

# Pyroprotein-Based Electronic Textiles with High Stability

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As demand for thin, lightweight, and portable electronic devices has grown, increasing interest has been focused on the development and applications of electronic textiles (e-textiles).<sup>[1–3]</sup> Due to their unique properties, including flexibility, portability, and electrical conductivity, e-textiles have been proposed for use in various fields such as fashion, medicine, sports, and even in military applications.<sup>[4,5]</sup> But before the practical use of e-textiles in real life, the flexible and electrically conductive fabrics and yarns have to be realized with commonly used textiles. Low-dimensional carbon-based materials have been considered promising candidates for the fabrication of e-textiles because of their lightness, high flexibility, good mechanical properties, and high electrical conductivity.<sup>[6–11]</sup> For those reasons, lots of studies on e-textiles fabricated using carbon nanotubes (CNTs),<sup>[12–17]</sup> graphene,<sup>[18–23]</sup> and hybrids of CNTs and graphene<sup>[24,25]</sup> have been reported. Among them, e-textiles have been fabricated by coating graphene oxide (GO) onto nylon-6, cotton, and polyester, using bovine serum albumin (BSA) as an electrostatic glue.<sup>[23]</sup> However, using BSA to coat GO onto currently used textiles leads the other chemicals, additional complicated steps, and thermal instability; first, the degradation temperature (melting point) of BSA is about 60–70 °C.<sup>[26]</sup> Second, in order to use BSA as a glue, pH level of BSA should be controlled with other chemical agent (HCl). Moreover, the high cost is inevitable for mass product because BSA is very expensive. In this regard, the fabrication method of e-textile without any glue such as BSA has to be developed.

Silk produced by silkworms and spiders is a semicrystalline biopolymer. Silk fibroin (SF) from *Bombyx mori* (*B. mori*)

silkworm cocoon has been used for high-quality clothing since ancient times due to its superior properties such as lightness, fineness, a pleasant feel, and a unique luster. And spider silk has been great attention due to its exceptional mechanical properties and good biocompatibility in recent.<sup>[27–30]</sup> Native *B. mori* silkworm cocoon fiber is composed of two types of protein; fibrous protein (silk fibroin, SF) and a glue-like protein (sericin).<sup>[31]</sup> After removing the sericins through a degumming process, SF has been used throughout history as textiles and biomedical sutures. The main components of SF are alanine, glycine, and serine (up to over 80%), which are linked by peptide bonding.<sup>[32]</sup> Namely, numerous hydrophilic amide groups providing hydrogen bonding sites exist in the SF main chain. In addition, the hydrophobicity is also shown in the formation of crystalline  $\beta$ -sheets in a silk.<sup>[33]</sup> Since GO also contains lots of oxygen functional groups such as epoxide (C–O–C), hydroxyl (–OH), and carboxyl (–COOH), GO can be attached to the SF by hydrogen bonding between the oxygen functional groups of GO and the amide groups of SF as well as hydrophobic interaction between GO and the crystalline  $\beta$ -sheets<sup>[34,35]</sup> without any glue such as BSA. Moreover, since spider web (SW) also consists of amino acids such as glycine, tyrosine, leucine, and glutamine,<sup>[36]</sup> it is expected that the SW can also be coated by GO without a BSA.

Here we report the development of e-textiles produced by coating GO on cocoon silk and SW without any glue. Cocoon silk textiles were made from SF obtained from *B. mori* silkworm through an electrospinning method.<sup>[37,38]</sup> The GO-coated SF (GO-SF) was reduced (rGO-SF) with hydroiodic acid (HI) to create good electrical conductivity.<sup>[39]</sup> The electrical conductivity of the rGO-SF was found to have a similar value to that of the e-textiles synthesized with GO and BSA ( $\approx 10 \text{ S cm}^{-1}$ ).<sup>[23]</sup> It was confirmed that this characteristic is maintained even after exposure to severe conditions, such as bending, temperature variation, and washing.

Using the same method, we also fabricated an e-textile with a commercially used silk textile. Moreover, the silk from cocoons and SWs is thermally transformed into compounds known as pyroproteins, which are stable at high temperatures.<sup>[40]</sup> Hence, the e-textiles were simply obtained by thermal treatment instead of a chemical reduction process. This study provides an easy way to fabricate e-textiles using biocompatible natural silk-based materials via a simple coating method without any glue such as BSA.

Figure 1a,b show the structure of the GO containing functional groups such as epoxy, hydroxyl, and carboxyl groups, and of the SF comprised of amide groups, respectively. As mentioned above, GO and SF with these functional groups can interact with each other by hydrogen bonding (see Figure S1, Supporting Information)

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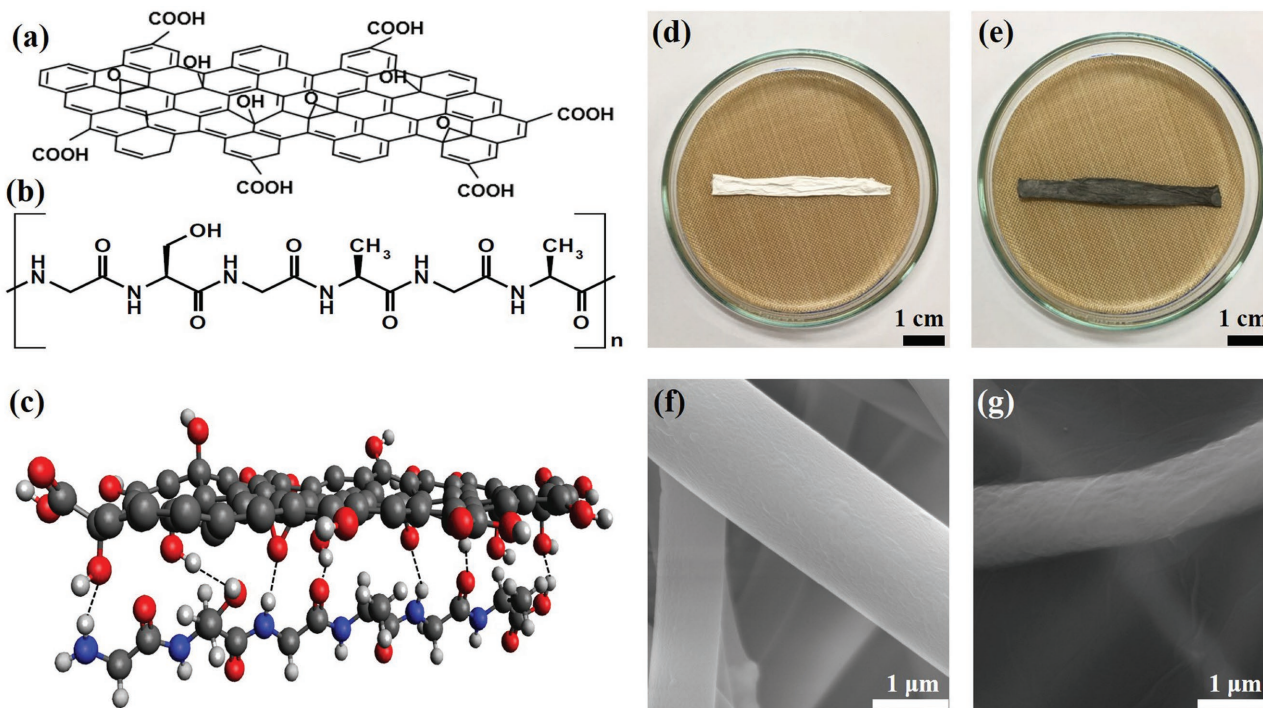
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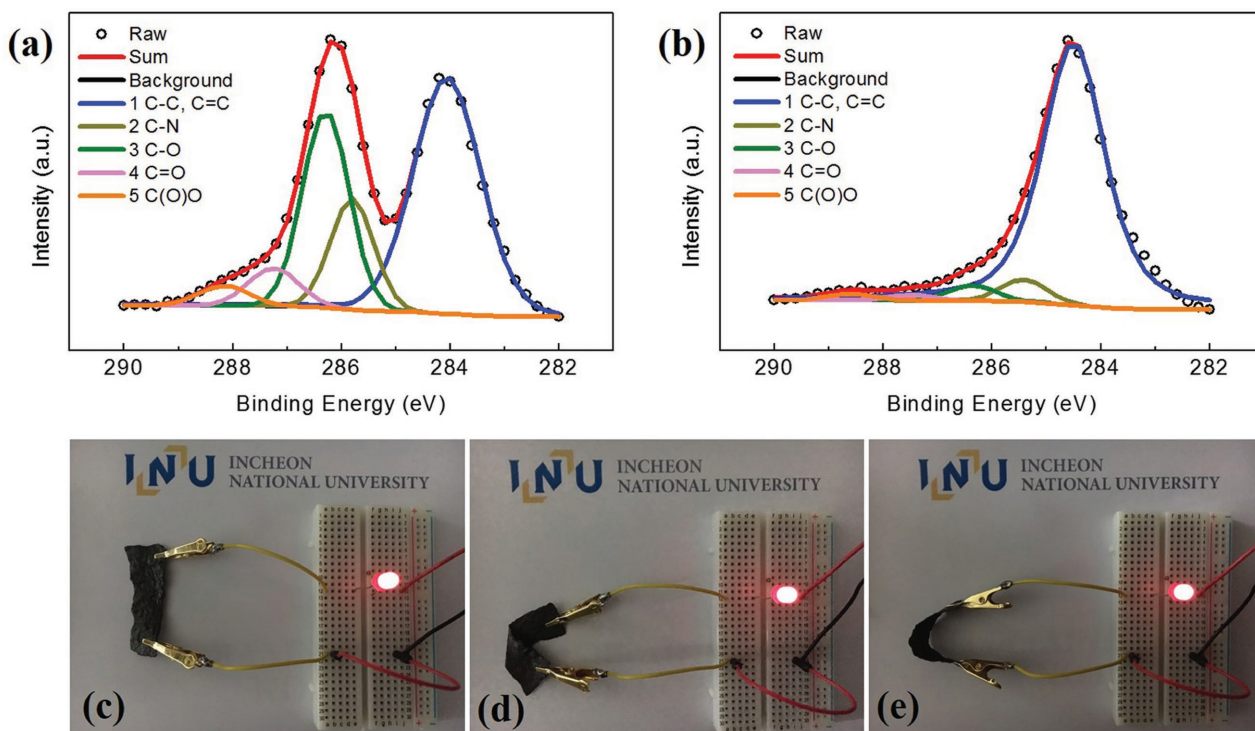




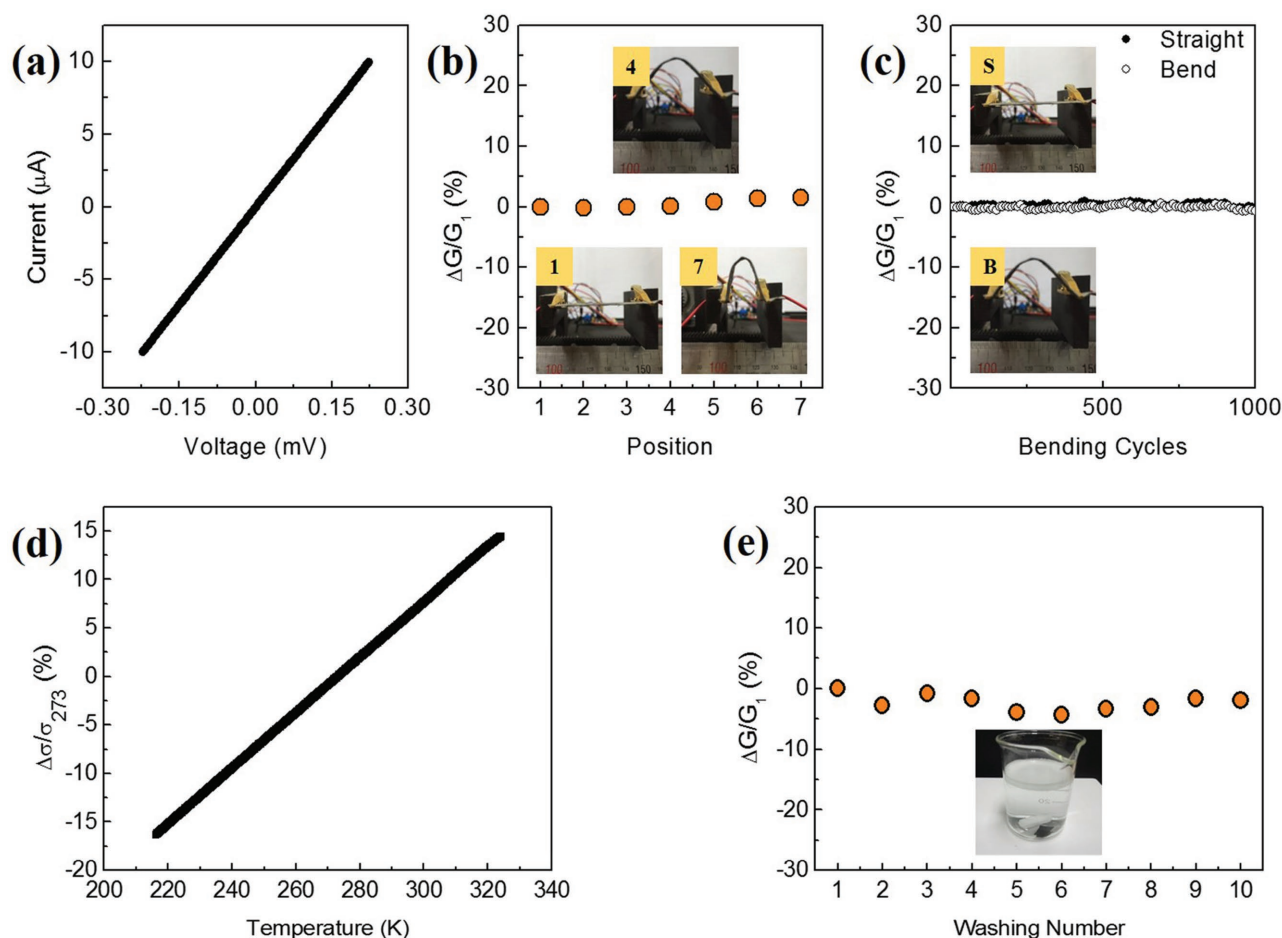
**Figure 1.** Coating GO onto SF. The structure of a) GO and b) SF. c) Hydrogen bond interaction between SF and GO (top: GO, bottom: SF, H: white, C: gray, O: red, N: blue). Optical images of d) electrospun SF and e) GO-SF. SEM images of f) electrospun SF and g) GO-SF. (scale bar = 1  $\mu\text{m}$ ).

as well as the hydrophobic interaction without any glue like BSA (Figure 1c). We fabricated GO-SF by simply dipping SF into a GO solution and drying in ambient conditions. The SF fabrics were

produced from a SF solution obtained from *B. mori* silkworm via electrospinning,<sup>[37,38]</sup> as shown in Figure 1d. The random distribution of the electrospun SF fibers forms the fabric.



**Figure 2.** Chemical reduction of GO-SF. a,b) XPS C 1s core-level spectra of GO-SF (a) and rGO-SF (b). c–e) Optical images of a red LED lamp connected to straight rGO-SF (c), folded rGO-SF (d), and bent rGO-SF (e).



**Figure 3.** Electrical properties of rGO-SF. a)  $I$ - $V$  characteristics of rGO-SF. b-e) Variation in electrical transport properties as a function of bending degrees (1 and 7 correspond to  $0^\circ$  and  $180^\circ$ , respectively) (b), bending cycles (c), temperature (d), and washing time (e).

The fabric was characterized by scanning electron microscopy (SEM) as shown in Figure 1f. The surface of the SF fibers in the electrospun SF fabric was very smooth before GO coating. However, numerous wrinkles were observed on the SF fibers after dipping into the GO solution (Figure 1g). It is possible that these wrinkles are GOs. To verify this more clearly, Raman spectroscopy was also performed (Figure S2, Supporting Information). Raman spectra of the GO-SF exhibited typical spectral characteristics of GO, including the D peak ( $1348\text{ cm}^{-1}$ ) and G peak ( $1589\text{ cm}^{-1}$ ).<sup>[41]</sup> These results indicate that GO was well coated onto the surface of the SF and bonded without any glue.

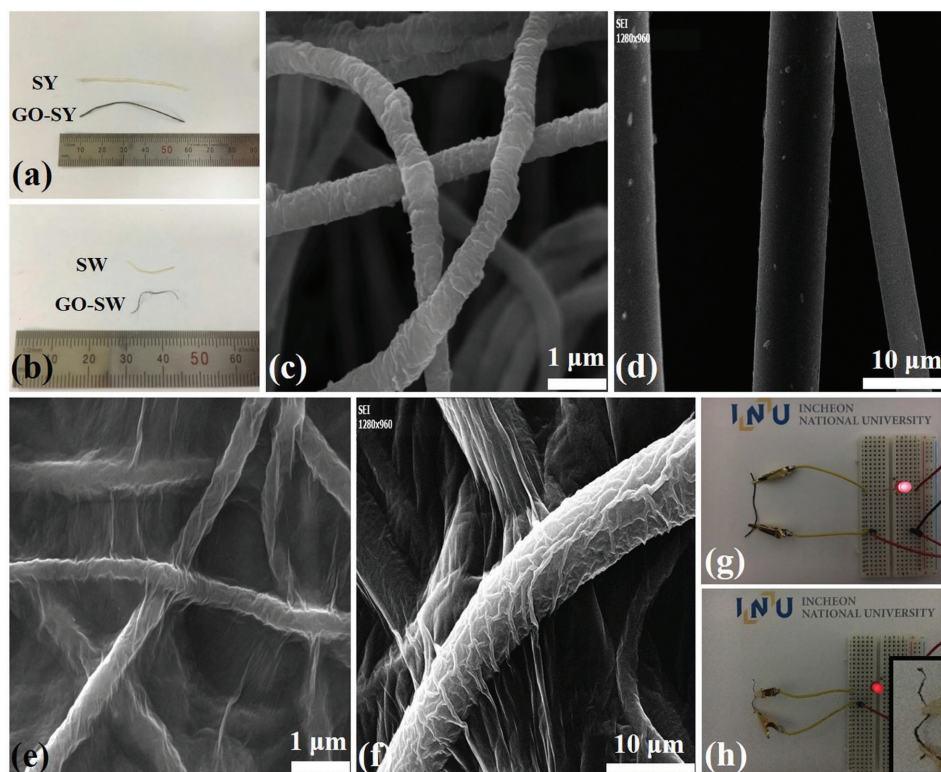
However, since GO is an electrical insulator, a reduction process of the GO on the SF must be performed to use them as e-textiles. One of the methods for reducing GO is by a chemical reduction with HI.<sup>[39]</sup> The amount of oxygen functional groups before and after reduction with HI was investigated by X-ray photoelectron spectroscopy (XPS). Figure 2a,b show the XPS C 1s core-level spectra of GO-SF and rGO-SF, respectively. The GO-SF has oxygen functional groups such as C-O, C=O, and C(O)O. After the reduction process, the oxygen functional groups significantly decreased from 27.28% to 3.16% for C-O,

from 5.74% to 3.16% for C=O, and from 2.97% to 1.15% for C(O)O, respectively. In contrast, the amount of C-C bonds dramatically increased from 49.66% to 89.93% (Table S1, Supporting Information). This means that the oxygen functional groups were detached from the GO by the chemical reduction, resulting in the restoration of C-C bonds.

To demonstrate the electrically conducting behavior of the rGO-SF, the rGO-SF obtained after the chemical reduction was connected to a red LED lamp. Using this simple circuit with the LED lamp, we confirmed that rGO-SF is an electrical conductor (Figure 2c). Moreover, Figure 2d,e shows the lighting of the LED lamp even when the rGO-SF was folded and bent.

To examine its electrical properties, the current-voltage ( $I$ - $V$ ) characteristics of the rGO-SF were measured using a conventional four-probe method. Highly symmetric and linear  $I$ - $V$  characteristics were observed (Figure 3a). The conductivity ( $\sigma$ ) obtained from the  $I$ - $V$  curve was  $11.63\text{ S cm}^{-1}$ , which is comparable to that of e-textiles fabricated with GO and BSA.<sup>[23]</sup>

Since constant electrical conductivity under various conditions is the most important factor for wearable and flexible electronic applications, the rGO-SF textiles were investigated for variation in conductance with bending, washing, and changes



**Figure 4.** Electronic yarns fabricated from SY and SW. a) Optical image of SY and GO-SY. b) Optical image of SW and GO-SW. SEM images of c) pristine SY (scale bar = 1.0  $\mu\text{m}$ ) and d) pristine SW (scale bar = 10  $\mu\text{m}$ ). SEM images of e) GO-SY (scale bar = 1.0  $\mu\text{m}$ ) and f) GO-SW (scale bar = 10  $\mu\text{m}$ ). Optical images of red LED lamp connected to g) rGO-SY and h) rGO-SW.

in temperature. The bending-cycle-dependent conductance was measured using a homemade bending device as shown in the inset of Figure 3b. Before measuring the bending-cycle-dependent conductance, the variation in conductance with respect to the bending degree was obtained (Figure 3b). It was found that even when the rGO-SF was bent gradually from position 1, the conductance remained almost constant. The conductance variation was less than 1.5%.

In addition, when the rGO-SF was stretched again (returned to position 1), the conductance was also returned to its original value at position 1. To demonstrate the durability of conductance during bending cycles, we measured the conductance of the rGO-SF over 1000 bending cycles (Figure 3c). The conductance of the rGO-SF did not change ( $<1.0\%$ ) even after 1000 cycles. This stability can be explained by the unchanged surface morphology after bending of the rGO-SF (Figure S3, Supporting Information).

The temperature dependence of the rGO-SF conductivity was also measured, considering the range of real-life weather (220–320 K, Figure 3d). Although the conductivity decreased with a decrease in temperature, the change was less than 16% compared with that at 273 K ( $\Delta\sigma/\sigma_{273\text{K}} < 16\%$ ,  $\Delta\sigma = \sigma(T) - \sigma_{273\text{K}}$ ).

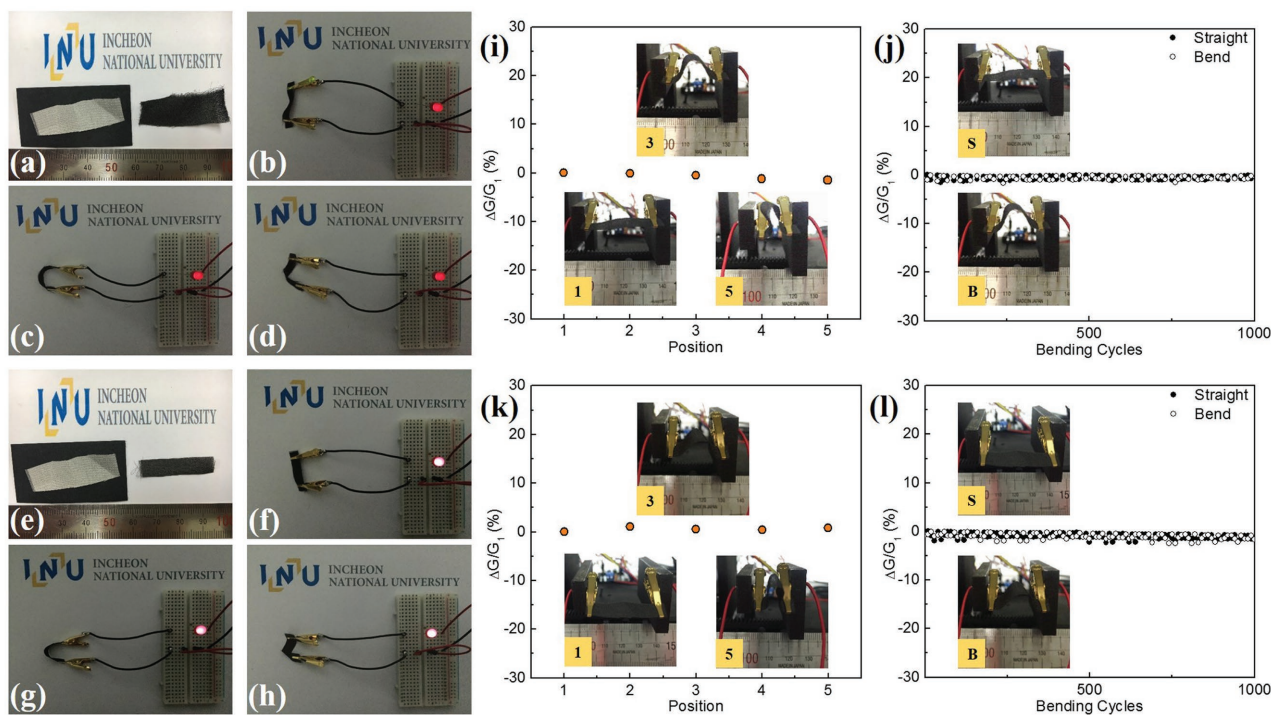
Finally, a washing test was also performed using a commercial detergent and stirring bar to confirm the material's stability against the chemical ingredient and mechanical stress (Figure 3e). The conductance as well as morphology of rGO-SF was almost maintained after washing (see Figure S4,

Supporting Information). From these results, we determined that the rGO was wrapped well onto the SF without any glue, and that the rGO-SF can be used in e-textiles in real life due to its good stability after bending, temperature changes, and washing.

We also fabricated rGO-coated silk yarn (rGO-SY) by hand-rolling the electrospun SF. It is worth noting that rGO-coated SW (rGO-SW) could also be synthesized by the same procedure as described above, because the SW consists of amino acids, like the SF. The optical images of hand-rolled SY, GO-coated SY (GO-SY), SW, and GO-coated SW (GO-SW) are shown in Figure 4a,b, respectively. The color was changed from white to black after the GO-coating process. This means the GO was well wrapped onto the SY and SW, as was confirmed by SEM.

Figure 4c,d are SEM images for the pristine SY and SW, respectively. The wrinkles were observed in GO-SY (Figure 4e) and GO-SW (Figure 4f). The electrical conductivity of the rGO-SY and rGO-SW after the chemical reduction process was proven with a red LED lamp (Figure 4g,h). The electrical conductivities were  $4.76 \times 10^{-1} \text{ S cm}^{-1}$  for rGO-SY and  $5.95 \times 10^{-4} \text{ S cm}^{-1}$  for rGO-SW, and the conducting property of both electronic yarns was maintained for bending (1000 bending cycles and stitch test) (Figure S5 and S6, Supporting Information).

Notably, the  $\sigma$  of rGO-SW is much lower than the  $\sigma$  of rGO-SY. The SF fibers of SY synthesized by the electrospinning method are formed randomly, and the fiber is much thinner



**Figure 5.** E-textiles with CSF obtained by the thermal reduction process. a) Optical image of pristine CSF (white) and rGO-CSF/C (black). b) Optical images of red LED lamp connected to b) straight rGO-CSF/C, c) bent rGO-CSF/C, and d) folded rGO-CSF/C. e) Optical image of pristine CSF (white) and rGO-CSF/T (black). Optical images of red LED lamp connected to f) straight rGO-CSF/T, g) bent rGO-CSF/T, and h) folded rGO-CSF/T. Variation in conductances of rGO-CSF/C and rGO-CSF/T as a function of i,k) bending degrees and j,l) bending cycles, respectively.

than the SW, as shown in SEM images. These thin fibers cause the increase of a surface area. As a result, lots of conducting channels are created. In addition, the vacant space between the SY fibers was much smaller than that of SW. This suggests that GO filled the vacant spaces between SY fibers, which results in the formation of additional conducting paths after the reduction process.

The cocoon and SW materials are known as pyroproteins because of their thermal stability at high temperature.<sup>[40]</sup> Hence, thermal energy can be adopted in the reduction process instead of a chemical reduction. To prove this property, we used a commercial silk fabric (CSF) and compared the electrical properties between two CSFs, one which was reduced chemically (rGO-CSF/C) (Figure 5a) and one thermally (rGO-CSF/T) (Figure 5e and Figure S7, Supporting Information). Both fabrics were connected with the red LED lamps (Figure 5b for rGO-CSF/C and 5f for rGO-CSF/T) and the light of both LED lamps was maintained even when the fabrics were bent and twisted (Figure 5c,d for rGO-CSF/C, and Figure 5g,h for rGO-CSF/T).

The difference in conductance of the rGO-CSF/C (Figure 5i,j) and the rGO-CSF/T (Figure 5k,l) was also measured as a function of position and bending cycles. Both rGO-CSFs demonstrated stable durability of conductance after 1000 bending cycles. It is worth noting that the light of the LED lamp connected to the rGO-CSF/T was brighter than that with rGO-CSF/C. The measured electrical conductivities were  $5.48 \times 10^{-4} \text{ S cm}^{-1}$  for rGO-CSF/C and  $1.2 \times 10^{-2} \text{ S cm}^{-1}$  for rGO-CSF/T (Figure S8, Supporting Information). The

relatively lower  $\sigma$  of rGO-CSFs compared with the  $\sigma$  of rGO-SF ( $\approx 10 \text{ S cm}^{-1}$ ) comes from the meshed structure of the CSF, as shown in Figure 5. Hence, we performed the thermal reduction with rGO-SF (rGO-SF/T) at  $250^\circ \text{C}$ . We obtained the conductivity of  $0.22 \text{ S cm}^{-1}$  and the temperature-dependent conductivity from 210 to 325 K, and also confirmed the stability of rGO-SF/T for the bending and washing with detergent (see Figure S9, Supporting Information).

Note that the  $\sigma$  of rGO-CSF/T is larger than that of rGO-CSF/C. This originates from the characteristics of the pyroproteins. The electrical conductivity of pyroprotein increases as the annealing temperature increases.<sup>[40]</sup> In other words, the CSF as well as the GO became more electrically conductive during the thermal reduction process, and therefore a larger  $\sigma$  was obtained in the thermally reduced GO-CSF.

Finally, we also investigated the electrochemical performance the rGO-SF for Li storage. Although the specific capacity became smaller after the second cycle, good cyclic stability was observed (Figure S10, Supporting Information). This indicates that these e-textiles fabricated by a simple method without any chemical agent during the coating and reduction process have potential utility as wearable energy materials as well as wearable electronic devices.

In conclusion, e-textiles were fabricated using GO and various silk-based materials including electrospun SF, SY, SW, and CSF without any glues such as BSA. The e-textiles produced in this way were electrically conductive and stable even in extreme conditions such as bending, washing, and temperature variation. Particularly, e-textiles were also produced using a thermal

reduction process by exploiting the pyroprotein property of cocoon silk and SW. In this study, we provide ways to fabricate functional e-textiles using simple methods without any chemical agent, and this study is expected to be easily adoptable in the present textile industry.

## Experimental Section

**Preparation of SF Solutions and Electrospinning:** Preparation of regenerated SF solution and electrospinning was achieved as a previous studies.<sup>[37,38]</sup> The procedure is described in the Supporting Information in detail.

**Preparation of rGO-SF by Chemical Reduction:** GO was prepared from graphite powder using the modified Hummers method.<sup>[42]</sup> GO solution (0.5 wt%) was prepared by dissolving GO into deionized (DI) water and bath sonicated for 1.0 h. The SF obtained from electrospinning was immersed into GO solution for 30 min at room temperature. After GO wrapping, the GO-SF was dried in a fume hood for 30 min. This procedure was repeated three times in order to coat GO onto SF evenly and it was reduced using the HI reduction method.<sup>[39]</sup> The GO-SF was immersed into solution that contained 2.0 mL of HI and 5.0 mL of acetic acid at room temperature for 1 h. The rGO-SF was rinsed with a saturated NaHCO<sub>3</sub> solution, DI water, and methanol, and then it was dried at room temperature in a fume hood.

**Thermal Reduction:** Thermal reduction was performed by a tube furnace (Daeheung Science). The sample was placed in an alumina boat and put into a tube furnace. It was heated to 250 °C as a rate of 5.0 °C min<sup>-1</sup> in a nitrogen atmosphere, and maintained the temperature (250 °C) for 10 min.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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