

Supporting Information

A supramolecular electrode with high self-healing efficiency at room temperature, recyclability and durability for dielectric elastomer generator

Wenpeng Zang^{1, 1}, Sijin Jin^{1, 1}, Shuxiong Fu¹, Yuhao Wang¹, Yingjie Jiang¹, Xueying
Liu¹, Nanying Ning^{*,1,2,3}, Ming Tian^{*,1,2,3} and Liqun Zhang^{1,2,3}

1. State Key Laboratory of Organic-Inorganic Composites, Beijing University of
Chemical Technology, Beijing 100029, China;

2. Beijing Advanced Innovation Center for Soft Matter Science and Engineering,
Beijing University of Chemical Technology, Beijing 100029, China;

3. Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education,
Beijing University of Chemical Technology, Beijing 100029, China;

⊥ Wenpeng Zang and Sijin Jin contributed equally to this work and they should
be regarded as co-first authors.

* Corresponding authors. Tel.: 86 10 64456158; Fax: 86 10 64433964.

E-mail addresses: tianm@mail.buct.edu.cn (M. Tian);

ningny@mail.buct.edu.cn (N. Ning)

Table S1 The content of CB and CG in each reference and experimental samples.

| Samples | PDMS (g) | CB (g) | CG (g) | BA (g) |
|---|----------|--------|--------|--------|
| CB ₄ /PBS-SN | 10 | 0.4 | 0 | 0.02 |
| CB ₄ /CG ₁₀ /PBS-SN | 10 | 0.4 | 1 | 0.02 |
| CB ₄ /CG ₃₀ /PBS-SN | 10 | 0.4 | 3 | 0.02 |
| CB ₄ /CG ₅₀ /PBS-SN | 10 | 0.4 | 5 | 0.02 |

Characterizations and measurements

Fourier transform infrared (FT-IR) spectra were recorded at a Bruker TENSOR 27 FT-IR spectrometer (Germany) from 4000 to 500 cm⁻¹ by transmission mode.

The optical images and microstructure of electrode were investigated by using optical microscope (JTVMS-1510T) and scanning electron microscope (SEM, S-4800), respectively.

The electrical conductivity (EC) of electrode under different strain was measured by a four-probe tester HPS 2661a and a Tensile apparatus (Instron 5567, USA). The durability of EC was characterized on a GX-80 motorized linear stage, which was used to stretch the DE film sandwiched with two electrodes, meanwhile, a Keithley 6500 digital multimeter was employed to record the resistance value in the tensile cycle. The capacitance under different strains was measured and recorded by a Digital Multimeter (DMM6500, Tektronix, USA). The input bias voltage was controlled by a high voltage DC source (AMP-20B20, Matsusada, Japan).

The electrode was loaded on the DE matrix and cut into dumbbell-shaped splines (length × width × thickness: 20 × 4 × 0.3 mm³). The influence of the electrode on the

mechanical properties of the DE matrix was tested by Tensile apparatus (Instron 5567, USA) at room temperature with a tensile rate of 500 mm/min.

In the energy harvesting process of DEG, it is often assumed that the DE film is an ideal material of incompressible and electrically insulated, and thus it is considered that there is no energy loss in such process. According to the charge conservation ($Q = C_1V_1 = C_2V_2$) and the energy storage calculation formula of capacitor, the energy generated ($\Delta E_{harvest}$) of DEG during a single cycle can be calculated according to the following formula:

$$E_{harvest} = E_{out} - E_{in}$$

$$= \frac{1}{2}[(C_2 + C_p)V_2^2 - (C_1 + C_p)V_1^2] = \frac{1}{2}(C_1 + C_p)V_1^2\left(\frac{C_1 + C_p}{C_2 + C_p} - 1\right) \quad (S1)$$

E_{out} and E_{in} in the formula respectively refer to the electrical energy output by DEG and the mechanical energy input of DEG. C and V represent the capacitance and the voltage of DE, respectively, and the subscripts 1 and 2 represent the stretching state and releasing state of the DE film, respectively. V_1^2 and V_2^2 represent the square of the voltage at the stretching state of the DE film and the square of the voltage at the releasing state of the DE film, respectively. C_p is the parallel transmission capacitor in the circuit, which mainly plays the role of anti-breakdown protection, and C_p is usually set to 1.3 times of C_1 .

At the same time of discharge, according to Joule's law, there will inevitably be a certain energy loss (ΔE_{loss} of electrode). Thus, equation (S2) can be obtained:

$$\Delta E_{loss} \text{ on electrode} = I^2 R_e t = \left(\frac{Q}{t}\right)^2 R_e t = \frac{(C_1 V_1)^2 R_e}{t} \quad (S2)$$

In the formula, I is the current flowing through the electrode during charging, R_e is the resistance of the electrode under different strains, t is the charge time, and Q is the charge quantity. Therefore, the electrode with low R_e (high electrical conductivity (EC)) can decrease the ΔE_{loss} on electrode during working cycle.

The crosslinking density of electrode was evaluated by a low field nuclear magnetic resonance (NMR) analyzer (Niumag Corporation, China) at 20 MHz proton resonance frequency and a magnetic field strength of 0.5 T. The samples (5 cm long and 0.5×0.5 cm in cross-sectional area, about 2 g) were placed in a cylindrical glass tube (18 mm in diameter) and then inserted into the probe of the low field NMR analyzer.

The basic principle of Low field NMR studying the structure and dynamics characterization of elastomers consists the spin-spin relaxation time T_2 . The spin-spin relaxation time T_2 depends on the mobility of chemical components of an elastomer. Normally, the stiffness of fractions like polymer chains and polymer-interfaces is described by correlation times of different orders. Thus, the transverse NMR relaxation decay can be separated by functions which can be identically referred to these fractions. The contribution of each fraction to the signal is proportional to its content in a sample. Usually, the nuclei of polymer network protons are quite movable and their T_2 vary within 0.3-15 ms depending on the crosslinking degree. The more heterogeneous structure of an elastomer caused by the network cross-linking, the wider the T_2 slow distribution. Based on the XLD Model, the crosslinking density (V_c) can be calculated by the following Equation:

$$V_c = \frac{\rho}{M_c} = \frac{5\rho N\sqrt{q}}{3C_\infty M_{ru}} \quad (\text{S3})$$

Where, ρ : density of sample; M_c : number average molecular weight of the elastomer (g/mol); N : the number of bonding of the main chain; q : the anisotropic factor; C_∞ : flexibility parameter of the elastomer chain; M_{ru} : molecular weight of monomer unit (g/mol).

The conductivity properties of the coated electrodes before and after self-healing were tested in situ on DE films. The electrode was first cut off without damaging DE films, and then the separated electrode was recontacted at room temperature for about 0.5, 1, 2 and 3 h, respectively. The self-healing efficiency of conductivity (SEC) was calculated by Equation S4.

$$SEC = \frac{\rho_{healed}}{\rho_{original}} \times 100\% \quad (\text{S4})$$

where $\rho_{original}$ and ρ_{healed} correspond to the conductivity for original and healed electrodes, respectively.

The recycling properties of the coated electrodes before and after self-healing were also tested under the help of solvent as following. The electrode was first removed from DE film, and then solved in cyclohexane. Finally, the electrode was recoated on DE film and reused in energy harvesting process.

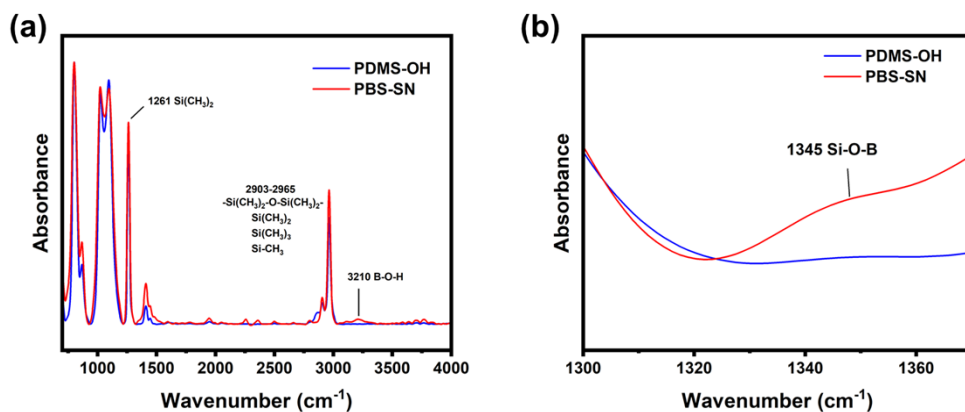


Figure S1. (a) FTIR spectra of hydroxyl-terminated polydimethylsiloxane (PDMS-OH) and PBS-SN; (b) Partial magnification of FTIR image.

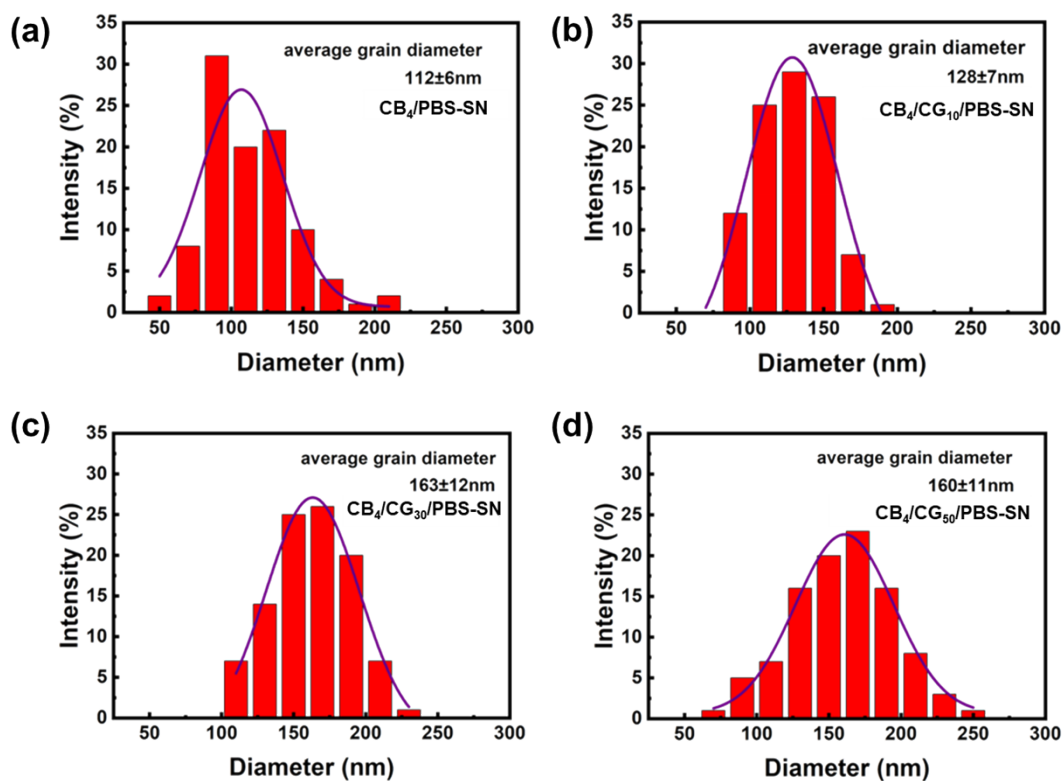


Figure S2. Particle size distribution of CB in (a) $\text{CB}_4/\text{PBS-SN}$ electrode, (b) $\text{CB}_4/\text{CG}_{10}/\text{PBS-SN}$ electrode, (c) $\text{CB}_4/\text{CG}_{30}/\text{PBS-SN}$ electrode and (d) $\text{CB}_4/\text{CG}_{50}/\text{PBS-SN}$ electrode.

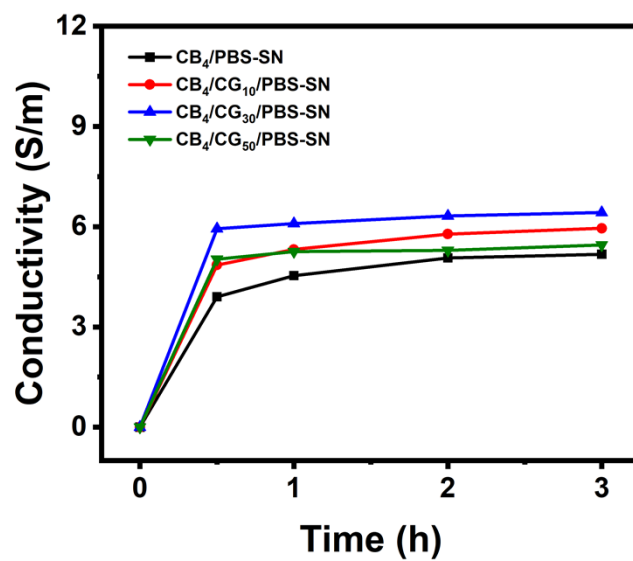


Figure S3. Variation of electrode conductivity with healing time.

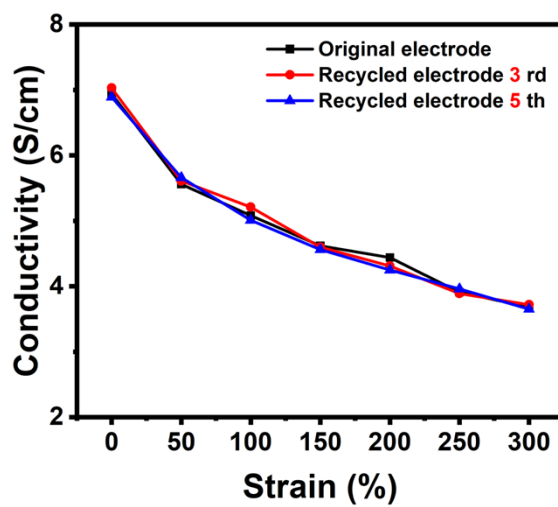


Figure S4. The conductivity-strain curves of CB₄/CG₃₀/PBS-SN electrode after multiple recycling.