Conductive Fibrous Materials

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Highly Conductive Aluminum Textile and Paper for Flexible and Wearable Electronics**

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The development of electronic devices with both excellent electrical conductivity and outstanding flexibility is an active and vibrant research field due to the inherent fragile nature of silicon-based electronics and the large demand for portable electronics, such as portable display, communication, computational, and identification products.[1–7] Flexible electronic devices (FEDs) consist of various functional organic and/or inorganic features on flexible substrates. In particular, electric circuits on flexible substrates are essential parts in the operation of FEDs. Flexible electric circuits can be generally fabricated by depositing the patterned conductive materials on a flexible substrate via conventional vacuum deposition or printing processes. However, flexible substrates applicable to the fabrication of highly conductive patterns by vacuum deposition and printing processes are mostly limited to impermeable thin-film plastic substrates because forming continuous patterns without disconnections is difficult on light fibrous substrates, such as fabric and paper, by a vacuum deposition or printing process. Moreover, the cost is other major obstacle when preparing flexible electric circuits using the vacuum deposition and printing processes owing to the requirement of expensive equipment and high operating outlays.

Fibrous materials, such as textile and paper, have excellent flexibility and foldability, and they can be easily cut and attached to flexible substrates simply by gluing or stitching. Furthermore, fibrous materials are easily accessible at an affordable price, and the processes for preparing patterns consisting of fibrous materials on a substrate are very simple and inexpensive. Once the fibrous materials has a high electrical conductivity and good mechanical endurance against external deformation, they become attractive for use in electronic fields, especially for the simple and low-cost preparation of electric circuits for flexible and wearable electronics.

Conductive fibrous materials are fabricated by the electroless silver (Ag) or nickel (Ni) plating onto the surfaces of chemical and/or natural fibers.[8] Although the electroless plating process is a useful tool for the deposition of metallic films onto the surfaces of nonconductive materials, it has a high cost when used for the uniform deposition of metallic film on fibrous materials owing to expensive processes and the price of the Ag and Ni. Furthermore, poor electrical conductivity and mechanical endurance against external deformation can occur in conductive fibrous materials which undergo electroless plating. Another well-established method is polymer coating, in which individual fibers are uniformly coated with a smooth and coherent layer of conductive polymers.[9–11] However, the electrochemical stability of polymer-coated conductive fibrous materials decays with age.[12] Recently, conductive carbons, such as carbon nanotube (CNT) and graphene, as well as activated carbon have been used in the production of conductive fibrous materials with reliable electrical conductivity and electrochemical endurance,[13–15] but their uses are mostly limited to electrodes in energy storage devices owing to their complicated processing and the high cost of CNT and graphene. Accordingly, a new process using inexpensive source materials that are also capable of high electrical conductivity is necessary for the simple production of versatile fibrous materials with excellent electrical properties and good mechanical endurance.

Aluminum (Al) is one of the most suitable metals owing to its advantages of high electrical conductivity at a low cost, so that its application to the low-cost production of fibrous materials with excellent electrical conductivity and mechanical endurance is very attractive.[16,17] However, the Gibbs free energies pertaining to the oxidation of Al and the reduction of aluminum ions (Al^{3+}) are extremely low and quite high, respectively, such that the deposition of Al film on the surface of a nonconductive material is rarely achieved by processes other than vacuum deposition. However, the vacuum deposition method is an expensive process requiring a vacuum chamber and other devices related to the vacuum, as well as requiring a large amount of energy to maintain the vacuum chamber at a low pressure and there is also a great loss of the source materials involved (less than 30% of the source materials is deposited on the target surface), signifying that

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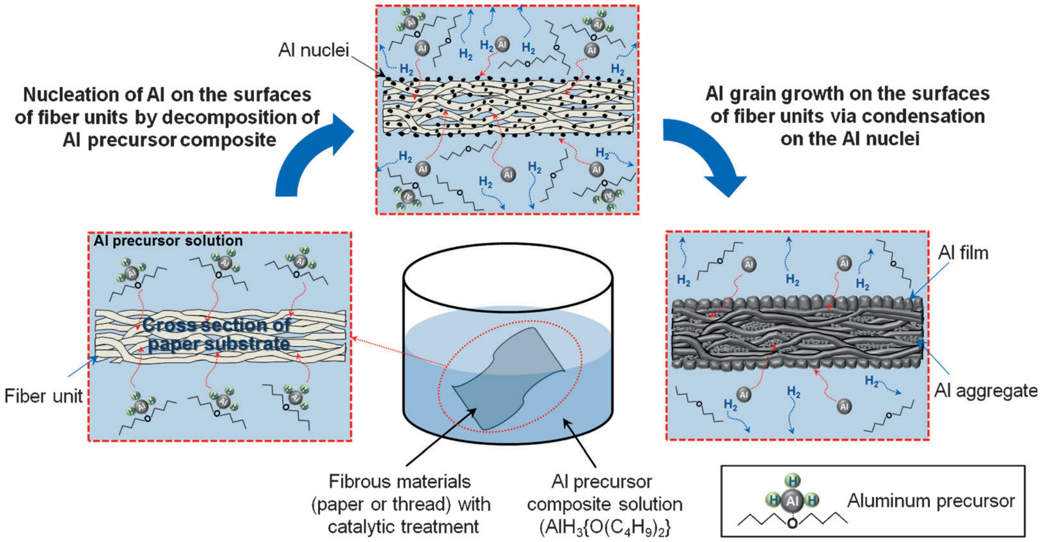

Figure 1. Schematic representation of the chemical solution (CS) process for fabrication of highly conductive Al fibrous materials by immersing the catalytically pre-treated fibrous materials into an Al precursor composite ($AlH_3\{O(C_4H_9)_2\}$) solution at room temperature.

the use of the vacuum deposition process is not optimal as a low cost means to prepare fibrous materials with excellent electrical conductivity and good mechanical endurance.

The reduction of Al_2O_3 or Al^{3+} is difficult to achieve by a physical or chemical process because of the extremely high energy required for this type of reduction. However, pure Al can be chemically prepared if an aluminum composite which is easily decomposed into Al and other chemicals is prepared by the reaction of aluminum salts with other metallic salts consisting of a metal with a reduction energy higher than that of Al. Equation (1)

$$AlCl_3 + 3\,LiAlH_4 \rightarrow 4\,AlH_3 + 3\,LiCl \rightarrow 4\,Al + 6\,H_2 + 3\,LiCl \qquad (1)$$

shows the chemical production of an Al precursor composite by a reaction of Al and Li salts and the further formation of pure Al by the decomposition of the produced Al precursor composites. This reaction has been very effectively applied to the preparation of pure Al materials.[17–23] In particular, Al films were successfully prepared on a substrate by a solution process using the reaction in Equation (1)[17,22,23] despite the fact that several complicated or expensive steps are necessary when using a solution process for the preparation of highly conductive Al films. Although the solution-stamping (SST) process introduced in our previous studies[17,22] is applicable to the preparation of a small-area Al film on a substrate, a large-area Al film is hard to prepare by the SST process because of bubble type defects stemming from its very complicated process. Therefore, the previously introduced solution processes are not adequate for the simple preparation of highly conductive fibrous materials.

Herein, we suggest a new chemical solution (CS) process for the direct deposition of densely structured Al features onto every single fiber in the fibrous material by the decomposition of an Al precursor composite without a vacuum deposition method. This approach was experimentally confirmed to be effective as a simple and low-cost fabrication process of highly conductive paper and textiles coated and packed with densely structured Al films and aggregates at room temperature.

Figure 1 shows a schematic diagram of our CS process. Because moisture absorbed in fibrous materials, such as paper and thread, causes the generation of non-conductive aluminum hydroxide ($Al(OH)_3$) and aluminum oxide (Al_2O_3), the moisture was removed before the CS process was performed. The decomposition of AlH_3 into Al and 1.5 H_2 occurs at about 165 °C[19] hence, the chemical preparation of Al cannot be performed at room temperature without a catalyst that decreases the activation energy of the decomposition process. The catalytic pretreatment of a fibrous material is thus a critical step for the fabrication of conductive fibrous materials at room temperature. We exposed the dried paper and thread to the fumed catalyst titaniumisopropoxide ($Ti(O\text{-}i\text{Pr})_4$) for about 10 min and subsequently immersed them into an Al precursor composite solution of $AlH_3\{O(C_4H_9)_2\}$, which was prepared by reaction of aluminum chloride ($AlCl_3$) with lithium aluminum hydride ($LiAlH_4$) in dibutyl ether ($O\text{-}(C_4H_9)_2$), for about 4 h. Unlike the SST process (described in Supporting Information S1), the Al precursor composite solution of $AlH_3\{O(C_4H_9)_2\}$ easily penetrates deeply into fibrous materials. As a result, the decomposition of $AlH_3\{O\text{-}(C_4H_9)_2\}$ into Al, H_2, and $O(C_4H_9)_2$ occurs at all of the fiber units. The nucleation of Al starts to occur on the surfaces of all of the fiber units at room temperature, and the nucleated Al grows eventually larger enough to cover the surface of each fiber unit and to fill the spaces among the fiber units. Detailed methods of the preparation of an Al precursor composite solution and the catalytic treatment of the substrate are described in Supporting Information S2.

Figure 2 a and b show the CS-processed paper and cotton thread, showing the microstructure and chemical elements of Al and carbon (C) as analyzed by means of SEM and energy dispersive spectroscopy (EDS) mapping. These figures clearly show that the white paper and the cotton thread become metallic gray after the CS process. An X-ray diffraction (XRD) analysis of the CS-processed paper revealed that the metallic gray materials were in good agreement with the FCC crystal structure of Al (see Supporting Information S3). On the paper and the thread, which consist of small cellulose fiber units (cross-section diameter of ca. 10 µm), the Al precursor composite solution behaves wholly differently than on a rigid

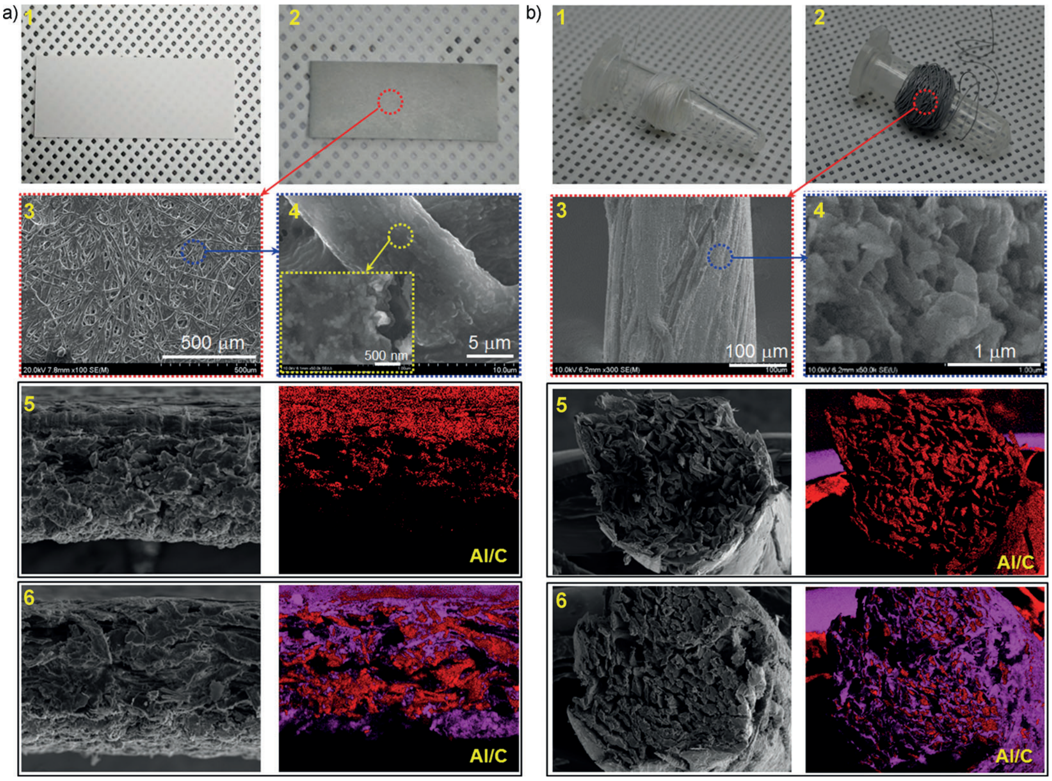

Figure 2. a) Paper substrate, 1) raw paper substrate before CS process, 2) CS-processed paper, 3) surface microstructure of CS-processed paper, 4) magnified microstructure of image (3), 5) cross-section microstructure of raw paper substrate and its mapping image for aluminum (Al) and carbon (C), 6) cross-section microstructure of CS-processed paper and its mapping image for Al and C. b) cotton thread, 1) raw cotton thread before CS process, 2) CS-processed cotton thread, 3) surface microstructure of the CS-processed cotton thread, 4) magnified microstructure of image (3), 5) cross section microstructure of raw cotton thread and its mapping image for Al and C, 6) cross-section microstructure of CS-processed cotton thread and its mapping image for Al and C; red dots C and purple dots Al.

substrate. A rigid substrate is impermeable to the Al precursor composite solution whereas paper and thread can soak up the precursor solution into the fibrous structure. Thus, the formation of Al films and aggregate materials occur both on the surface and inside the fibrous materials, unlike the SST process, in which the Al film forms only on the substrate surface. As shown in the microstructures of the CS-processed paper (Figure 2a: parts 3, 4) and thread (Figure 2b: parts 3, 4), densely structured Al films and aggregates consisting of very fine Al particles (ca. 10 to 300 nm) were formed on every fiber unit of the fibrous materials. This was confirmed by the EDS mapping results for raw and CS-processed fibrous materials (Figure 2). Because the main component of the paper substrate and the cotton thread is cellulose, only carbon (Figure 2, red dots) was detected in the EDS mapping images of the raw fibrous materials, however, after the CS process, both C and Al (purple dots) were well distributed throughout the cross-sections of fibrous materials. It was also experimentally confirmed that the other types of fibers, such as polyester thread, could also undergo the preparation of highly conductive Al fibers by the CS process (Supporting Information S4).

Because paper and thread consisting of numerous small fiber units are extremely hygroscopic, densely structured Al features formed on and among fiber units may be easily damaged by moisture and oxygen. Thus, it was necessary to investigate the electrical and mechanical properties of the CS-processed fibrous materials as well as their long-term stability. Figure 3 shows the electrical resistances of the CS-processed Al papers and threads with their immersion times in the Al precursor composite solution. The CS-processed paper and thread show excellent electrical properties with an electrical sheet resistance (ESR) of less than 250 mΩ/□ (less than ca. 25 mΩ/□ for the Al paper prepared under the optimized conditions) and electrical linear resistance (ELR) of less than 30 Ω/10 cm (less than ca. 2 Ω/10 cm for the Al thread prepared under the optimized conditions), respectively. These are superior to SST-processed Al paper (ca. 2 Ω/□)[17] or commercialized conductive thread (ca. 1000 Ω/10 cm). LED lamps connected by all of the CS-processed Al papers and threads flashed well when a DC current was applied. Furthermore, their electrical resistances showed an initial decrease but afterward showed stable values as the immersion time of the paper and thread into the Al precursor composite solution increased. The electrical resistance of a densely structured conductive film is inversely proportional to its thickness. As shown in Figure 2, fibrous materials, such as paper and thread, have highly porous structure, therefore, the thickness of conductive film increases and reaches to a stable value once the conductive film fully fills all the spaces in the fiber units. Accordingly, the improvement of electrical properties of the CS-processed Al paper and thread result from the densely structured Al films formed on the fiber units becoming thicker with increasing immersion time. (Methods for investigating electrical properties of CS-processed Al paper and thread are described in Supporting Information S5.)

The mechanical properties of the CS-processed Al paper and thread were investigated by performing bending and cyclic folding tests (the test methods are explained in

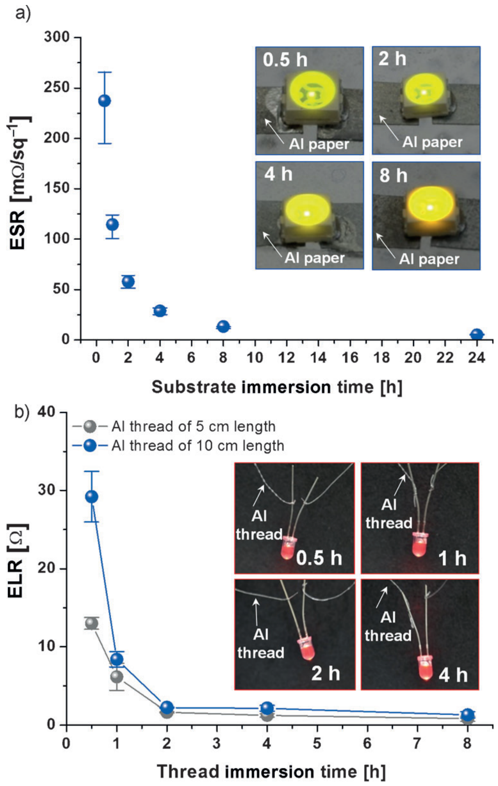

Figure 3. Electrical properties of Al processed paper and cotton thread. a) Electrical sheet resistance (ESR) of CS-processed Al paper versus immersion time in the Al precursor composite solution. b) Electrical linear resistance (ELR) of CS-processed cotton thread versus immersion time in the Al precursor composite solution. Insets: LED lamps connected to the CS processed Al paper and thread, respectively.

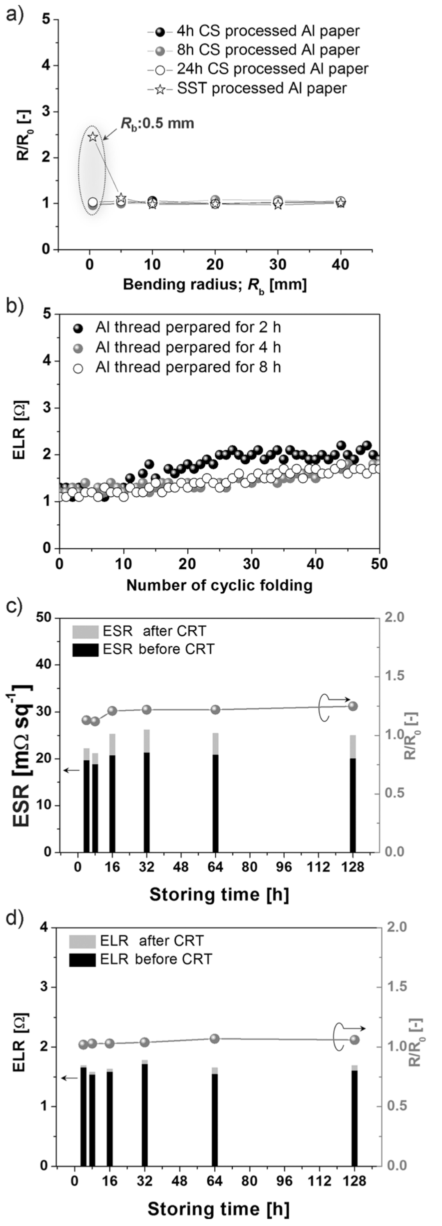

Figure 4. a) ESR change of CS-processed Al paper under bending radius and their comparison to that of the SST-processed Al paper. b) ELR change of CS-processed Al threads during the 50-times intensive cyclic folding test. Electrical resistances of c) CS-processed Al papers and d) threads before and after an accelerated test of their long term stability. CRT = corrosion resisting testing.

Supporting Information S6). Figure 4a shows the normalized ELR when CS- and SST-processed Al papers with a size of 50 mm (L) × 5 mm (W) were bent to a 0.5–40 mm radius (R_b). All the CS-processed Al papers showed the very stable electrical resistances regardless of the bending radius. Furthermore, the Al paper bent at R_b of 0.5 mm appeared to be nearly folded (Supporting Information S6). Nevertheless, the ELR, as measured after the bending tests for all of the CS-processed Al papers, rarely changed from the initial values ($\leq \approx 1.5\,\Omega$) of the flat Al papers. The SST-processed Al paper bent at R_b of 5–40 mm was also very stable, but bent at R_b of 0.5 mm it showed a twofold increase of electrical resistance. Deterioration of electrical conductivity after the bending test is mainly caused by damage to the conductive features.[17] Optical microscopy (OM) of the samples bent at R_b of 0.5 mm confirmed that many cracks were present in SST-processed Al paper, while no cracks were observed in the CS-processed Al paper (Supporting Information S7). These results indicate that the CS-processed Al paper is stable against external deformation, but the SST-processed Al features on the paper are too thin to have be stable enough against folding deformation.

Unlike the paper, the CS-processed thread was very slender and wavy such that a bending test was not a proper assessment method for it. Thus, a cyclic folding test was conducted to investigate its mechanical properties, and this result is shown in Figure 4b. Although the cyclic folding test was highly intensive (one cycle of a folding test involved the folding of the Al thread to +180°, folding it back to 0°, refolding it to −180°, and then folding it back to 0° again, Supporting Information S6), the ELR of the CS-processed Al thread increased by a factor of 1.45–1.55 after 50 cycles of folding deformation. Optical microscopy (Supporting Information S8) showed minor damage at the folded part of the Al thread, not present before the folding test. However, the minute damage is only on the surface of the Al thread, which is also filled with densely structured Al features. Therefore, a serious deterioration of the electrical conductivity was not caused by the intensive folding test. In particular, considering its initial very low ELR ($\leq 1.3\ \Omega$), the CS-processed Al thread maintained good electrical conductivity throughout the intensive folding tests. These findings indicate that the Al features are not easily damaged by bending and folding deformation.

The long-term stability of the CS-processed Al paper and thread against oxygen and moisture was evaluated by measuring their electrical resistances after they were stored in a harsh environment with a relative humidity of 80 % and a temperature of 80 °C for 4–128 h (Figure 4 c and d). The electrical resistances of the CS-processed Al paper and thread had initial values of approximately 20 mΩ/□ and 1.6 Ω/10 cm, respectively, and increased by factors of somewhat less than 1.25 and 1.07 after they were stored in the harsh environment for a week (final values of ca. 25 mΩ/□ and ca. 1.7 Ω, respectively). Thus the effects of oxygen and moisture on the electrical properties of the CS-processed Al paper and thread were marginal. The reaction of Al with oxygen and/or moisture is so active that a thin Al oxide layer (3–10 nm) always exists on the surface of Al films. Once the Al oxide layers are formed, the oxidation or hydroxylation of Al films does not show any further significant progress.[17,22] Because the CS-processed Al paper and thread consist of fiber units with very densely structured Al films we believe that they are capable of long-term stability even in harsh environments.

An electric circuit board can easily be fabricated by trimming the CS-processed Al paper and attaching it to a substrate. Furthermore, an electric circuit on a fabric substrate for wearable electronics can be prepared by stitching with the CS-processed Al threads. Figure 5 a shows a LED lamp mounted on electric circuits fabricated by attaching the trimmed Al paper on a name card, showing excellent flexibility. As the CS-processed Al paper had excellent electrical conductivity, the LED lamp flashed on as DC current was applied, and continued flashing even after large bending deformation. Figure 5 b shows a very simple electric circuit consisting of four trimmed Al papers and two backstitched Al threads. The trimmed Al papers were glued onto the surface of a cotton substrate and were connected by backstitched Al threads. Despite fact that the backstitched Al threads were twisted several times, a blue LED lamp flashed well when DC current was applied to the circuits. Furthermore, to demonstrate the scalability of this current technology to larger paper (□ 100 mm × 100 mm) and cotton textile (□ 50 mm × 50 mm) substrates, it was experimentally confirmed that large pieces of Al-coated conductive paper and cotton textile with excellent electrical conductivity levels (the electrical sheet resistance levels of the Al paper and cotton textile materials are 19 mΩ/□ and 43 mΩ/□, respectively, Supporting Information S9) could be easily reproduced by the CS process.

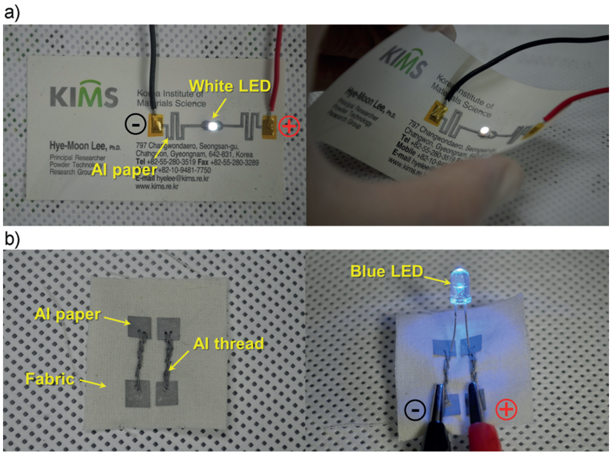

Figure 5. Photos of LED lamps mounted on a simple electrical circuits prepared by attachment of the trimmed Al conductive papers on a paper substrate (a) and by attachment of trimmed Al conductive paper to a cotton fabric and connecting between the attached Al conductive papers using the backstitched Al conductive thread (b).

In conclusion, we applied a new chemical solution (CS) process to the preparation of highly conductive Al fibrous materials (textile and paper) for the creation of electric circuits for flexible and wearable electronics at room temperature. The CS-processed fibrous materials were observed to be fully coated and packed with densely structured Al features, and their comparison to materials prepared by other solution processes revealed that the CS process was superior for the preparation of Al fibrous materials with high electrical conductivity and mechanical endurance against serious bending and folding deformations. These excellent electrical and mechanical properties were also confirmed through simple electric circuit demonstrations even during serious bending and folding deformation. Moreover, the highly conductive fibrous materials coated and packed with densely structured Al features were easily scaled up for large-area flexible and wearable electronic devices. Accordingly, we expect that the simple and low-cost CS process introduced herein will make great contributions to the development of improved electric circuits and electrodes for flexible and wearable electronics and advanced electromagnetic interference (EMI) shielding materials as well.

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