Supplementary Information

Highly Stretchable Strain Sensors with Reduced Graphene Oxide Sensing Liquids for Wearable Electronics

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Table of contents
1. Materials and Methods
2. Supplementary Table
3. Supplementary Figures
4. Mechanism Analysis
5. Supplementary References
1. Materials and Methods

Material: The KMnO$_4$, H$_2$SO$_4$ (98%), H$_3$PO$_4$ (85%), H$_2$O$_2$ (30%), HCl (37%), N$_2$H$_4$-H$_2$O (≥85%) and NH$_3$-H$_2$O (≥25%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Natural graphite flakes (325 meshes) was provided by Alfa-Aesar. The Ecoflex rubber (00-30) was provided by Smooth-On and the acrylic tape (3mm thick, 4965PV0) was purchased from TESA. All these reagents were used without further purification.

Preparation of GO: GO was synthesized by the oxidation of 325 meshes graphite flakes based on the modified Hummers method. Typically, natural graphite flakes (3.0 g) was dispersed in a mixture of concentrated H$_2$SO$_4$/H$_3$PO$_4$ (360:40 ml) under stirring in an ice bath, KMnO$_4$ (18 g) was added slowly to keep the temperature of the suspension lower than 20°C. Then, the reaction system was transferred to a 40°C oil bath and vigorously stirred for about 30 min. Then, 50 ml deionized water (DI) was added, stirred for another 15 min at 95°C. Successively, additional 150 ml water was added, and 5 ml H$_2$O$_2$ was added drop wise until gas generation was completed, turning the color of the solution from dark brown to yellow. Bright-yellow suspension was treated by filtration, and the resulting solid material was washed 3 times with 1:9 HCl aqueous solutions (50 ml) to remove metal ions, and then, washed with DI to remove the residual acid. Finally, the resulting solid GO was dried in air and dispersed in DI to form 0.5 mg/ml GO aqueous dispersion for use.

Preparation of rGO foams: GO dispersion was reduced to rGO according to a previously reported method. The resulting homogeneous GO dispersion (0.5 mg/ml, 50 ml) was mixed with 50 ml DI, 17.5 µl N$_2$H$_4$-H$_2$O and 350 µl NH$_3$-H$_2$O in a 250-ml reaction flask. After being vigorously stirred for a few minutes, the reaction system was set in a 95°C oil bath for 1 h. When the reaction was completed, gauze was used to filter out a small amount of residue. Successively, the as-obtained rGO foams were collected and then diluted to a desired concentration.

Fabrication of rGO/DI liquids strain sensor: The cleaned PET substrate (100µm thick) was cut into size of 40mm×30mm and was patterned in a rectangular shape (30mm×10mm×3mm) with acrylic tape covered around the PET. Then, the rectangular shape was filled up with 2g mixed Ecoflex rubber (mass ratio A: B=1:1) after a wire (d=1mm) was left in the middle. When the rubber was cured after 2 hours, the acrylic tape was detached from the PET slide. The wire was pulled to one end as the conductor and left a cylindrical cavity (30mm long, d=1mm). Another wire (d=1mm) was used to block the cylindrical cavity after the as-obtained rGO/DI liquids injected into. Finally, the translucent and highly
stretchable strain sensor (30mm×10mm×3mm) was manufactured after sealing and peeling off the PET. The length of sensing fluid is 20 mm.

**Characterizations and testing:** The Raman spectrum was obtained by utilizing confocal Raman spectroscopy (Horiba JY-HR800) with an Ar⁺ laser source at room temperature (λ=633nm). JEOL scanning electron microscope (SEM, JSM-6490) was employed to observe the morphology of synthesized materials. The electromechanical properties of the strain sensors were measured with semiconductor characterization system (Keithley 4200) and a digital source meter (Keithley DMM-7510).

### 2. Supplementary Table

#### Table S1. The performance comparison of strain sensors ("-" means Not Shown)

<table>
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<tr>
<th>Material</th>
<th>Maximum GF</th>
<th>Stretchability</th>
<th>Limit of detection</th>
<th>Durability</th>
<th>Reference</th>
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<tr>
<td>Carbon fiber+ZnO NWs</td>
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<td>[3]Nanoscale 2013</td>
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<td>Ag NP</td>
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<td>[6]Nanoscale 2014</td>
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<td>Graphene-Nanocellulose paper</td>
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<td>[7]. Adv. Mater. 2014</td>
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<td>Laser scribed graphene</td>
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<td>Ag NWs+elastomer</td>
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<td>[9]ACS Nano 2014</td>
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<td>[12]. Adv. Funct. Mater. 2015</td>
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<td>Graphene foams+PDMS</td>
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<td>[16]. ACS Nano 2015</td>
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<td>Graphene foam+PI</td>
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<td>2000</td>
<td>[17]. ACS Nano 2015</td>
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### Table 3. Nanocomposites

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<tr>
<th>Material Description</th>
<th>Ag NWs</th>
<th>Fish scale-like rGO/tape film</th>
<th>Self-Assembly Graphene film</th>
<th>MoS$_2$+Graphene film</th>
<th>Ag NWs+rubber</th>
<th>Graphene+TPU foam</th>
<th>PVA/MWCNT/PEDOT:PSS</th>
<th>Graphene foam+CNT</th>
<th>RGO+DI liquids</th>
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2015 [18]. Nano Letter 2015

Fish scale-like rGO/tape film 16 [19]. ACS Nano 2016


PVA/MWCNT/PEDOT:PSS 5.2 [24]. Nanoscale. 2017


RGO+DI liquids 31.6 400% 0.1% 10000 This work

3. Supplementary Figures

**Figure S1.** Digital photographs of a) natural graphite flakes, b) GO suspension, c) rGO foams, and d) rGO/DI liquids.
**Figure S2.** SEM images of rGO foams from rGO/DI liquids a) 1 mg/ml, b) 6 mg/ml.

**Figure S3.** a) Resistance-time curves of DI (2 ml), RGO/DI liquids (1 mg/ml, 6 mg/ml, and 5 ml), b) Resistances of DI (1 ml), RGO/DI liquids (1 ml) and 6 mg pure rGO solid.

**Figure S4.** Schematic illustration of fabricating the rGO/DI liquids strain sensor a) PET substrate, b) patterned in a rectangular shape (30 mm×10 mm×3 mm), c) a wire (d=1 mm) was installed above the PET substrate, d) filled up with 2 g mixed Ecoflex rubber and cured after 2 hours, e) filled up with the sensing liquids, f) sealed and peeled off the PET.
Figure S5. Schematic illustration of the pressure measurement setup a) Unload, b) Load.

The pressure applied in the vertical direction and it can be considered equal to the weight measured by the electronic balance. It means $F=mg$. The pressure act on the slide (10 mm wide) which was always contacted the upper surface of the device (10 mm wide). Therefore, the pressure acting area is a constant equivalent to the size of the slide (10 mm wide, 15 mm long) during the pressure applied.

Figure S6. Mechanical stability of cycling pressure rGO/DI liquids strain sensor a) 1000 cycles, b) 14000 cycles.
Figure S7. The method of calculating the strain during the stretch applied.

\[
\varepsilon = \frac{L - L_0}{L_0}
\]

Figure S8. Top-view images of the rGO/DI liquids (6mg/ml) a) Unload, b) Loading with 5 kPa, c) Relax, d) Stretch with 5%.
**Figure S9.** The typical resistance-time curve of the rGO/DI liquids strain sensor upon cyclic stretching/releasing to 200%, 300% and 400% (stretching rate = releasing rate = 2.5 %·s⁻¹).

**Figure S10.** Mechanical stability of cycling tensile rGO/DI liquids strain sensor under a) small strain from 0.1% to 1%, b) large strain from 200% to 400%.
Figure S11. The durability of the sensor over the time from 0 hour to 72 hours after fabrication, and the response curve of the device recycled the sensing liquid.

4. Mechanism Analysis

On the basis of the Figure 2, the sensing mechanism of rGO/DI liquids strain sensor is theoretically analyzed as follows.

The initial resistance of this strain sensor, $R_0$, can be depicted by equation S1:

$$R_0 = R_D + R_r = \rho \frac{l}{S} + R_r$$  \hspace{1cm} \text{(S1)}

Where $R_D$ is the inherent resistance of DI, $R_r$ is the contact resistance of rGO foams at 0% strain or 0kPa. $\rho$, $l$, $S$ is the resistivity, length and cross-sectional area of DI respectively. We reasonably assume $R_D$ is much larger than $R_r$, based on the Fig. S4 that compared to DI ($10^6 \Omega$), the resistance of the rGO/DI liquids is closer to the rGO solid ($10^5 \Omega$).

At a pressure of $P$, the resistance $R$ is described as:

$$R_p = R_D' + R_r' = \rho \frac{l}{S'} + R_r'$$ \hspace{1cm} \text{(S2)}

Where $R_r'$ is the contact resistance of rGO foams at the pressure of $P$.

The resistance of DI will increase according to the reduce of cross-sectional area ($S \geq S_1$). However the contact resistance of rGO foams will decrease according to micro-contact effect of rGO foams in the liquids. The final change in resistance $\Delta R$ is a combination of both. It is believed that the resistance change in $R_r$ is much larger than $R_D$, based on the Fig. 3c that
the resistance of strain sensor decreased during the pressure applied. The electronic resistance variation ratios \((\Delta R/R_p)\) chosen to express the change of current during different pressures in the deformation process is mainly determined by the change of \(R_r\). \[^{[26]}\]

Therefore, the pressure sensitivity of rGO/DI liquids strain sensor determined by the micro-contact effect of rGO foams in the liquids can be calculated as follows:

\[
S = \frac{\delta(\Delta R/R_0)}{\delta P} = \frac{\delta\left[(R_0 - R_p) / R_0\right]}{\delta P}
\]

(S3)

During the stretching process, the resistance \(R\) is described as:

\[
R_\varepsilon = R_D + R'_r = \rho \frac{l_1}{S_1} + R'_r
\]

(S2)

Where \(R'_r\) is the contact resistance of rGO foams at the strain of \(\varepsilon\).

Both the DI resistance and the contact resistance will increase because the shape of the sensing liquids becomes slender \((S > S_l, l < l_i)\). After the sensor being stretched to a strain of \(\varepsilon\), the gauge factor (GF) of stretch can be calculated as follow:

\[
GF = \frac{\delta(\Delta R/R_0)}{\delta \varepsilon} = \frac{\delta\left[(R_\varepsilon - R_0) / R_0\right]}{\delta \varepsilon}
\]

(S5)

5. Supplementary References