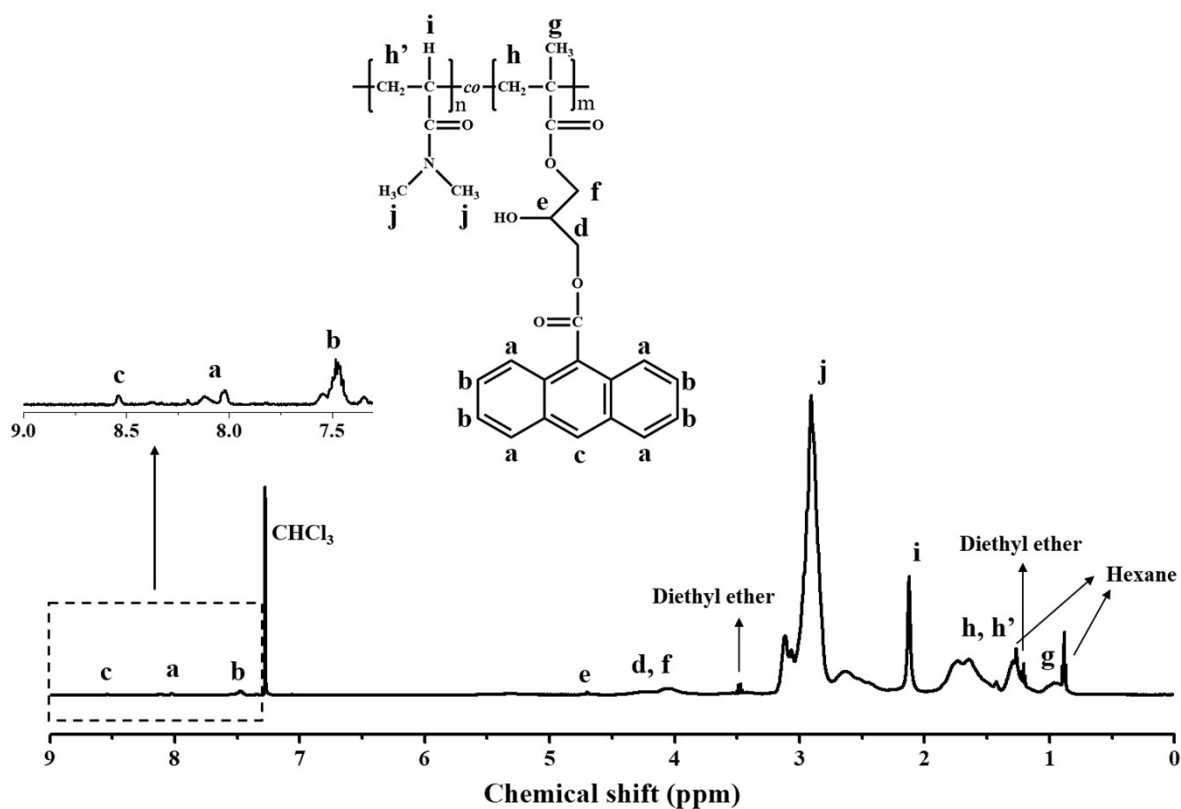
To prepare the fluorescent probe containing  $\text{Zn}^{2+}$ -elastomer film, 4 mL Anca-modified PDMA dioxane solution with 0.4 g Anca-modified P(DMA-*co*-GMA), 2 mL of XNBR dioxane solution (10 w/v%), 20  $\mu\text{L}$  of EGDMA (0.021g, 0.1mmol), 15  $\mu\text{L}$  of photo initiator (0.1 mmol) and 18  $\mu\text{L}$  of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  methanol solution (50 w/v%, 0.026 mmol) were mixed and sonicated (power of 180 W) for 30 min (a DL-180B sonicator from Zisun, Shanghai). Then, the mixture was molded in the PTFE mold ( $40 \times 40 \times 7 \text{ mm}^3$ ). After exposed to UV light ( $1 \text{ mW/cm}^2$ , 365 nm) for 20 min, an organogel was obtained. Through subsequent drying of the as-prepared organogel, a fluorescent probe containing  $\text{Zn}^{2+}$ -elastomer film was obtained.

#### 4. Characterization

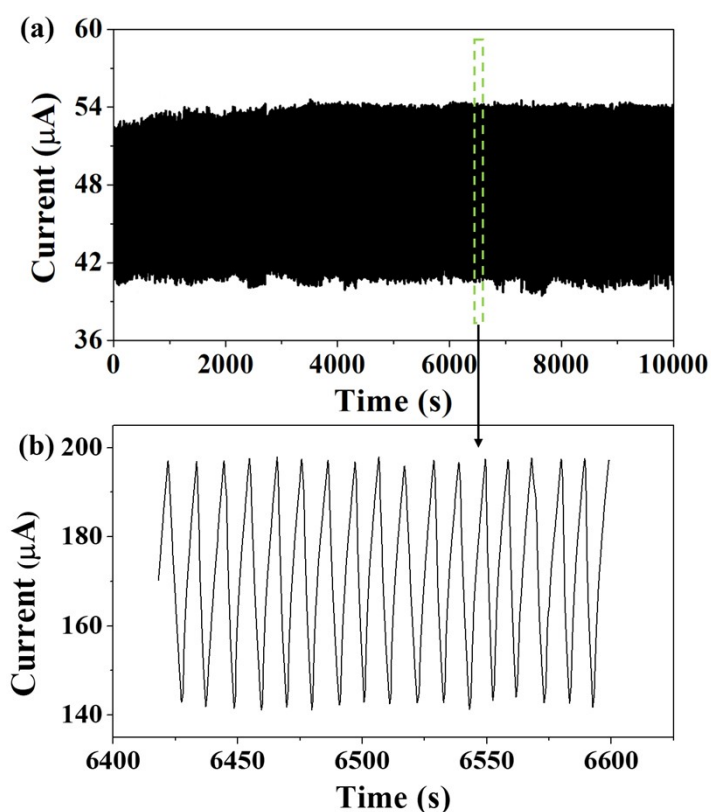
UV irradiation experiments were carried out using a 365 nm UV lamp (UV-20A, 1 mW/cm<sup>2</sup>, Shanghai-Yaozhuang) to prepare IPN elastomeric films. The dispersion of CNTs were characterized by transmission electron microscope (TEM, FEI Tecnai G2 F20 S-TWIN). Ultrathin sections for TEM were prepared using a Leica Ultracut UCT ultramicrotome. The Ni<sup>2+</sup> and Zn<sup>2+</sup> distribution in the elastomer was investigated by a scanning electron microscopy (SEM) instrument (Su-70, Hitachi, Japan) operated at 15 kV coupled with an energy dispersive X-ray (EDX) spectrometer (EDAX, AMETEK Materials Analysis Division, USA). Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on a Bruker Ascend 500 MHz spectrometer using CDCl<sub>3</sub> as the solvent for Anca-modified PDMA. A confocal laser scanning microscope (CLSM, Leica TSC SP8 FALCON) was used to observe the distribution of Anca-modified PDMA and XNBR phases. Uniaxial tensile tests on the elastomer films (thin strip samples of 25 × 10 × 0.4 mm<sup>3</sup>) were carried out on an MTS Criterion Model 43 material testing machine with a loading cell of 100 N and a tensile speed of 50 mm min<sup>-1</sup> at 25 °C.

The V-I and discharging measurements of galvanic cells were conducted on an IT8511A+ electronic load using electrodes of a surface area of 16 cm<sup>2</sup>. The elastomer films for those measurements were 4 cm in length and 0.4 mm in thickness. The discharging behaviors of all cells were conducted at a discharging current of 12.5 μA and a stop voltage of 0 V. All measurements were carried out at 25 °C.

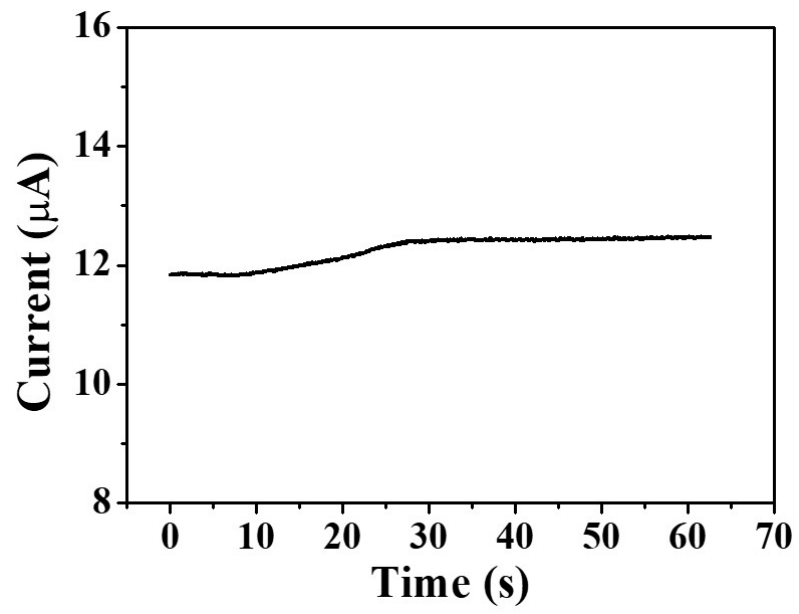
A Keithley 2000 multimeter was used to measure the pressure and temperature-sensitive current changes of the soft sensors throughout this work. To measure the current variation of the soft sensor (diameter of 1.5cm, area of 1.77cm<sup>2</sup>) upon heating, a Cossim PRT-8A hot plate (from 25 to 60°C, the heating rate is 10 °C/min) was used. The 1000 heating (40 °C)/cooling(30 °C) cycles at a switching frequency of ~0.1 Hz were also conducted to investigate the durability and repeatability. The Keithley 2000 multimeter was also chosen to measure the influence of force on the soft sensor (4 × 4 cm<sup>2</sup>) using an Metravib DMA +1000 dynamic mechanical analyzer with a fatigue mode for cyclic loading (frequency of 2.5 Hz, 25 °C, displacement of 0.05mm,0.03mm and 0.01mm). A multichannel signal recorder Toprie TP700 was applied to record the multichannel current changes of the electronic skin at 25 °C.



**Figure S1.**  $^1\text{H}$  NMR spectra of Anca-modified PDMA using  $\text{CDCl}_3$  as the solvent.



**Figure S2.** (a) The current changes of the SE sensor when alternatively subjected to 1000 heating (40  $^{\circ}\text{C}$ )/cooling(30  $^{\circ}\text{C}$ ) cycles at a switching frequency of  $\sim 0.1$  Hz. (b) The enlarged part of the current changes in (a).



**Figure S3.** The influence of finger temperature on the current signals of one “pixel” from the electronic skin.