Supporting information

**Temperature-dependent microstructure of PEDOT/PSS films: insights from morphological, mechanical and electrical analyses**

Jian Zhou,*a Dalaver H. Anjum,b Long Chen,b Xuezhu Xu, c Isaac Aguilar Ventura,a Long Jiangc and Gilles Lubineau* a

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**Fig. S1** Illustration on preparation of PEDOT/PSS self-standing nanofilm on TEM copper mesh.

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*King Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia; E-mail: zhouj588@gmail.com; gilles.lubineau@kaust.edu.sa; Tel:+966(12)8082983
bKing Abdullah University of Science and Technology (KAUST), Advanced Nanofabrication, Imaging and Characterization Core Laboratory, Thuwal 23955-6900, Saudi Arabia
cNorth Dakota State University, Department of Mechanical Engineering, Fargo, ND 58108, United States
Fig. S2 Energy-dispersive X-ray spectroscopy (EDX) spectra of PEDOT/PSS nanofilm investigated under TEM.

Fig. S3 TG curves of pristine and annealed PEDOT/PSS film.
Fig. S4 Cryo-TEM images of (a) carbon film, (b) PEDOT/PSS nanofilm on carbon and (c) High magnification of (b).

Table S1 Diameter of PEDOT/PSS grains measured from BF-TEM and HAADF-STEM images at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Diameters in BF-TEM</th>
<th>Diameters in HAADF-STEM</th>
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</thead>
<tbody>
<tr>
<td>RT (26 °C)</td>
<td>33±4 nm</td>
<td>63±12 nm</td>
</tr>
<tr>
<td>LT (-177 °C)</td>
<td>27±9 nm</td>
<td>47±13 nm</td>
</tr>
<tr>
<td>HT (100 °C)</td>
<td>43±7 nm</td>
<td>52±10 nm</td>
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</table>
**Fig. S5** Microstructure of PEDOT/PSS nanofilm at 150 °C. (a) BF-TEM image of PEDOT/PSS nanofilm collected at a thinner place. Inset is the TEM diffraction pattern. (b) HAADF-STEM image of PEDOT/PSS nanofilms collected at a thinner place. (c) HAADF-STEM image of PEDOT/PSS nanofilms collected at a thicker place.