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# Highly conductive PEDOT:PSS treated by sodium dodecyl sulfate for stretchable fabric heaters†

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In this study, the conductivity of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) was greatly enhanced by using sodium dodecyl sulfate (SDS) without damaging the fabric substrates. We suggest that blending and dipping methods using SDS which is compatible with natural and synthetic fabrics dramatically increase the conductivity of PEDOT:PSS to as high as  $1335 \text{ S cm}^{-1}$ . Additionally, a highly stretchable fabric heater with high conductivity was successfully fabricated using SDS-modified PEDOT:PSS. The fabric heaters exhibited reversible electrical behaviour with cyclic loading of a tensile strain even larger than 80%. The increase in resistance with the tensile strain was significantly smaller than the calculated value for a rigid substrate because the fabrics with a weave structure exhibited interfibrillar contact effects with strain. For example, the resistance was increased by a factor of only 2.62 with 80% strain. The Joule heating behaviours of the fabric heaters were demonstrated at several different applied voltages and ambient temperatures, and the heat capacity and convective heat transfer coefficient were  $2 \text{ J K}^{-1}$  and  $30 \text{ W m}^{-2} \text{ K}^{-1}$ , respectively. The results demonstrated that the method suggested in this work is not only efficient for greatly improving the conductivity but also simple and cost-effective for fabricating highly conductive and stretchable fabrics with various e-textile applications.

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## 1. Introduction

Wearable heaters have recently attracted great interest as the demand for wearable and stretchable devices has grown.<sup>1–7</sup> Wearable heaters must be light-weight, comfortable to wear, and have the feel of a fabric.<sup>8,9</sup> However, conventional heating materials based on metal or metal wires have limitations, such as heaviness, inconvenience, and different textural properties between the heating material and fabric. To address these problems, many researchers have explored alternatives to metals, such as conducting polymers,<sup>10–12</sup> graphite,<sup>13,14</sup> graphene,<sup>15</sup> and carbon nanotubes.<sup>16–19</sup> Among these materials, conducting polymers are light-weight, processable, and flexible.<sup>20</sup> Since fabrics such as cotton and synthetic fabrics are not conductive, conducting materials must be loaded into the fabric; the simplest method for loading of fabrics is dipping the fabric into a solution containing the conductive polymer because fabrics can be well impregnated with aqueous solutions.<sup>21</sup> Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) is one of the most successfully commercialised conductive polymers owing to its high mechanical flexibility and excellent thermal stability.<sup>22</sup> However, the

electrical conductivity of pristine PEDOT:PSS is less than  $1 \text{ S cm}^{-1}$ , which is too low to be utilised in heaters. High conductivity is a crucial factor affecting the conversion of electrical energy into thermal energy.

The conductivity of PEDOT:PSS has been reported to be increased by the addition of dielectric organic solvents, such as dimethyl sulfoxide (DMSO),<sup>23</sup> or by post-treatment with a strong acid.<sup>24</sup> However, the use of DMSO may irritate human skin, and fabrics are vulnerable to acid, preventing the use of post-treatment with a strong acid. Therefore, to improve the performance of PEDOT:PSS for application in the development of wearable heaters, it will be necessary to increase the conductivity of PEDOT:PSS without causing damage to the fabric.

Sodium dodecyl sulfate (SDS), one of the ionic surfactants that have been generally used in detergents for laundry, is effective for increasing the conductivity of PEDOT:PSS. It was reported that the conductivity of PEDOT:PSS film can be increased to  $80 \text{ S cm}^{-1}$  by adding SDS into PEDOT:PSS aqueous solution (hereafter, simply denoted by blending method).<sup>25</sup> However, previous study on the effect of anionic surfactants in PEDOT:PSS have not been studied in detail for achieving high conductivity.

In this study, we report the most effective and simple process using SDS for fabrication of highly conductive PEDOT:PSS, and SDS-modified PEDOT:PSS was evaluated as a conductive material in fabric heaters. The Joule heating properties of the stretchable fabric heater was also described.

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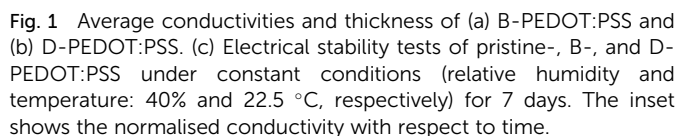
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## 2.1 Fabrications of PEDOT:PSS films and fabric heaters

## 2.2 Characterization of PEDOT:PSS films and fabric heaters

The Joule heating behaviours of fabric heaters were investigated under constant voltages (6, 9, and 12 V) supplied by a DC power source (RDP-305; SMART). We measured the temperatures of the heaters using a digital thermometer (UT320; UNI-T) and observed their IR images using a thermal camera (ThermApp TH, ThermApp). The resistances of the fabric heaters with or without strain were obtained from  $I$ - $V$  characteristic curves of the samples using a source meter (4200-SCS; Keithley). The joule heating experiment was carried out at an ambient temperature of 26 °C. The experiment at 4 °C was also carried

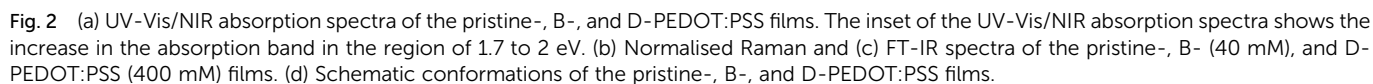
The stability test was performed under constant conditions (relative humidity and temperature were 40% and 22.5 °C, respectively) for 7 days. As shown in Fig. 1c, the conductivities of B-PEDOT:PSS and D-PEDOT:PSS films remained almost unchanged, while the pristine PEDOT:PSS film underwent severe degradation. The normalised conductivity ( $\sigma/\sigma_0$ ) with respect to time is shown in the inset in Fig. 1c, where the value



To investigate the mechanism of conductivity enhancement through the blending and dipping methods, the analysis of chemical bonding states of PEDOT:PSS films was carried out using absorption spectroscopy. The absorption spectra of the PEDOT:PSS films formed by SDS blending (40 mM) and SDS dipping (40, 100, 200, and 400 mM) are shown in Fig. 2a. Notably, the D-PEDOT:PSS films showed significant decreases in absorbance at 5.5 eV, where a strong absorption band originated from the aromatic rings of PSS.<sup>28</sup> This result demonstrated that insulating PSS in the film was selectively removed. A small increase in absorbance in the region from 1 to 2 eV was also observed, indicating the generation of polaronic states in

The conformational change of PEDOT:PSS could also affect the bonding energy between constituent atoms in PEDOT:PSS.<sup>32</sup> Thus, FT-IR analysis was performed to investigate the change of bonding energy. As shown in Fig. 2c, the FT-IR spectrum of the pristine PEDOT:PSS showed peaks at 1209, 1143, and 1089  $\text{cm}^{-1}$  which are originated from to C–O–C bond stretching in the ethylene dioxy group.<sup>33,34</sup> The C–S bond stretching peaks in the thiophene ring were observed at 977, 827, and 690  $\text{cm}^{-1}$ .<sup>33,34</sup> The peaks assigned at 1544 and 1342  $\text{cm}^{-1}$  correspond to C=C and C–C bonds, respectively.<sup>33,34</sup> These peaks in the FT-IR spectrum of D-PEDOT:PSS shifted to higher bonding energies, while the FT-IR spectrum of B-PEDOT:PSS was similar to that of pristine-PEDOT:PSS. In particular, the peak of 1342  $\text{cm}^{-1}$  corresponding to the C–C bond shifted to 1432  $\text{cm}^{-1}$ , which means that the C–C bonding energy increased due to the PSS removal by SDS dipping.

Distinct changes in the surface morphologies of B- and D-PEDOT:PSS films were observed by atomic force microscopy (AFM). The AFM images of topography in Fig. 3a, c and e demonstrate that the rms roughness ( $R_q$ ) values of the pristine- and B-PEDOT:PSS films were 1.3 and 1.4 nm, respectively, and the  $R_q$  of D-PEDOT:PSS films increased to 2.2 nm. Fig. 3b, d and f show phase images in which the positively charged (bright) and negatively charged (dark) phases corresponded to


$$R_{\text{St}} = \frac{1}{\sigma} \frac{l(1 + \varepsilon')}{w(1 - \nu_s \varepsilon')h(1 - \nu_f \varepsilon')} \quad (2)$$



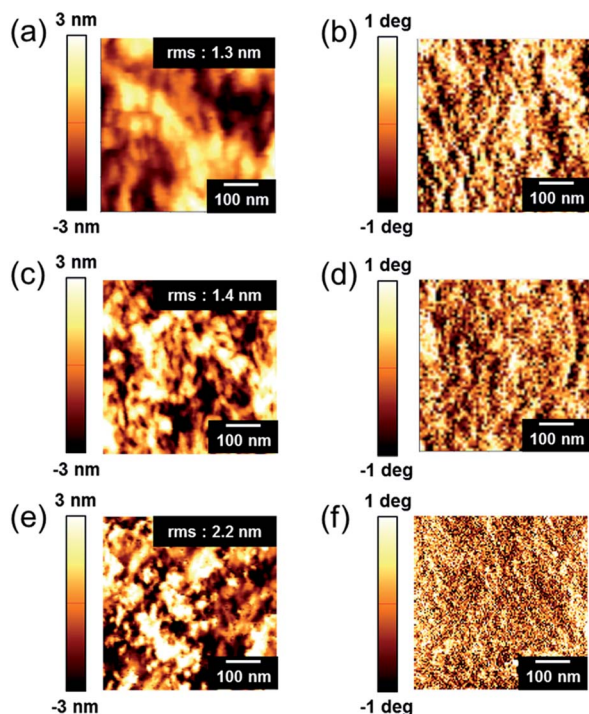


Fig. 3 AFM images of the pristine- [(a) and (b)], B- [(c) and (d)], and D-PEDOT:PSS films [(e) and (f)]. The left (a, c, e) and right (b, d, f) images are photographic and phase images, respectively. The concentrations of SDS used for blending and dipping methods were 40 and 100 mM, respectively. All images were obtained for an area of 250 nm  $\times$  250 nm.

where  $\nu_s$  and  $\nu_f$  are the Poisson's ratio of the substrate and film, respectively, and  $\epsilon'$  is the fractional strain defined as  $\epsilon' = \epsilon/100\%$ . Then, the normalised resistance,  $R_{St}/R_0$ , can be simply expressed by eqn (3),

$$\frac{R_{St}}{R_0} = \frac{1 + \epsilon'}{(1 - \nu_s \epsilon')(1 - \nu_f \epsilon')} \quad (3)$$

The woven structure of the fabric related to the Poisson's ratio determines its structural and mechanical properties.<sup>38</sup> Thus, the  $\nu_s$  values of cotton and polyurethane used as fabric substrates in this work were measured to be 0.48 and 0.2, respectively. The reported  $\nu_f$  of PEDOT:PSS was 0.3532. As shown in Fig. 5a, we plotted  $R_{St}/R_0$  with respect to  $\epsilon$  for BD-PEDOT:PSS-cotton (solid line), where the resistances were directly measured from the current ( $I$ )–voltage ( $V$ ) characteristic curves of the samples. The method of  $I$ – $V$  measurement is described in detail in Fig. S7.† The  $R_{St}/R_0$  values calculated using the  $\nu_s$  and  $\nu_f$  mentioned above are shown in Fig. 5a (dotted line). The measured  $R_{St}/R_0$  values with  $\epsilon \leq 20\%$  were consistent with the calculated values, and the differences between them increased with  $\epsilon$  when  $\epsilon > 20\%$ . For example, at  $\epsilon = 80\%$ , the measured  $R_{St}/R_0$  of the BD-PEDOT:PSS-cotton was 2.62, while the calculated  $R_{St}/R_0$  was 4.05. The significantly small increase in the real  $R_{St}$  with  $\epsilon$  compared with the calculated value must be caused by the woven structure of the fabric. The stretching of the fabric improves the alignment and intercontact of the fibres, thereby reducing its resistance.<sup>39,40</sup> Hereafter, we call this effect the “interfibrillar contact effect”.

Next, the cyclic  $\epsilon$ -loading/unloading tests were performed for BD-PEDOT:PSS-cotton was also performed and the result was shown in Fig. 5b. The  $R_{St}/R_0$  shows reversible behaviour with cyclic  $\epsilon$ -loading/unloading. The inset in Fig. 5b shows the changes in  $R_{St}/R_0$  during a cycle of  $\epsilon$ -loading/unloading. The difference of  $R_{St}/R_0$  between  $\epsilon = 0\%$  (blue arrow) and 20% (red arrow) was only 0.09. However, the difference gradually decreased with the strain, and finally showed reaching a negative value. For example, the difference was decreased from 0.09 to  $-0.20$  when the strain increased from 20% to 80%. The results clearly indicated that the interfibrillar contact effect increased with  $\epsilon$  due to the increase of in the interfibrillar contact area along with the axis of  $\epsilon$  until the cotton was torn at  $\epsilon > 80\%$ .

We also carried out  $I$ – $V$  measurement and cyclic  $\epsilon$ -loading/unloading tests for BD-PEDOT:PSS-polyurethane, which was stretchable even with an extreme strain greater than 150%. The

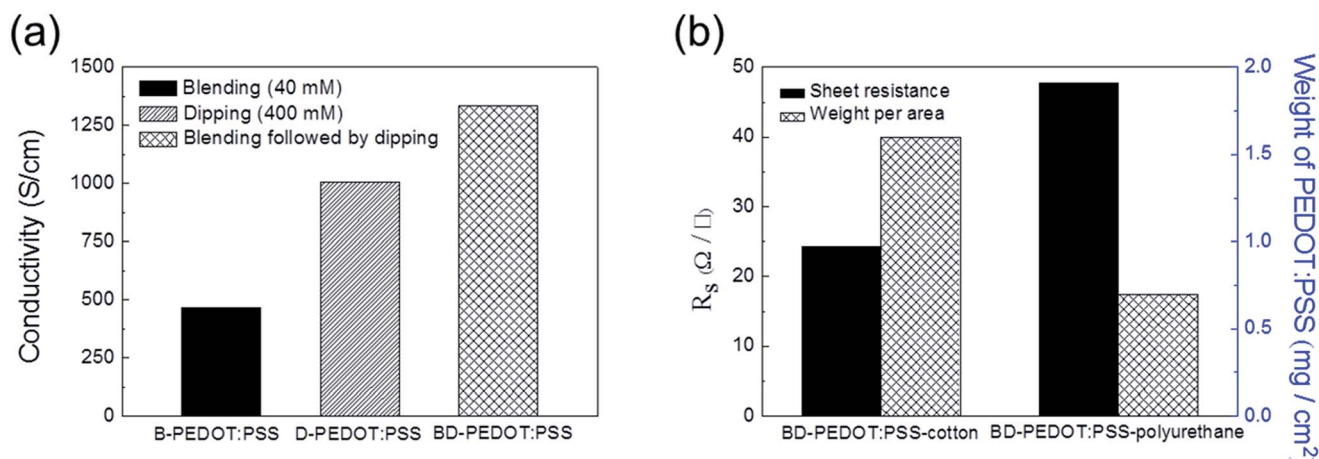


Fig. 4 (a) The highest conductivities of B-, D-, and BD-PEDOT:PSS films spin-coated on glass. (b) Sheet resistance ( $R_s$ ) and weight of PEDOT:PSS of BD-PEDOT:PSS-cotton and polyurethane.

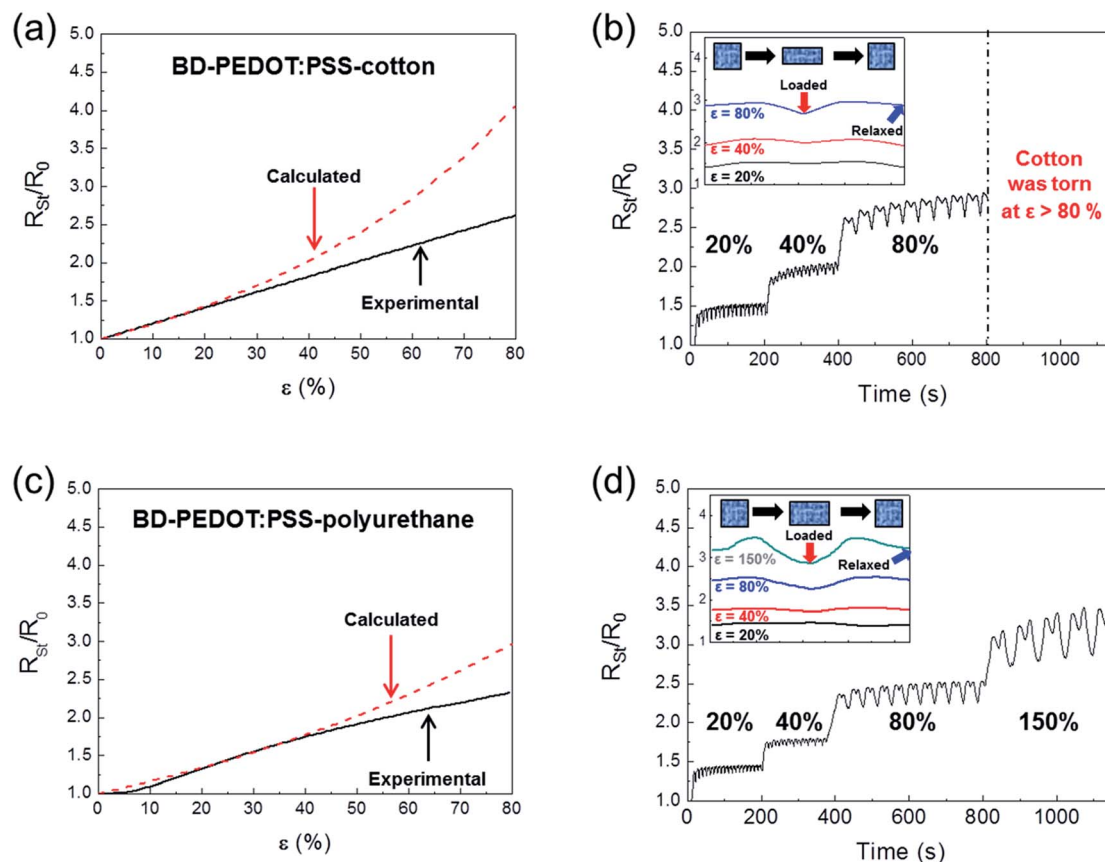


Fig. 5 Normalised resistance results of (a) BD-PEDOT:PSS-cotton and (c) BD-PEDOT:PSS-polyurethane with respect to tensile strain. The dotted and single curves correspond to the calculated and experimental data, respectively. Cyclic loading tests for (b) BD-PEDOT:PSS-cotton and (d) BD-PEDOT:PSS-polyurethane. The insets of (b) and (d) show changes in  $R_{St}/R_0$  during a cycle of  $\epsilon$ -loading.

calculated and experimental  $R_{St}/R_0$  curves for BD-PEDOT:PSS-polyurethane are shown in Fig. 5c. The measured  $R_{St}/R_0$  values with  $\epsilon = 40\%$  coincided with the calculated values, and the difference between them then increased with  $\epsilon$  when  $\epsilon > 40\%$ . The results of cyclic  $\epsilon$ -loading/unloading tests for BD-PEDOT:PSS-polyurethane are shown in Fig. 5d. Interestingly, the  $R_{St}/R_0$  values of BD-PEDOT:PSS-polyurethane were saturated after only a few cycles of  $\epsilon$ -loading/unloading, even with an  $\epsilon$  value as large as 80%, and the results consistently showed reproducible curves by  $\epsilon$ -loading/unloading. The inset of Fig. 5d clearly demonstrates that the interfibrillar contact effect was still effective with  $\epsilon = 150\%$ .

In this work, we introduce the term “critical interfibrillar contact strain ( $\epsilon_{CIC}$ )”, above which the experimental  $R_{St}/R_0$  values begin to deviate from the values calculated using Poisson's ratios; when  $\epsilon > \epsilon_{CIC}$ ,  $(R_{St}/R_0)_{exp} < (R_{St}/R_0)_{cal}$  for a positive interfibrillar contact effect. As shown in Fig. 5a and c, the  $\epsilon_{CIC}$  of BD-PEDOT:PSS-polyurethane ( $\nu_s = 0.2$ ) was 40%, while the  $\epsilon_{CIC}$  of BD-PEDOT:PSS-cotton ( $\nu_s = 0.48$ ) was 20%. These results implied that the value of  $\nu_s$  was related to  $\epsilon_{CIC}$  and that larger  $\nu_s$  values resulted in smaller  $\epsilon_{CIC}$  values. Moreover, higher  $\nu_s$  values could more effectively facilitate increased interfibrillar contact effects during stretching.

As shown in Fig. 5b and d, the relaxed resistance,  $R'_0$ , even after one cycle of  $\epsilon$ -loading/unloading, was larger than  $R_0$ , and

$R_{St}/R_0$  was not recovered to the initial value of 1.0. This may be explained by the permanent deformation of the conducting films owing to cracking or peeling. To investigate the reason for this deformation, we used optical microscopy and scanning electron microscopy (SEM) before and after  $\epsilon$ -loading for the BD-PEDOT:PSS-cotton, which was relatively weak against strain compared with BD-PEDOT:PSS-polyurethane. Fig. 6a shows optical and SEM images of the BD-PEDOT:PSS-cotton before and after  $\epsilon$ -loading. These optical images showed that the BD-PEDOT:PSS-cotton (purple colour) was uniformly coated by PEDOT:PSS. The SEM image in Fig. 6b does not show any visible fractures after loading 40% of  $\epsilon$ . However, the PEDOT:PSS films showed signs of peeling at  $\epsilon = 150\%$  (ESI Fig. S8†). In a previous study, a compressive force perpendicular to the stretching direction was exerted on the film during stretching, leading to the formation of cracks when the Poisson's ratio of the substrate was larger than that of the film,<sup>36</sup> and we observed cracks in SDS-modified PEDOT:PSS coated on polydimethylsiloxane, even after loading 40% of  $\epsilon$  (ESI Fig. S9†). These results demonstrated that the woven structure significantly relieved stress from the compressive force; therefore, BD-PEDOT:PSS-fabric exhibited excellent stretchability while maintaining low resistance. This low resistance behaviour with a very large  $\epsilon$  may be a noticeable advantage of conductive fabric applications compared with conventional plastic applications.



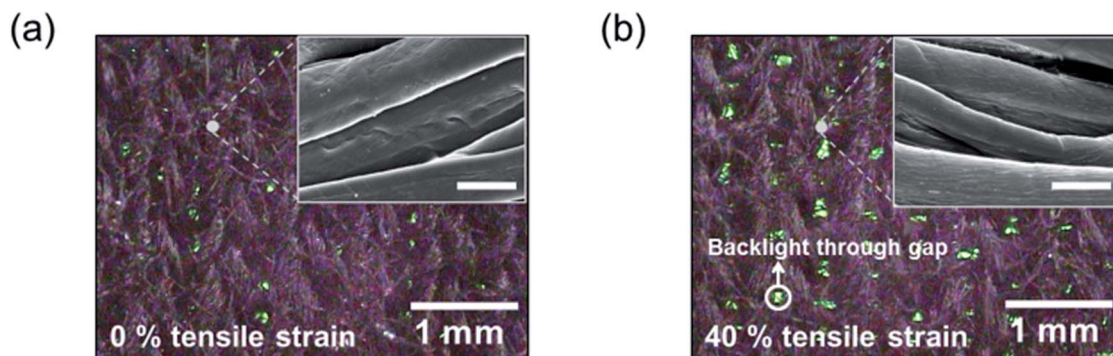


Fig. 6 Optical and SEM images of the BD-PEDOT:PSS-cotton before (a) and after (b) loading 40% tensile strain. The scale bar of the SEM image is 10  $\mu\text{m}$ .

Using the BD-PEDOT:PSS-cotton, we fabricated a flexible heater to determine the applications of stretchable conducting fabrics and evaluated the Joule heating behaviours of this heater. Fig. 7a shows the temperature ( $T$ )-time ( $t$ ) profiles for the BD-PEDOT:PSS-cotton, which had an  $R_s$  of  $24 \Omega \square^{-1}$ . When a bias voltage (6, 9, or 12 V) was applied, the temperature of the fabric heater increased and saturated to a certain temperature within 60 s. For example, the saturated temperature ( $T_{\text{sat}}$ ) of BD-PEDOT:PSS-cotton was  $99.6^\circ\text{C}$  when 12 V was applied. The heat capacity ( $C$ ) and convective heat transfer coefficient ( $h$ ) could be also obtained by comparing the experimental data with the  $T$ - $t$  curve calculated using a power balance equation.<sup>41</sup>

In general, a power balance equation<sup>41</sup> between the input power and heat loss by convection ( $Q_{\text{conv}}$ ) and radiation ( $Q_{\text{rad}}$ ) can be described as shown in eqn (4),

$$\frac{V^2}{R} = Q_{\text{conv}} + Q_{\text{rad}} + C \frac{dT}{dt} \quad (4)$$

where  $V$  and  $R$  are the input voltage and resistance, respectively.  $Q_{\text{conv}}$  and  $Q_{\text{rad}}$  are expressed as shown in eqn (5) and (6),

$$Q_{\text{conv}} = hA(T - T_0) \quad (5)$$

$$Q_{\text{rad}} = e\sigma A(T^4 - T_0^4) \quad (6)$$

where  $A$ ,  $T_0$ ,  $e$ , and  $\sigma$  are the convective heat transfer coefficient, the surface area of the heater ( $10.8 \text{ cm}^2$ ), initial temperature, surface emissivity of the heater (0.98), and Stefan-Boltzmann constant ( $5.67 \times 10^{-8} \text{ W m}^2 \text{ K}^{-4}$ ), respectively. Because  $R$  increased with  $T$ , the temperature coefficient of resistance ( $\alpha$ ) was introduced, and  $\alpha$  was  $0.001 \text{ K}^{-1}$  by measuring the current with respect to the temperature. The power balance equation (eqn (4)) can be expanded by using eqn (5) and (6), as expressed in eqn (7),

$$\frac{V^2}{R_0 \{1 + \alpha(T - T_0)\}} = hA(T - T_0) + e\sigma A(T^4 - T_0^4) + C \frac{dT}{dt} \quad (7)$$

where  $R_0$  is initial resistance. When the values of  $C$  and  $h$  were  $2 \text{ J K}^{-1}$  and  $30 \text{ W m}^{-2} \text{ K}^{-1}$ , respectively, the calculated curve

coincided quite well with the measured data of BD-PEDOT:PSS-cotton, as shown in Fig. 7a.

To evaluate the potential of stretchable PEDOT:PSS-fabric heaters, the Joule heating behaviours were investigated with different  $\varepsilon$  values. As shown in Fig. 7b, the value of  $T_{\text{sat}}$  decreased slightly from  $99.6$  to  $97.7^\circ\text{C}$  at  $\varepsilon = 10\%$ . Additionally, the  $T_{\text{sat}}$  was  $80.4^\circ\text{C}$  at  $\varepsilon = 80\%$ . The values of  $T_{\text{sat}}$  with respect to  $\varepsilon$  were plotted in Fig. S10.† As inferred from Fig. 5a, the experimental values of  $T_{\text{sat}}$  with  $\varepsilon > 20\%$  were larger than the calculated values due to the interfibrillar effect. These results indicated that the BD-PEDOT:PSS-fabric was a promising material for application in highly stretchable heaters.

In practical applications, fabric heaters may be used in a cold environment. Therefore, the heating behaviours were also investigated in a low-temperature environment ( $4^\circ\text{C}$ ) and compared with the heating behaviours at room temperature ( $26^\circ\text{C}$ ). As shown in Fig. 7c, the  $T_{\text{sat}}$  of BD-PEDOT:PSS-cotton was  $88.0^\circ\text{C}$ , while the value at room temperature was  $99.6^\circ\text{C}$ . Furthermore, a longer time was needed to reach saturation at  $4^\circ\text{C}$  than at  $26^\circ\text{C}$ . This result could be explained by changes in  $h$  depending on environmental conditions (the speed of convection currents, etc.).<sup>42</sup>

We also obtained photographs and infrared images of a human hand wearing the fabric heater, as shown in Fig. 7d. In this experiment, the input voltage was as mild as 6 V to avoid the potential danger of burns. The maximum ( $T_{\text{max}}$ ) and minimum temperatures ( $T_{\text{min}}$ ) were  $46.1$  and  $41.9^\circ\text{C}$ , respectively, before bending the finger, and  $46.9$  and  $42.6^\circ\text{C}$ , respectively, after bending the finger. The results clearly show that BD-PEDOT:PSS-fabric can be adaptable even for the finger joint or elbow requiring very high stretchability ( $\varepsilon > 100\%$ ).

As described above, because a few cycles are needed to reach a stable reversible behaviour, a cycle-aging process at a certain  $\varepsilon$  is essential for practical applications requiring consistent reproducible performance. Fig. 8 shows the  $R_{\text{st}}/R_{0,\text{sat}}$  values of BD-PEDOT:PSS-fabrics during a cycle of 80%  $\varepsilon$ -loading/unloading, where  $R_{0,\text{sat}}$  is the saturated resistance of a sample at  $\varepsilon = 0\%$  after suffering from cycle-aging processing at  $\varepsilon = 80\%$ . The results showed that the differences between the maximum and minimum  $R_{\text{st}}/R_{0,\text{sat}}$  values for BD-PEDOT:PSS-cotton and





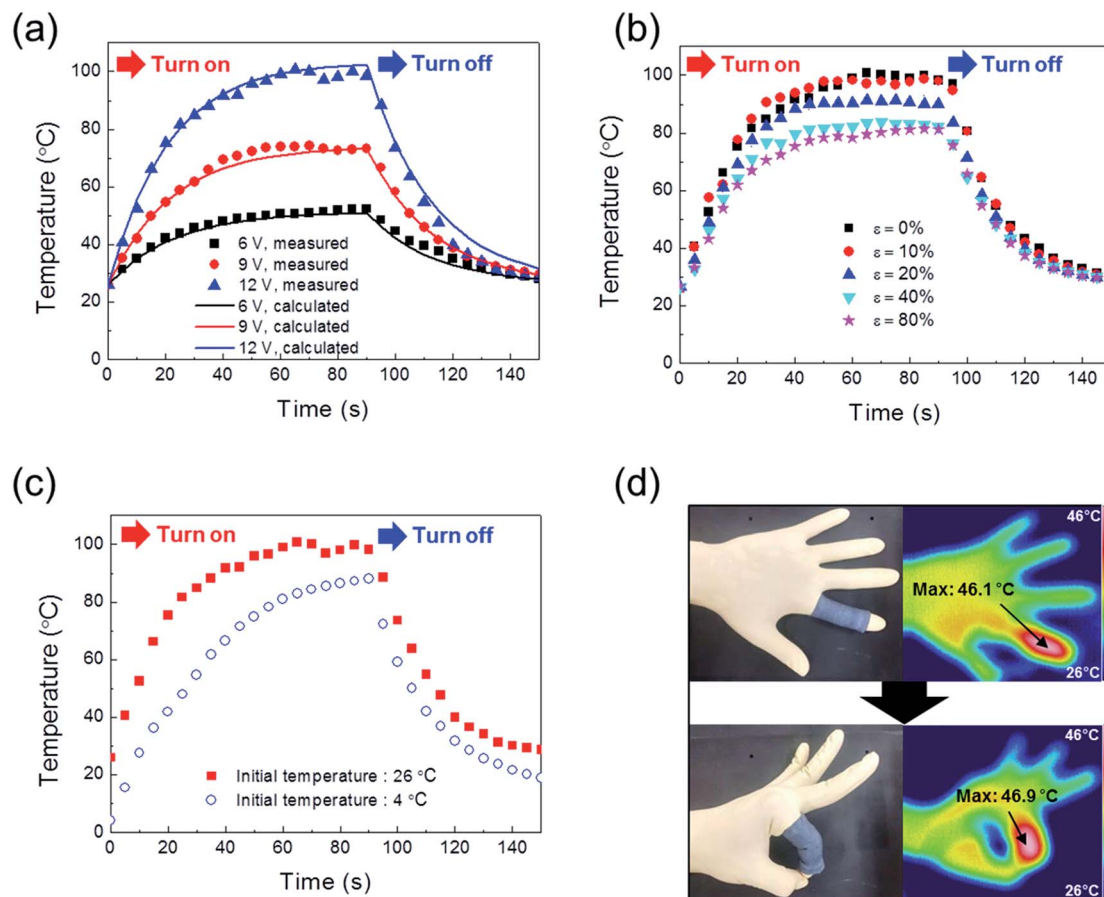


Fig. 7 (a) Temperature–time dependence curve with application of different bias voltages (6, 9, and 12 V). The solid lines are fitted curves calculated from a power balance equation between input power and heat loss. (b) Joule heating properties as a function of tensile strain at an applied voltage of 12 V under different ambient temperatures (4 and 26 °C). (d) Photographs and IR images of the heaters before and after bending fingers. The applied bias voltage was 6 V.

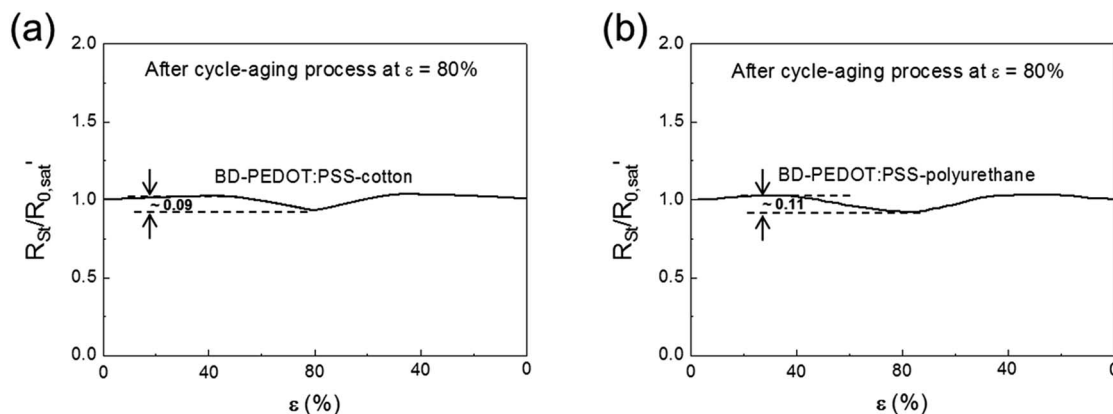


Fig. 8 The  $R_{st}/R_{0,sat}$  values of (a) BD-PEDOT:PSS-cotton and (b) BD-PEDOT:PSS-polyurethane during a cycle of 80% loading after performing the cycle-aging process at  $\epsilon = 80\%$ .

polyurethane were 0.09 and 0.11, respectively; these values are so small that stretchable device performance would not be noticeably changed with respect to variations in  $\epsilon$  during practical operation.

## 4. Conclusions

In summary, we demonstrated, for the first time, that conductivity of PEDOT:PSS as high as  $1335 \text{ S cm}^{-1}$  could be obtained by





combining the blending and dipping methods with an anionic surfactant, SDS, which were compatible with natural and synthetic fabrics. We also fabricated highly conductive and stretchable fabric heaters using SDS-modified PEDOT:PSS. The mechanisms of conductivity enhancement by SDS dipping and blending methods were elucidated; specifically, the SDS dipping method selectively removed insulating PSS domains, leading to enhancement of the interchain interactions between conducting domains, whereas SDS blending caused conformational change of PEDOT chains. The fabric heaters fabricated using SDS-modified PEDOT:PSS exhibited reversible electrical behaviours with cyclic loading of a tensile strain greater than 80%. The interfibrillar contact effect of the woven fabrics caused a significant but small increase in resistance compared with the calculated value for a rigid substrate. The heat capacity and the convective heat transfer coefficient of BD-PEDOT:PSS-cotton obtained in this work were  $2 \text{ J K}^{-1}$  and  $30 \text{ W m}^2 \text{ K}^{-1}$ , respectively. The effective, simple, and cost-effective method proposed in this work should be useful for fabricating highly conductive PEDOT:PSS-fabric and could expand the use of e-textiles in stretchable applications.

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