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Photoenhanced Patterning of Metal Nanowire Networks for Fabrication of Ultraflexible Transparent Devices

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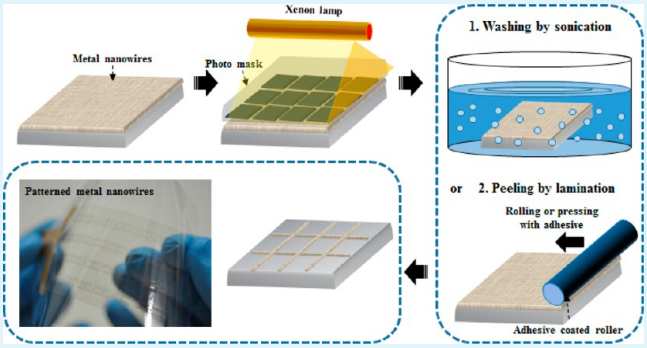
Supporting Information

ABSTRACT: Network structures of metal nanowires are a promising candidate for producing a wide range of flexible electronic devices, but only if they can be suitably patterned and retained on various materials. Here we present a new approach to the patterning of metal nanowires by employing intense-pulsed-light (IPL) irradiation to reduce the process to just two steps: irradiation and the subsequent removal of nonirradiated nanowires. This ultrasimple method eliminates the need to employ chemical reagents for etching or improving the adhesion of nanowires, and is compatible with Ag nanowires (AgNWs), Cu nanowires (CuNWs), and most transparent polymers. Furthermore, it is not reliant on additional processes, such as coating, heating, developing, and etching to make a patterned nanowire structure. Using this simple method, ultraflexible and transparent devices such as touch sensor, heater and light emitting diode with an exceptionally high mechanical stability have been successfully fabricated. This new method is expected to be directly applicable to the fabrication of a wide range of high-performance, low-cost, biocompatible, and wearable devices.



KEYWORDS: *transparent electrode, metal nanowire, wearable device, intense pulsed light, flexible electronics*

INTRODUCTION

Wearable, shape-deformable transparent electrodes are of great importance to various future applications, such as energy harvesting devices,[1−5] electronic skin for tactile sensing,[6−10] and flexible displays that can be worn directly on the eye.[11,12] The intrinsically high conductivity, flexibility, and porous network structure of metal nanowires, such as Ag nanowires (AgNWs) and Cu nanowires (CuNWs), has seen them emerge as most promising candidates for such applications,[13−20] but their use in wearable electronics is dependent on how easily they can be formed into suitable patterns on flexible surfaces. Creating a regular pattern of metal nanowires is possible through conventional photolithography and etching, but requires precise control over the photoresist (PR) thickness and time/intensity of light exposure, as well as a delicate optimization of development and etching.[21−23] These conditions can only realistically be achieved with a rigid and planar substrate, creating an urgent need to develop a simpler approach suitable for any kind of substrate regardless of its shape and consisting materials.

Inkjet printing is one of the most well-known options for simple and direct patterning, but has several drawbacks that hinder its practical use with patterning nanowires.[24,25] First, nanowires with a high aspect ratio tend to block the jet nozzle, greatly limiting the applicable length for continuous, reliable printing, and reducing the figure of merit of any electrode produced in this manner. Second, printing line in a width of smaller than 100 μm is still challenging that is deemed necessary for achieving high quality tactile or touch sensors. Third, inkjet printing is not capable of achieving the sharply defined shapes needed for complex patterns. Last point to be indicated is that it generally requires surface treatments for hydrophobicity, which could adversely affect coatings of overlying materials. The recent introduction of laser ablation for the selective elimination of metal nanowires is gradually being accepted by industry, as this makes it possible to eliminate the costly and laborious photolithography and etching processes from the patterning of metal nanowires.[26−28] However, it introduces its own detrimental side effects in the form of thermal damage to materials in proximity to the irradiated nanowires and the unavoidable loss of noble metal (Ag) through the ablation. Spray coating with a patterned shadow mask is yet another alternative, but has not been able to meet industrial demands with regards to patterning quality.[29,30] Most importantly, regardless of which of the aforementioned patterning

Received: October 4, 2015
Accepted: December 21, 2015
Published: December 21, 2015

DOI: 10.1021/acsami.5b09386
ACS Appl. Mater. Interfaces 2016, 8, 480−489

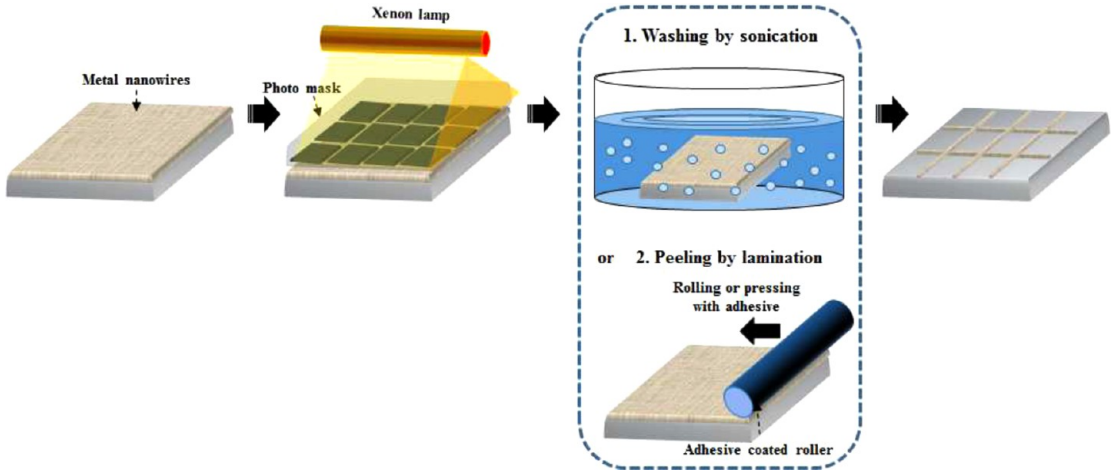


Figure 1. Patterning of metal nanowire-based electrodes by intense-pulsed-light.

methods is used, there is still a need for additional processes or materials to improve the adhesion and mechanical stability of the patterned nanowires when applied to a flexible polymer.[31−33]

To address the current limitations of fabricating patterned nanowire structures, for the first time, we herein propose a totally new approach based on selective irradiation of photonic energy. This is a method that is extremely simply to implement, as it does not require any chemical etchants or reagents to make patterns or improve the adhesion of the nanowires, which implies that the developed approach does not need additional coating process. Instead, nanowires can be patterned by washing in liquids or simply using a commercial Scotch tape (see Movie S1), and the remaining nanowires adhere surprisingly well to polymers. Both AgNWs and CuNWs have been successfully patterned by this approach on various flexible transparent polymers. Moreover, as one of this is a wet-type pattern-making approach, any detached nanowires can potentially be reused. Finally, the feasibility of this new approach is tested by applying it to the ultrasimple fabrication of flexible and transparent devices, for example, a touch sensor, patterned heater and pixelated light-emitting-diode (LED).

RESULTS AND DISCUSSION

The fundamental procedure for patterning is schematically illustrated in Figure 1, in which a dispersion of AgNWs or CuNWs in isopropyl alcohol (IPA) is first deposited onto the surface of a polymer to form a transparent and conductive network. This approach was confirmed to be compatible with various polymers, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and colorless-polyimide (cPI) film. After it was dried to remove the solvent, the nanowire electrodes were irradiated with intense-pulsed-light (IPL) using an appropriate voltage for the material being used (2.5 kV for PET and PEN, and 3.0 kV for cPI). IPL system uses nonlaser high intensity light sources that make use of a high-output flash lamp to produce a broad wavelength output of noncoherent light, usually in 500 to 1200 nm range. A film-type photomask typical of that employed in photolithography was also used to divide the nanowire area into two distinct parts: one being subjected to IPL, while the other was shielded by the shadowing pattern of the mask. These photoaffected nanowire films were patterned by either a wet-type approach, in which the sample is immersed in a liquid and ultrasonified, or a dry-process of "attach and detach" using commercial tape. With either method, the nonirradiated nanowires were successfully removed without detaching irradiated nanowires from the polymer substrate, leaving a nanowire network on the film with a pattern that is the inverse of the shadowing mask. Thus, a network of nanowires can be patterned on a flexible substrate by IPL irradiation followed by ultrasonic washing or attachment/detachment with tape.

To understand the mechanism by which patterning is achieved with IPL, we first analyzed its effects on the electrical and optical characteristics of AgNW electrodes on a cPI substrate. Figure 2a shows the change in sheet resistance (R_s) of the films with increasing exposure to IPL irradiation, and from the inset image, it is clear that there is an initial decrease in R_s of about 10−20% within the first few irradiation pulses. The fact that this occurs regardless of the actual time of exposure can be explained by the fact that IPL irradiation delivers highly intensive photonic energy to the AgNWs over the course of hundreds or thousands of microseconds, eventually heating it nearly to its melting point. When this occurs, Ag atoms diffuse and cause the AgNWs to plasmonically weld together, and the poly(vinylpyrrolidinone) capping layer is removed from their surface.[34−36] This heat absorption also increases the temperature of nearby AgNWs and can potentially activate the underlying polymer, causing it to react with the surface of the AgNWs or become thermally damaged if the irradiated energy is excessive.[34] Figure S1 shows examples of this latter scenario, wherein an excess of photothermal energy led to the polymer damaged. This photothermally induced damage is responsible for the steep increase in R_s observed after the initial 10−20% when IPL exposures of 1000 and 2000 μs were used. It is also known that the repetition of exposures exceeding 1000 μs reduces the transmittance of the electrodes, while at the same time increasing the cPI film haziness (Figure S2) and burning out the edges of the film. To avoid such damage, multiple instances of shorter exposure (500 μs) were used, with a 3 s interval between each exposure. Figure 2b and 2c show respectively the effect this had on the transmittance and haziness (the ratio of diffused transmission and total transmission) of the AgNW electrodes, namely that allowing sufficient time for the AgNWs to cool between each exposure prevents any significant deterioration of their optical properties. Indeed, even with up to 16 repetitions of irradiation, the transmittance was reduced by less than 0.5% and the haziness increased by less than 0.1% over the entire wavelength range tested.

DOI: 10.1021/acsami.5b09386
ACS Appl. Mater. Interfaces 2016, 8, 480−489

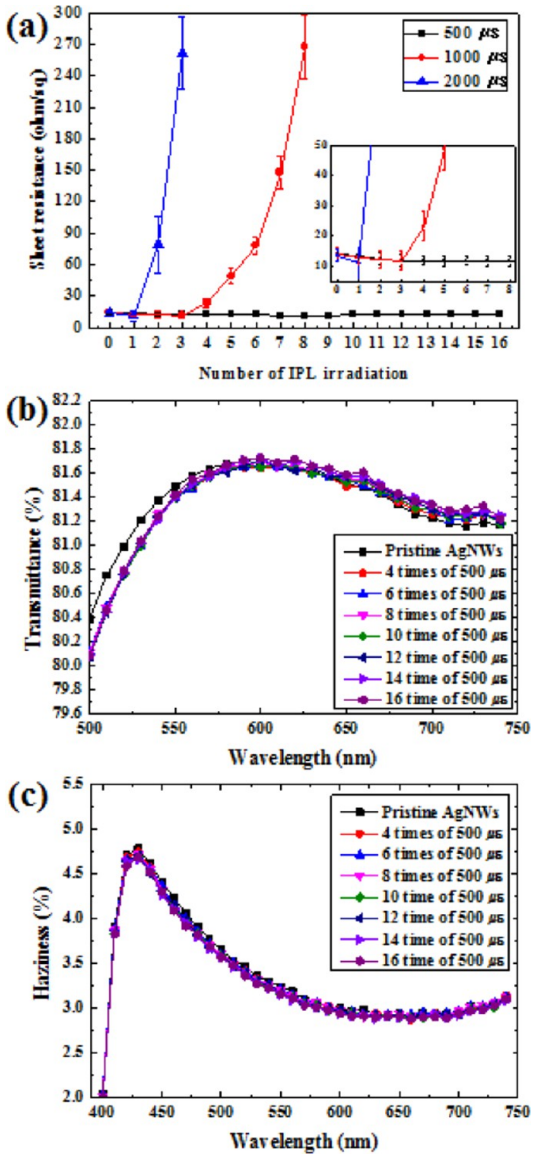


Figure 2. (a) Sheet resistance of AgNW electrodes (comparison of 500, 1000, and 2000 μs irradiations), (b) transmittance (pulse length = 500 μs), and (c) haziness (pulse length = 500 μs).

Given that the goal of this study is to ultimately produce a patterned network of nanowires, the irradiated areas need to be able to resist the external energy used to detach the non-irradiated areas from the surface of the polymer. To test this, an AgNW sample was prepared on a cPI substrate through IPL irradiation (10 pulses of 500 μs duration), followed by immersion in an isopropyl alcohol (IPA) bath with sonication of up to 40 s. Figure 3a shows the effect of varying the duration of sonication on the R_s of the sample, with the measured resistance reaching a maximum stability after 17 s, but increasing from 20 s onward due to a loss of network rigidity. This suggests that the patterning of nanowires should be kept to less than 20 s, particularly under the conditions used in this study. The effects of increasing or decreasing the number of irradiation pulses on the mechanical stability of the samples was also assessed by measuring the R_s after 10 applications of the tape test and 15 s of sonication (Figure 3b). From this, it was deduced that under the conditions applied for patterning, at least 8 repetitions of IPL irradiation are needed to maintain the stability of resulting electrode. However, it was also known that this depends on the materials used for a substrate as well as a system setup employed, for example, only 2 repetitions were sufficient for the PET film possibly because of its low melting temperature. On the basis of these results, optimal conditions for preparing and patterning an AgNW network on a cPI substrate were concluded to be as follows: 10 repetitions of IPL irradiation with a 3 s interval between each; two repetitions of attachment/detachment with 3 M magic tape, or alternatively, 15 s of sonication in an IPA bath.

The microstructures of the AgNW electrodes were analyzed by field-emission scanning electron microscope (FESEM) and atomic force microscope (AFM), their surface being divided on the basis of whether it was irradiated by IPL or not (Figure 4a). The area shielded by the shadowing pattern of the photomask (area B) can be seen in Figure 4b to contain nanowires with visible gaps between them, this porous structure being mainly attributed to the low surface energy of the cPI substrate. That is, the untreated, nonpolar surface of polymers typically results in problems in relation to adhesion, coating, colloid stabilization, and lamination with other materials, resulting in the poor coating and adhesion of metallic materials. This weakness is often overcome by adding a transparent adhesive or binding material, but this also tends to have the effect of reducing optical transmittance, increasing haziness and causing a deterioration of color neutrality. In contrast, the area exposed multiple times to IPL through the film of the mask (area A) can be seen in Figure 4c and 4d to consist of nanowires that are glued to the substrate through fusion with the underlying polymer. This indicates that the increased temperature of the

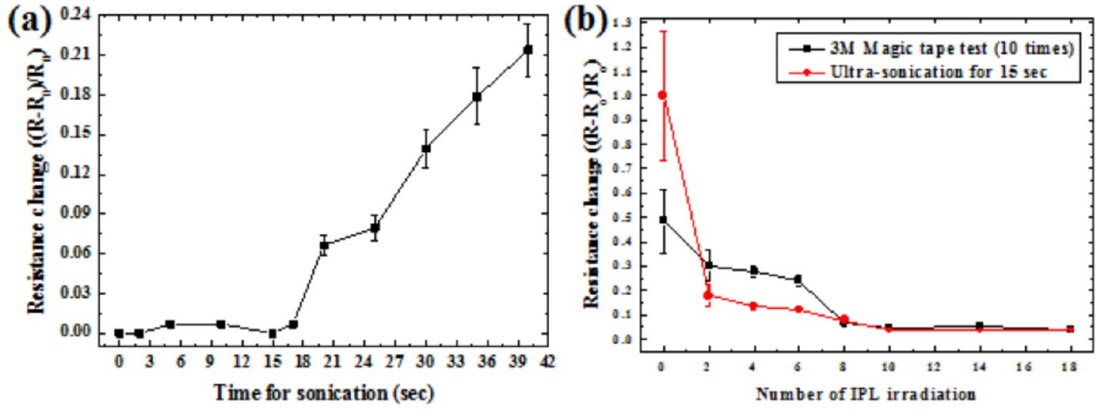


Figure 3. (a) Effect of ultrasonic washing time on resistance and (b) the effect of IPL irradiation on the stability of the electrode.

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ACS Appl. Mater. Interfaces 2016, 8, 480−489

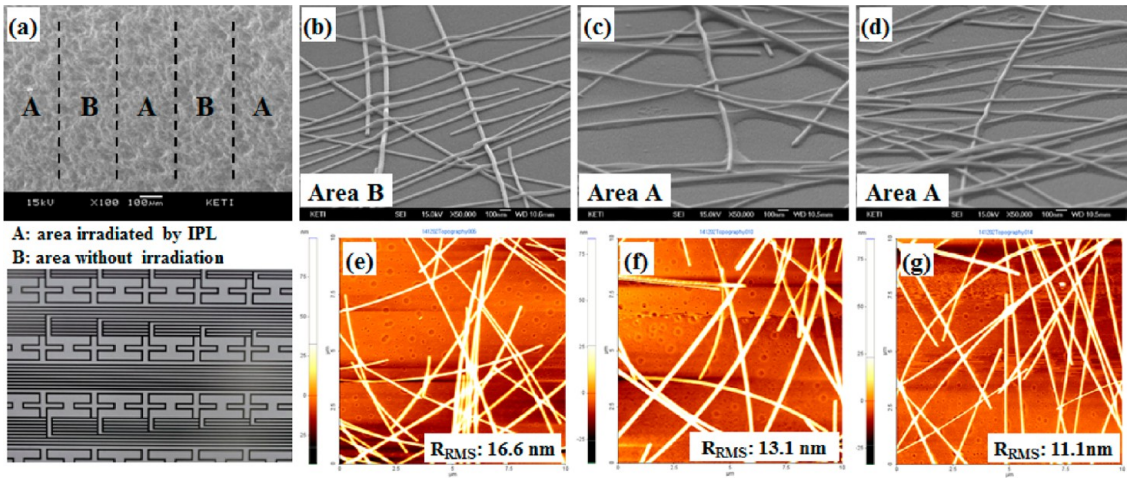

Figure 4. (a) Effect of IPL irradiation on AgNW networks treated by IPL with a photo mask (A indicates an area treated by IPL, B is an area without treatment). (b–d) FESEM and (e–g) AFM images. (b and e) Area B and (c and f) area A with six repeated treatments. (d and g) Area A after ten repeated treatments.

nanowires causes the polymer to partially melt and flow around the lower parts of the AgNWs, with the high thermal conductivity of Ag causing a rapid cooling of the AgNW/polymer interface and subsequent partial embedding of wires in the polymer surface. To confirm this, the sample was immersed in a silver etchant to remove the AgNWs from the surface. As shown in Figure S3, this revealed only a few Ag oxides in area B, but clear evidence of polymer fusion in area A. Another noticeable feature is that the roughness of the AgNW film was decreased by the repetition of IPL irradiation; a comparison of Figure 4e, 4f, and 4g shows that the root-mean-square roughness (R_{RMS}) of the pristine AgNW networks continuously decreased with increasing repetition of irradiation. This was particularly evident after 10 pulses of IPL irradiation, which had the effect of reducing the R_{RMS} from 16.6 to 11.1 nm through what is believed to be the partial burying of structures between each irradiation cycle. This gives a new insight into the potential application of metal nanowire electrodes in thin-film devices, as this has still now been hindered by a high surface roughness.[37,38] From previous works on the optimization of processing parameters, it is known that metal nanowires partially buried in a polymer surface are difficult to remove by physical means.[34−36] However, this new approach avoids this issue by using IPL to create a distinctly different form of adhesion between the nanowire and polymer. The only condition for this is that the polymer must be a thermoplastic material like cPI, PET, PEN, and many other polymers to ensure that it is melted by the induced heat.

Prior to the fabrication of any specific device by this new approach, the mechanical durability of the AgNW electrodes on cPI was tested before and after IPL irradiation by subjecting them to bending curvatures ranging from 700 to 50 μm (Figures S4 and S5). Figure 5a and 5b show the change in resistance in response to inward (compressive stress) and outward (tensile stress) bending, respectively, as a function of the bending radius; the change in resistance is expressed as $(R - R_0)/R_0$, where R is the resistance after bending and R_0 is the initial resistance. Note also that the applied strain is equal to the thickness of the film divided by twice its bending radius. A comparison of the untreated and IPL treated samples reveals the latter to be more flexible and mechanically stable, yet there is almost no increase in resistance with inward bending at any of the bending radii used. Indeed, even with outward bending of 20 μm thick electrode the increase never exceeds 20%, at a bending radius of 50 μm (which is equivalent to a strain of 20%). A buckled structure with a cPI thickness of 5 μm was also formed of an AgNW electrode on cPI to measure the smallest curvature that could be created using the preparation method illustrated in Figure S6. To the best of our knowledge, this is one of the smallest bending curvatures ever reported for such a material. An example of these fabricated buckles (curvature <10 μm) is shown in Figure 5c, and this was found to increase the resistance of the AgNW electrode by ∼30%. Subsequent long-term cyclic (1 Hz) bend testing to an inward and outward radius of 500 μm found that the irradiated film has an excellent bending fatigue strength, with Figure 5d also showing that the irradiated samples have an improved mechanical stability. Furthermore, those samples irradiated 10 times were more stable than those irradiated 6 times, with resistance increasing by less than 10% after 50 000 cycles. This high mechanical flexibility originates from the unique structure created by IPL irradiation, wherein AgNWs become partially embedded in the surface of polymer. This is a significant feature from an engineering perspective in that it means that no additional process or material is needed to enhance its flexibility or mechanical stability, with just the irradiation scheme of photonic energy proposed here being sufficient. In particular cases with PET or PEN substrate, this high adhesion and mechanical stability could be achieved by only one or two repetition of the irradiations.

This proposed IPL irradiation mechanism was used for the ultrasimple fabrication of transparent and flexible devices for a range of different practical applications: touch sensor, patterned heater, and pixelated LED. Figure S7 gives two examples of the fabrication of a metal nanowire pattern on a polymer film for the devices, wherein the AgNW electrodes formed on a cPI substrate were exposed to IPL irradiation with a screening photomask, which was followed by tape attachment, rubbing, and detachment to form a complicated pattern of nanowires. Movie S1 shows the simplicity of this process using a piece of Scotch Magic tape on a cPI film. The other, even simpler method is "washing with sonication", which is effective enough to produce a single-layer touch sensor (Movie S2). The AgNW patterns fabricated on a cPI film by these methods are presented

DOI: 10.1021/acsami.5b09386
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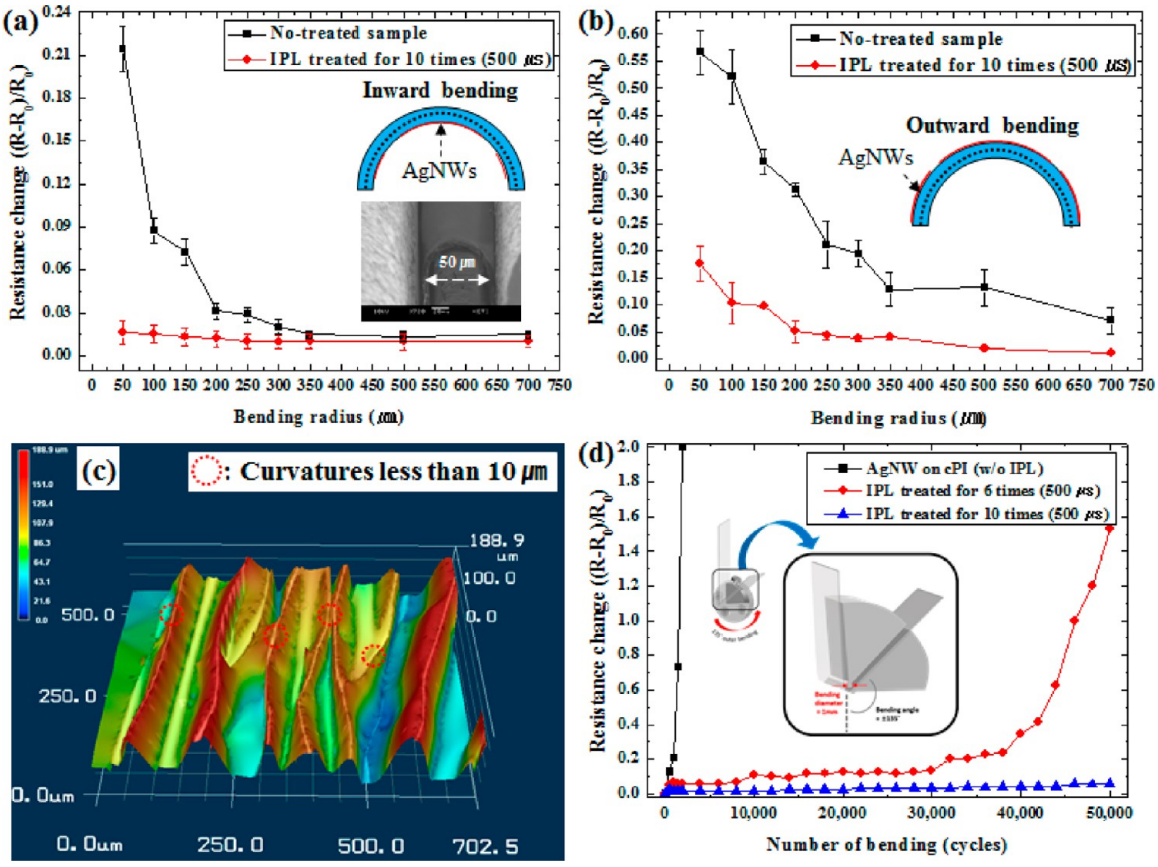

Figure 5. Mechanical stability of an AgNW electrode on cPI: (a) inward and (b) outward bending stability with varying radius, (c) irregular buckles (taken by a 3D laser confocal microscope) formed by a method described in Figure S6, and (d) cyclic bending stability of AgNW electrodes (radius of curvature = 500 μm).

in Figure 6; the first two are produced by two repetitions of tape attachment/detachment, while the others were formed by 15 s of ultrasonication. It is evident from this that both proposed methods create very ordered patterns of various shapes with high, sharp edges, and despite the simplicity of the second approach, a resolution finer than 70 μm is possible without any significant defects. As discussed earlier, this is attributed to the thermoplastic properties of the underlying polymer, meaning that other materials popular in industry such as PET and PEN could also be used. This is confirmed in Figure S8, which shows that AgNW patterns formed on PET and PEN are comparable in quality to those on cPI.

One thing of particular value with patterning by ultrasonic washing is that it allows any detached nonirradiated nanowires to be reworked, as the fact that it does not rely on chemical reagents means that the detached wires should retain their original shape and structure. Furthermore, the use of IPA as the washing liquid ensures that any detached nanowires are redispersed in the liquid and can conceivably be coated onto another substrate. To test this notion, two samples were prepared for comparison: the first being coated with a pristine AgNW dispersion, while the other was fabricated using reclaimed AgNWs. Both samples were found to have an identical R_s value of 130 ohm/sq, but there was a 1−1.5% drop in transmittance and 0.5−1% increase in haziness when reworked AgNWs were used (Figure 7). Subsequent FESEM imaging (Figure S9) revealed this degradation in performance to be caused by the presence of particles and shortened nanowires. Of course, given that all current approaches to the patterning of metal nanowires employ a chemical solution or physical process to neutralize conductivity,[21−30] any reworkability of the removed nanowires is certainly a significant step forward. Furthermore, the purification of the AgNW dispersion is not a particularly onerous task, meaning that there is a very real possibility of further improving this capability.

It is also worth noting here that this newly developed approach is intended to be a universally acceptable method capable of patterning nanowires regardless of their composition. CuNWs were also used for patterning, which as shown in Figure S10, still produced a well-defined pattern shape. Another practical example demonstrated by this method is shown in Figure S11, and involves lighting an LED through a mixed structure of AgNWs, CuNWs, and an AgNW/CuNW composite. It is the percolated porous structure of the nanowire electrodes and adhesion-based patterning mechanism that makes it possible for more than one material to be simultaneously formed on a substrate. In this case, AgNWs were first partially patterned on a polymer film, then a pattern of CuNWs was applied to other areas with specifically designed areas of overlap creating a composite structure of AgNWs and CuNWs. This unique structure presents a possible solution to the cost issue of AgNW-based devices by allowing for the substation of cheaper nanowires in noncritical areas. For example, a transparent sensor can be made from an AgNW network, but the nonvisible connector or circuit can be formed from CuNWs or an AgNW/CuNW composite.

A capacitance-sensing type sensor was first fabricated from a single-layered AgNW electrode that contained both transmitter

DOI: 10.1021/acsami.5b09386
ACS Appl. Mater. Interfaces 2016, 8, 480−489

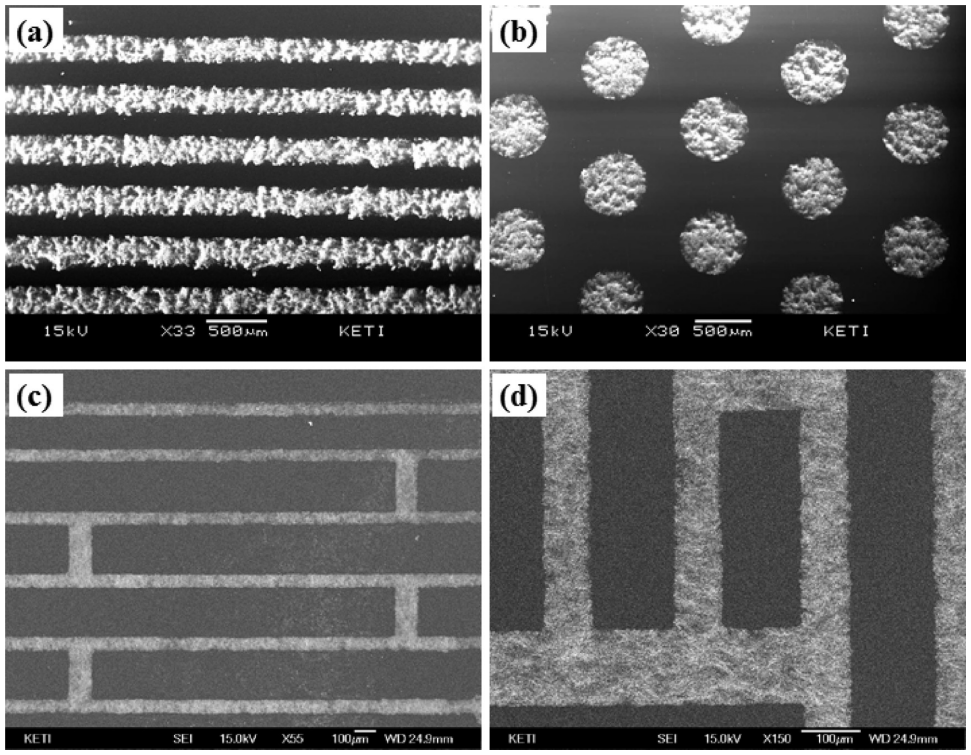

Figure 6. SEM images of various AgNW patterns fabricated on cPI film by (a–b) tape attachment and detachment or (c–d) ultrasonic washing.

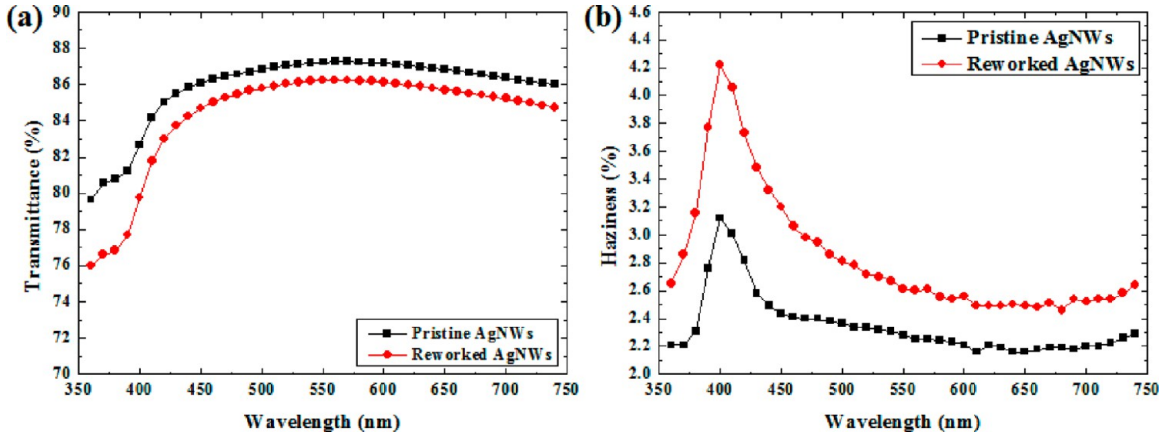

Figure 7. Comparison of optical properties for pristine and reworked AgNW/cPI electrodes: (a) transmittance and (b) haziness (R_s of both electrodes was identically 130 ohm/sq).

(T_x) and receiver (R_x) patterns. As only AgNWs formed by a single coating were used for both the sensor area and signal transit circuit, the resulting panel was totally transparent (higher than 88% in transmittance of AgNW areas at 550 nm). To provide an interconnection with the driving module, an anisotropic conductive film (ACF) was used without any significant increase in contact resistance between the AgNWs and conductive particles in the ACF. The photo in Figure 8a of this sensor after it was bonded to a flexible printed circuit board (FPCB) shows a very clear sensor area, with the FPCB remaining firmly attached when bent to a curved shape. By connecting this FPCB to an inductance–capacitance–resistance (LCR) meter utilizing a probe station, the change in capacitance created by the electric field could be measured. Figure 8b shows the values measured before and after finger touch for both a fresh sensor and one subjected to 100 cycles of bending to a curvature of 200 μm. Note that in either case the decrease in measured capacitance (~0.7–0.8 pF) was well within the detectable range, meaning that the capability to sense touch was not deteriorated by repeated bending. The functionality of the fabricated sample was successfully demonstrated by its ability to recreate lines drawn on its surface, as shown in Movie S3. Further examples of lines and circles drawn on the surface are also provided by the movie. This is the first example of the full-scale (100 mm in diagonal length) transparent touch sensor (transmittance higher than 85% within whole visible wavelength), which was fabricated by an extremely simple and facile approach (only one coating of nanowires and two steps for patterning).

The AgNW networks patterned on a cPI were also tested for its ability as a flexible transparent heater. A sample is shown in Figure S12 with two sets of heaters laid out on upper and lower

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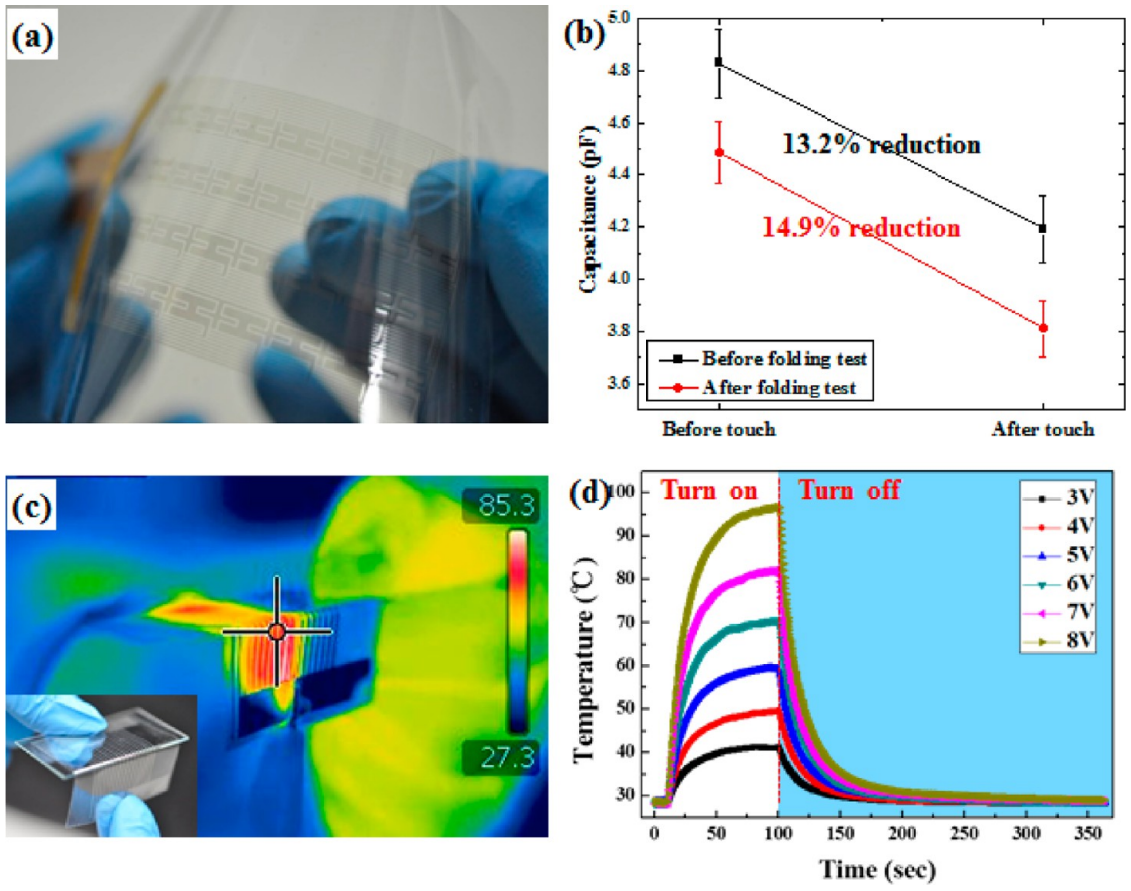

Figure 8. (a) Flexible touch panel and (b) its variation in capacitance when touching sensor areas before and after folding 100 times to a 200 μm radius of curvature. (c) An infrared camera image of a transparent heater folded over an edge of a glass slide (also see an inset photograph for the shape of the sample). (d) Temperature profiles of the fabricated transparent heater (R_s = 15.5 ohm/sq, transmittance = 85.3% at 550 nm of wavelength) under its operation at different input voltages.

side of the cPI. The DC voltage was supplied by a power supply to the fabricated transparent heater through an AgNW pad at either side of the film. One of the heaters was Joule heated with various applied voltages up to 8 V, and an infrared image was obtained at 7 V as shown in Figure 8c. To demonstrate its heating capability as well as high mechanical stability, the heater film was folded over an edge of a glass slide while the voltage was applied to heat the electrode. A sample rolled over a human finger with an application of the same voltage was also shown in Figure S13. It was shown that the patterned electrodes were heated to higher than 80 °C with unheated gaps clearly formed between them. In Figure 8d are shown the temperature profiles obtained from the fabricated transparent heater (R_s = 15.5 ohm/sq, transmittance = 85.3%) at different voltages applied from 3 to 8 V. The temperature responses of the heaters were directly measured with a thermocouple mounted on the top surface of the electrodes. Because of the high conductivity, the temperature can be rapidly increased from room temperature to ~100 °C with an applied voltage of 8 V, which means that the highly transparent, flexible and efficiently heatable micropatterns could be successfully fabricated by the 2-step patterning technology (irradiations and washing). The high heating capability implies the efficient transduction of electrical energy into Joule heating, which may be attributed to the high conductivity of the patterned AgNW electrodes.[39] We also fabricated a flexible pixelated LED with an application of an inorganic phosphor (blue emitting material) and dielectric layer sandwiched by two identical AgNWs/cPI patterned electrodes. The schematic description of the devices is illustrated in Figure S14. Figures 9 and S15 show the fabricated pixelated

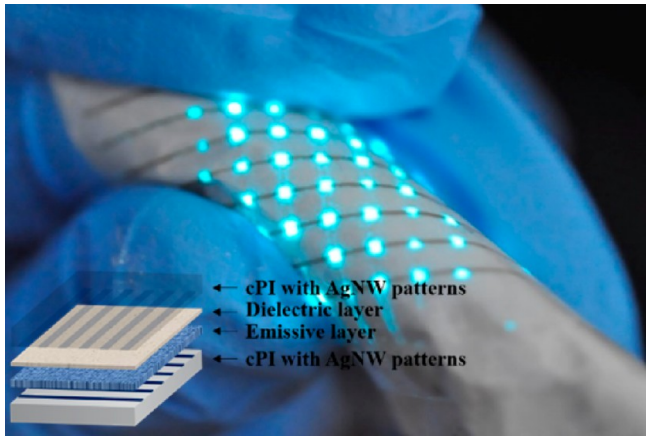

Figure 9. Flexible pixelated LED, which was fabricated with an inorganic phosphor (blue emitting material) and dielectric layer sandwiched by two identical AgNW/cPI patterned electrodes.

inorganic LEDs wrapped over a finger and an edge of the glass slide, respectively. Thanks to the high mechanical stability and enhanced smoothness of the AgNW networks patterned on the cPI, the electrodes were not damaged at all by ensued ink

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ACS Appl. Mater. Interfaces 2016, 8, 480−489

coating, drying and lamination, and no pixel was found to be dead. By these exampled demonstrations, it could be deduced that we did not have to employ any of the complicated procedure for patterning nanowires, materials for enhancing adhesion and conductivity, or transferring nanowire patterns onto the polymers to realize the mechanically stable and transparent sensors, heaters, or even pixelated LEDs: it was verified that only two steps were needed: irradiation of high energy light and washing.

CONCLUSION

A new scheme for the fabrication of precisely patterned metal nanowire-based electrodes on various polymers has been introduced based on IPL irradiation, which through microscopic observation, has been found to induce fusion between the polymer and metal nanowires, thereby ensuring a high force of adhesion. Patterning of the metal nanowires by limiting the IPL-irradiated areas through the use of a conventional photomask represents a simple process in that it is not reliant on other materials or additional processes such as coating, heating, developing and etching. The exception to this is the use of ultrasonic washing or tape laminating to remove the nonirradiated nanowires, though in the case of the former this offers the advantage of allowing the nanowires to be reused. Through this simple approach various transparent and ultraflexible devices can potentially be fabricated, ranging from a fully transparent touch sensor to a transparent microheaters and pixelated LEDs based on a single layer of AgNWs. It is therefore believed that this method represents an important step toward the simple fabrication of high-performance/ultraflexible biocompatible and wearable devices.

EXPERIMENTAL PROCEDURES

Patterning of a Metal Nanowire Electrode on a Polymer Film. The procedure used for the fabrication of the patterned transparent electrode is schematically illustrated in Figure 1. Here, a transparent polymer film (cPI, PET, or PEN) was first cleaned using detergent, deionized water, and isopropanol. Next, a dispersion of AgNWs (Nanopyxis Ltd., Korea) or CuNWs (Nabond Ltd., China) was deposited by spin or spray coating, and then carefully dried under infrared illumination for 10 min. A photomask (a glass in thickness of 2.3 mm comprising a patterned chrome masking layer) typical of that used for photolithography was then carefully placed on the metal nanowire electrodes, which were then exposed to repeated 500 μs pulses of intense light from a photonic sintering system (Polytec Ltd., Sinteron 2000, USA) operating at a voltage input of 2.5 (for PET and PEN) or 3.0 kV (for cPI). To detach the nonirradiated nanowires, two simple methods were used: dipping the sample in an ultrasonic bath filled with water or alcohol for 15 s, and attaching/detaching with a commercial adhesive (3M, Scotch 810 Magic Tape, USA).

Formation of Mixed Structure of AgNW, CuNW, and AgNW/CuNW Composite. A transparent polymer film (cPI, PET, PEN, or PUA) was first cleaned, and then a dispersion of AgNWs was deposited by spin or spray coating, which was then carefully dried under infrared illumination for 10 min. A film mask was placed on the first metal nanowire electrodes, which were then exposed to repeated pulses of intense light using the same process used for the removal of nanowires. A same procedure using a CuNW dispersion was carried out to form its electrode with a different shape.

Evaluation of Electrode. The microstructure of the nanowire networks was investigated by FESEM (JEOL Ltd., JSM6700F, Japan). Their optical transmittance was measured using a UV−visible spectrophotometer (Jasco, V-560, Japan). The sheet resistance was measured by a noncontact measurement system (Napson Corporation, EC-80P, Japan), and the surface roughness was measured by AFM (Park Systems, XE-100TM, USA). The mechanical stability of the patterned electrodes was evaluated by two different methods. The first of these was to evaluate the actual foldability of the films using small bending radii of 700 to 50 μm, in which the sheet resistance before and after folding was used as an indicator of the folding endurance. An automatic bend testing machine (Toyoseiki Ltd., MIT-DA, Japan) was used to measure the long-term reliability under repeated bending cycles, with this particular device causing the electrodes to alternately experience outward bending (tensile stress) and inward bending (compressive stress) to a radius of 0.5 mm (~2% tensile and compressive strain) until the point of cyclic fatigue failure. The electrodes were bent at a cycle rate of 1 Hz, and their resistance was measured during both the inward and outward bending cycles. Bending curvatures were measured by a laser confocal microscope (KEYENCE, VK-9710K, Japan).

Fabrication and Evaluation of Devices. A touch panel with a single-layered electrode was fabricated with a specially designed sensor pattern. The AgNW electrode (R_s = 42 ohm/sq, transmittance = 88.1% at 550 nm) was patterned on a cPI film to produce a capacitive-type touch sensor, which was then bonded to a flexible printed circuit board (FPCB) using an anisotropic conductive film (ACF; Dexerials, CP20431-35AG, Japan). This was then connected to a driving module, and the capacitance before and after applying a finger touch was measured by an inductance−capacitance−resistance (LCR) meter (Hewlett-Packard, 4284A, USA) connected to a probe station (MS Tech, 5500B, Korea) in order to verify the functionality of the fabricated touch panel. In regard of a fabrication of heater, An AgNW dispersion was also coated onto a cPI film, resulting in R_s of 15.5 ohm/sq and transmittance of 85.3% at 550 nm of wavelength. Two sets of separated heaters (line width = 500 μm) were formed by the optimized patterning scheme. A DC power supply (Keithely, 2400 Sourcemeter, USA) was employed to induce Joule heating, and a thermometer (Keithely, 2701 Multimeter, USA) was used to measure the temperature and make the temperature profiles. An infrared camera (FLIR, T335, USA) was also employed to obtain the temperature distribution on the surface of heater during an application of voltage. For fabrication of flexible LEDs, two sheets of identical AgNWs/cPI patterned electrodes (R_s = 17.1 ohm/sq, transmittance = 86.3% at 550 nm) were first fabricated by the identical method. A dielectric ink (ND-8010E, NET, Korea) was spin-coated on one of the electrodes, while the phosphor ink (NET-7030, NET, Korea) was coated onto the other electrode, both of them followed by drying at 50 °C for 2 min. Then the passivated electrode was laminated face to face with the phosphor-coated electrode tilted at an angle of 90° as illustrated in Figure S17. The lamination was conducted at 120 °C and maintained for 10 min. To supply power to the fabricated LEDs, an AC power supply (EXTECH, 6620, Taiwan) was used.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b09386.

Thermally damaged AgNW/cPI electrodes, Optical properties of AgNW/cPI electrodes, FESEM microstructures of the AgNW film surfaces, procedure for bending test of the fabricated films, bending test for mechanical characterization of the fabricated films, fabrication procedure for a buckled transparent electrode, patterning procedures, SEM images for the line patterns fabricated by tape attachment and detachment, FESEM images of the AgNW networks, Cu nanowire electrodes patterned on a cPI film, demonstration of nanowire character, transparent heater, fabricated AgNW/cPI heater, alternating current electroluminescence device, and alternating current electroluminescence devices (PDF)

Patterning by tape attachment and detachment (AVI)

Patterning by washing with sonication in IPA (AVI)

Sensing touch with a fabricated capacitive sensing panel (AVI)

DOI: 10.1021/acsami.5b09386
ACS Appl. Mater. Interfaces 2016, 8, 480−489

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J.-W.K. designed and supervised the research and wrote the paper. C.H.S. fabricated and evaluated the electrodes and devices. C.J.H. and B.K.J. have given useful ideas for developing experimental methods. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the New & Renewable Energy Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20153030012110).

ABBREVIATIONS

IPL, intense pulsed light
AgNW, silver nanowire
CuNW, copper nanowire
PR, photoresist
IPA, isopropyl alcohol
PET, polyethylene terephthalate
PEN, polyethylene naphthalate
cPI, colorless-polyimide
R_s, sheet resistance
FESEM, field-emission scanning electron microscope
AFM, atomic force microscope
R_{RMS}, root-mean-square roughness
T_x, transmitter pattern
R_x, receiver pattern
ACF, anisotropic conductive film
FPCB, flexible printed circuit board
LCR, inductance-capacitance-resistance
LED, light-emitting-diode
DC, direct current
AC, alternating current

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DOI: 10.1021/acsami.5b09386
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