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ORIGINAL REPORT



Surface-functionalized silver nanowires on chitosan biopolymers for highly robust and stretchable transparent conducting films

Zeno Rizqi Ramadhan^a, Joo Won Han^a, Dong Jin Lee^a, Siti Aisyah Nurmaulia Entifar^a, Juhee Hong^a, Changhun Yun^b and Yong Hyun Kim^a

^aDepartment of Display Engineering, Pukyong National University, Busan, Republic of Korea; ^bCenter for Nano-Photonics Convergence Technology, Korea Institute of Industrial Technology (KITECH), Gwangju, Republic of Korea

ABSTRACT

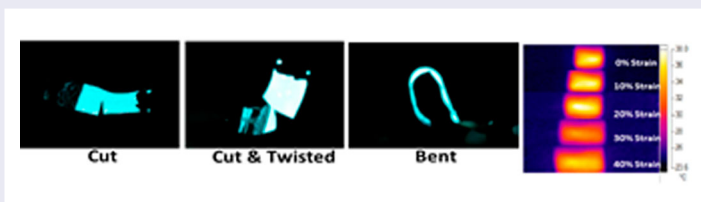
We develop highly robust and stretchable conductive transparent electrodes based on silver nanowires (AgNWs) deposited on functionalized chitosan biopolymer substrates. 11-aminoundecanoic acid is introduced as a surface modifier for enhancing the chemical bond. The chemically functionalized AgNW films achieve a low sheet resistance of 12.2 ohm/sq with a high transmittance of 88.9%. In addition, stretchable alternating current-driven electroluminescent devices and stretchable transparent heaters have been fabricated with AgNW/chitosan thin-films which can be cut, stretched, bent, and twisted without performance degradation. With this approach, stretchable electronics prepared on bio-compatible substrates can be easily applied to curved surfaces or human skins.

ARTICLE HISTORY

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KEYWORDS

Transparent electrodes; chitosan; silver nanowires; stretchable electronics; wearable electronics



IMPACT STATEMENT

We demonstrate highly robust and stretchable transparent conductive electrodes based on the AgNWs/chitosan biopolymer with the organic surface modifier. The films can realize future biocompatible wearable electronics on the human body.

1. Introduction

Recent development in the wearable electronics enables for utilizing various electronic components to the human body, which can collect biofeedback or can operate as displays, energy harvesting devices, power supplies, or personal thermal management devices [1]. Especially for the functionalized artificial electronic skin, highly stretchable, bendable, and biocompatible conductors are of great necessity. Optically transparent stretchable conductors enable electronic components in electronic skins to be visually imperceptible. When applying the stretchable electronic devices to the human body, it should be conformal to skins and have robust contact and minimized human rejection.

Chitosan obtained by deacetylation of chitin, which is the second most abundant polysaccharide in nature, attracts a great interest for biomaterials due to its biodegradable, non-toxic, interesting physicochemical, and biopharmaceutical characteristics [2]. Chitosan is suitable for a variety of tissue engineering applications due to the desirable properties for a tissue scaffold. In addition, chitosan films are potentially favorable materials as biodegradable, transparent, elastomeric substrates due to their many advantages such as simple and cheap fabrication process from fishery waste, outstanding optical transmittance, and mechanical softness [3]. Thus, chitosan has a great potential to be utilized as an ideal substrate for green electronics. However, the strong

CONTACT Yong Hyun Kim ✉ yhkim113@pknu.ac.kr Department of Display Engineering, Pukyong National University, Busan 48513, Republic of Korea

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hydrophobicity of chitosan surface needs a surface modification for its applications to functional substrates for electronics [4]. In this respect, various physicochemical, mechanical, and biological surface functionalization methods have been investigated [5]. However, most surface functionalization methods cannot be directly applied to polymeric substrates due to randomly oriented polymer chains with no particular anchoring sites [6].

The development of high performance transparent elastic conductors is another issue in the applications of wearable electronics. Indium tin oxide (ITO) is the most commonly used transparent electrode material for optoelectronic devices. However, the intrinsic brittleness, the high material cost, and the elevated processing temperature of ITO limit its application in low-cost, flexible, and stretchable devices [7]. For this reason, the need to develop alternative transparent electrodes as alternatives to ITO has been rapidly grown. Currently, conductive polymers, metal nanowires, and graphene have been widely investigated as alternatives to ITO [7,8]. In particular, the silver nanowire (AgNW) is one of the promising materials for alternative transparent electrodes due to its high transmittance, high conductivity, and excellent mechanical flexibility, and easy, low-cost solution processability [7]. It is reported that the sheet resistance of AgNWs embedded in the crosslinked poly(acrylate) matrix increased by ~ 2.3 times at 50% tensile strain [9]. Hu et al. demonstrated that AgNWs on polyurethane substrates exhibited the increase in resistance by a factor of ~ 5.4 at 60% strain [10]. Graphene oxide-coated AgNWs on silane-modified polydimethylsiloxane (PDMS) substrates reported by Lee et al. showed the resistance increase by a factor or ~ 2.8 at 40% strain [11]. Liu et al. reported that spray-coated AgNWs transferred on PDMS substrates lead to the increase of sheet resistance by 1.9 times at 100% strain [12].

Here, we demonstrate highly stretchable and mechanically robust, transparent conductive AgNWs on chitosan biopolymer thin-films. 11-aminoundecanoic acid (11-AA) is introduced as an organic surface modifier to enhance the wettability and adhesiveness of AgNW/chitosan films. The chemical treatment using 11-AA greatly reduces the sheet resistance of AgNWs by two orders of magnitude, resulting in simultaneously enhanced electrical, mechanical properties as well as the chemical stability of AgNW networks. The highly stretchable transparent conductive electrodes based on 11-AA treated-AgNWs/chitosan thin-films achieve a low sheet resistance of 12.2 ohm/sq and a high transmittance of 88.9%. The enhancement of bonding properties between the AgNW and chitosan is attributed to the favorable formation of hydrogen and covalent bonds from 11-AA treatment. Based on the

optimized AgNW/chitosan films, approximately 160 μm -thick stretchable alternating current-driven electroluminescent (ACEL) devices and transparent heaters are realized. The biocompatible chitosan substrates used in stretchable electronic devices are expected to minimize the mismatch in physical properties at the electronic/skin interfaces. We expect that the novel stretchable transparent conductive AgNWs prepared on biocompatible polymer substrates using the surface modification strategy provide an important progress for realizing high performance wearable electronics with an artificial skin.

2. Experimental details

Preparation and characterization of chitosan thin-films: Acetic acid was mixed with deionized water at a concentration of 1–3 vol. %. Deacetylated chitosan (Sigma Aldrich) with high molecular weight was dissolved in the acetic acid solution at a concentration of 1–2 wt.% and was stirred for 1 h. Subsequently, glycerol was added into the solution (0–40 wt.% in chitosan) and stirred for 30 min again. The solution was filtered by a centrifugation at a spin-speed of 5000 rpm for 30 m. The solution was poured into a Petri dish and dried at room temperature. Transmittance of films was examined by a UV–visible spectrophotometer (Perkin Elmer). The thermal stability of chitosan films was measured by thermal gravimetric analysis.

Preparation and characterization of AgNWs: The films were prepared in air ambient with a humidity of around 40%. 11-AA (Sigma Aldrich) was used as a surface modifier for highly hydrophobic chitosan films. For the preparation of 11-AA, 11-aminoundecanoic acid was dissolved in deionized water with a concentration of 0.14 wt.%. The 11-AA solution was spin-coated onto the plasma-treated chitosan substrates at a spin-speed of 500 rpm for 10 s, and subsequently annealed at 100°C for 10 min. AgNW solutions (0.3 wt% in deionized water, Nanopyxis Co., Ltd) were spin-coated onto the 11-AA-treated chitosan substrates with various spin-speeds for 30 s. The AgNW films were annealed at 100°C for 10 min. The sheet resistance of AgNW films was measured by van der Pauw method with a source measurement unit (Keithley 2401). The transmittance of films was recorded by a UV-vis spectrophotometer (Perkin Elmer). Surface images were measured using SEM (Hitachi S-2700). The resistance under tensile strains was examined by a Keithley sourcemeter with a custom-made motion stage.

Fabrication and characterization of stretchable ACEL and stretchable transparent heater devices: The devices were fabricated in air ambient. The three-layered AgNWs were spin-coated onto 11-AA treated-chitosan thin-films

at a spin-speed of 5000 rpm. Polyvinylidene fluoride (PVDF, $M_w = 530,000$ g/mol, Sigma Aldrich) as a dielectric layer was dissolved in *N,N*-dimethylformamide (10 vol.%) and spin-coated onto the AgNW/chitosan films at a spin-speed of 500 rpm for 10 s. ZnS used as an emitting layer was with mixed with ethyl cellulose (ZnS: ethyl cellulose = 60 vol.%: 40 vol.%) and spin-coated on the PVDF layer at a spin-speed of 1000 rpm for 20 s. ZnS is a widely used emitting material for stretchable ACELs. As a top electrode, AgNWs were double-coated onto ZnS emitting layers by spin-coating at a spin-speed of 1500 rpm for 30 s and annealed at 100°C for 10 min. All devices were tested in air ambient. Performances of ACEL devices were characterized by a spectrophotometer (CS-2000, Minolta) with an AC source-measure unit system under air ambient conditions.

For the fabrication of stretchable transparent heater devices, AgNWs were triple-coated onto chitosan films by spin-coating at a spin-speed of 5000 rpm for 30 s. Aluminum tapes were attached on both edges of the AgNW electrodes and wired to the DC power supply. Thermal properties and infrared (IR) images were examined using an IR camera (TiS45, Fluke).

3. Results and discussion

Chemical structures of chitosan and 11-AA are shown in Figure 1. The chitosan with high molecular weight is prepared with acetic acid and glycerol which successfully improve the stretchability of chitosan thin films as plasticizers. The best performing chitosan thin-films in

terms of the stretchability are obtained where chitosan is dissolved in acetic acid solutions at a concentration of 1 wt.% and glycerol (glycerol:chitosan = 0.4:1 weight ratio) is introduced. The synthesized chitosan thin-films show an outstanding thermal stability. The transmittance of chitosan thin-film is 95.1% (at a wavelength of 550 nm), which is much higher than that of glass substrates (91.0%). The chitosan thin-films reveal a very flat surface as residual solids are thoroughly removed by the centrifugation process. The resulting thickness of chitosan thin-film is around 18 μm .

To overcome the poor adhesion properties between AgNWs and highly hydrophobic chitosan substrates caused by the weak van der Waals forces, we introduced 11-AA as a surface modifier. The surface functionalized nanoparticles or nanowires with 11-AA treatment have been made in several reports [13–15]. Schematic of bonding mechanism between AgNWs and the chitosan substrate is shown in Figure 1(c). The chitosan thin-films are pretreated with oxygen plasma to form -OH functional group on the surface of films. As the 11-AA solutions are spin-coated on the plasma-treated chitosan, the functional groups of primary amine ($-\text{NH}_2$) of 11-AA form a hydrogen bond with polyvinylpyrrolidone (PVP) surrounding nanowires. In addition, the carboxyl group (COOH) of 11-AA results in the strong covalent bonds with chitosan substrates. The resulting hydrogen and covalent bonds induced by the primary amine and carboxyl groups of 11-AA, respectively, remarkably enhance the adhesion between the nanowires and the chitosan substrate.

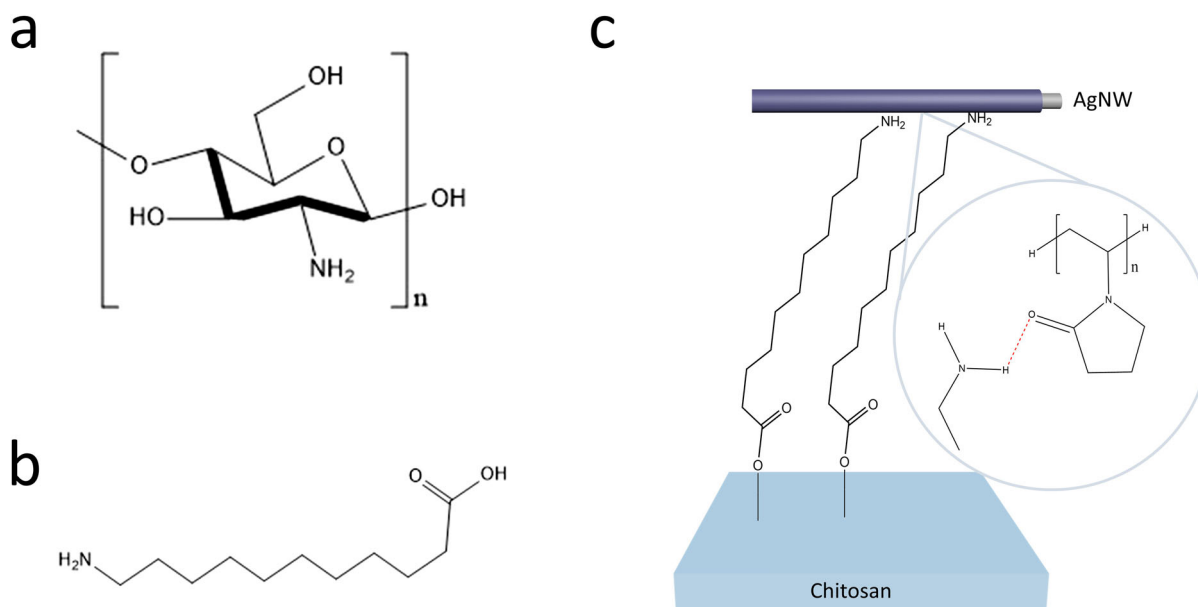


Figure 1. (a) Chemical structures of chitosan and (b) 11-aminoundecanoic acid. (c) Schematic of bonding structures between AgNW networks and chitosan thin-films.

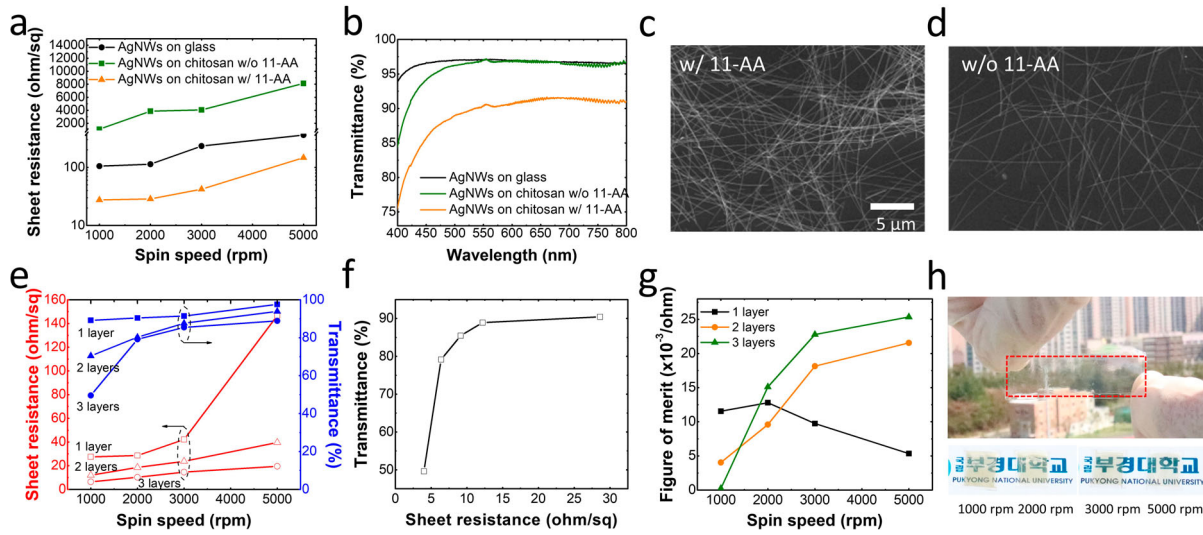


Figure 2. (a) Sheet resistance of AgNWs (single layer). (b) Transmittance of AgNWs (2000 rpm, 1 layer). SEM images of AgNWs (2000 rpm, 1 layer) on the chitosan films (c) with and (d) without 11-AA treatment. (e) Sheet resistance and transmittance of AgNWs on the chitosan films with 11-AA treatment. (f) The behavior of sheet resistance and transmittance of three-layered AgNWs (various spin-speeds) on the chitosan films with 11-AA treatment. (g) Figure of merit values of AgNWs on the chitosan films with 11-AA treatment. (h) A photograph of three-layered AgNWs (5000 rpm) on chitosan thin-films (a red dotted line). Photographs of AgNWs on chitosan thin-films prepared with various spin-speeds (the bottom images).

Figure 2(a) shows the behavior of the sheet resistance of AgNWs prepared on chitosan substrates with and without 11-AA treatment. The AgNWs (2000 rpm, 1 layer) on the untreated chitosan substrates exhibit a very high sheet resistance of 3871.6 ohm/sq due to the poor formation of nanowire networks on highly hydrophobic chitosan films. The 11-AA treatment significantly improves the electrical properties of AgNWs on the chitosan thin-films with a reduction of sheet resistance by two orders of magnitude. The sheet resistance of 11-AA-treated AgNWs (2000 rpm, 1 layer) is 28.6 ohm/sq, which is rather lower than that of the untreated AgNWs deposited on glass substrates (113.1 ohm/sq). The AgNW networks (2000 rpm, 1 layer) prepared on the chitosan films with 11-AA treatment show a ultrahigh transmittance of 97.1% at a wavelength of 550 nm. Whereas, the transmittance values of AgNWs deposited on the untreated chitosan film or on the glass substrate are only 90.4 as shown in Figure 2(b). The enhanced electrical properties of AgNWs with 11-AA treatment are attributed to the excellent surface modification function of 11-AA which effectively improves the adhesion between AgNWs and chitosan films. Figures 2(c,d) show scanning electron microscope (SEM) images of AgNWs on chitosan thin-films with and without 11-AA treatment. It is observed that 11-AA treatment could leads to a reduction of the haziness of nanowires on PDMS substrates. In this regard, the further optimization process with 11-AA will be conducted

for simultaneously improving electrical and optical properties of AgNW/chitosan films in future work.

Figure 2(e) shows the electrical and optical properties of AgNWs on chitosan thin-films prepared with various spin speeds and the number of AgNW layers. The sheet resistance and transmittance decrease with decreasing spin-speeds as expected. A lowest sheet resistance of 4.0 ohm/sq with a transmittance of 49.6% is observed for films prepared at a spin-speed of 1000 rpm. Figure 2(f) displays the behavior of electrical and optical properties for three-layered AgNWs prepared with different spin-speeds. The observed properties well correspond to the coverage of AgNWs. To find the optimum electrical and optical conditions, we calculate figure of merit (*FoM*) of AgNWs (Figure 2(g)):

$$FoM = \frac{T^{10}}{R_s}$$

where T is the transmittance at a wavelength of 550 nm and R_s is the sheet resistance. The highest *FoM* of 0.0254/ohm is observed for AgNW films (5000 rpm, 3 layers) with a sheet resistance of 12.2 ohm/sq and a transmittance of 88.9%.

We investigate the relative changes of the resistance for AgNW/chitosan thin-films under the tensile strain (Figure 3(a)). The AgNW/chitosan films treated with 11-AA (dissolved in acetic acid at a concentration of 0.14 wt.%) exhibit a resistance increase by only 3.1 fold when stretched up to 90%. In contrast, untreated films

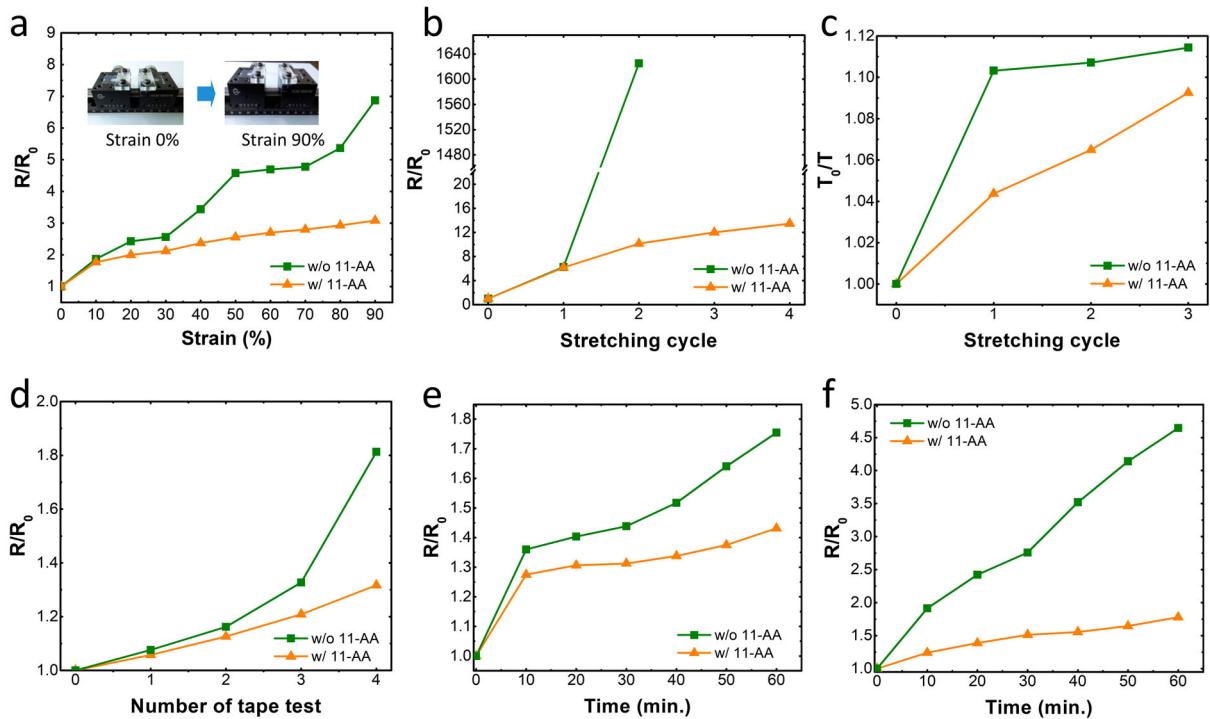


Figure 3. (a) Resistance changes of AgNWs on the chitosan films treated with and without 11-AA (0.14 wt.%) under tensile strains. (b) Resistance and (c) transmittance changes of films as a function of stretching cycles (20% strain). (d) Resistance changes of films as a function of the number of tape test. Resistance changes of films, which are dipped in (e) ethanol and dipped in (f) deionized water.

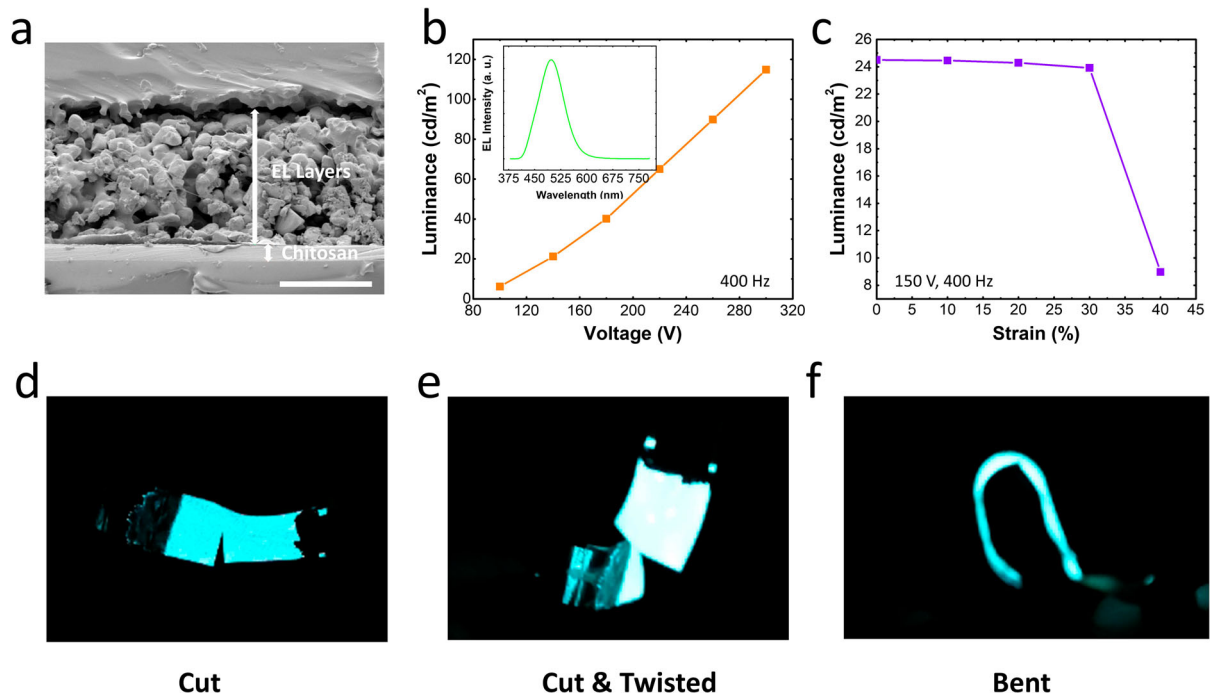


Figure 4. (a) The cross-sectional SEM image of the ACEL device prepared on the chitosan thin-film (scale bar: 100 μm). (b) The luminescence of the ACEL device. The inset shows the electroluminescence intensity. (c) Luminescence of the ACEL device under various tensile strains. Photographs of the illuminating ACEL devices being (d) cut, (e) cut and twisted, (f) and bent.

show a rapidly increase in resistance by 6.9 fold under a strain of 90%. It is observed that the chitosan films are torn off above 90% strain. The introduction of 11-AA also

remarkably reduces resistance and transmittance changes after several stretching cycles of the 20% strain (Figures 3(b) and (c)). Additionally, the tape attach-release

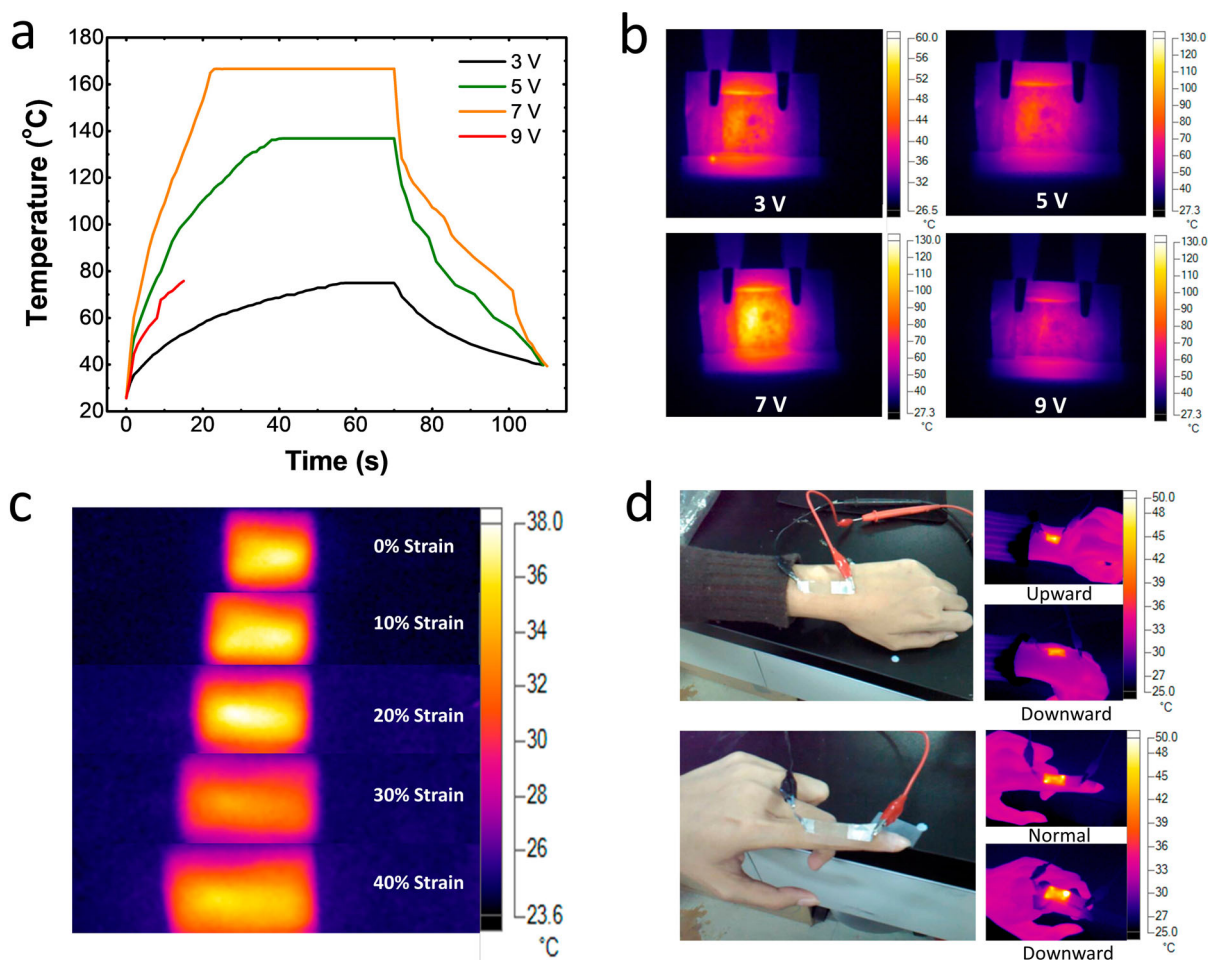


Figure 5. (a) Temperature changes of stretchable transparent heater devices based on AgNW/chitosan thin-films as a function of time and applied voltages. (b) Corresponding IR images of stretchable transparent heater devices. (c) IR images of the stretchable transparent heater devices under various tensile strains. (d) Photographs and IR images of stretchable transparent heater devices worn on the wrist and finger.

test is performed to investigate the adhesion properties of films (Figure 3(d)). The 11-AA treated AgNW/chitosan films reveal highly robust characteristics with a small resistance change. We also investigate the chemical stabilities of AgNW/chitosan thin-films which are dipped in ethanol and deionized water (Figures 3(e,f)). The 11-AA treatment results in the outstanding chemical stability of films due to the enhanced adhesion properties of AgNW/chitosan films. The 11-AA-treated films with the greatly enhanced stretchability and the chemical stability promise as a highly robust stretchable electrode for developing wearable and stretchable devices.

Stretchable ACEL devices based on 11-AA (0.14 wt.%) treated AgNW/chitosan films as the stretchable transparent conductors have been demonstrated. AgNWs with the highest *FoM* values are used in the devices. It is noted that the thickness of ACEL devices based on AgNW/chitosan films is only about 160 μm , including the thickness of substrates, as shown in

Figure 4(a). A maximum luminance of 114.78 cd/m^2 is achieved at a voltage of 300 V with an emission spectrum at 498 nm (Figure 4(b)). Figure 4(c) shows the strain-dependent characteristics of the stretchable ACEL devices. The luminance of ACEL device slightly drops from 24.49 to 23.91 cd/m^2 until the strain reaches 30%, showing very stable emitting performances. The ACEL devices can be cut, stretched, bent, and twisted without performance degradation, illustrating outstanding elastic behaviors (Figure 4(d–f), movie S1 and S2). The outstanding stretchability of our device is promising for practical applications in stretchable electronic devices at human skins, since human skins exhibit a linear elastic behavior until a tensile strain of $\sim 15\%$ [16].

We also develop soft, stretchable transparent heaters (18 μm -thick) based on AgNW/chitosan films treated with 11-AA (0.14 wt.%). Figure 5(a) shows the transient temperature evolution of AgNW/chitosan heaters operated by Joule heating as a function of applied DC voltage

for an operation time of 70 s. The gradients of temperature evolution depend on the power consumption of heaters, except for the device applied with a voltage of 9 V. The highest temperature of 166.5°C is exhibited at a voltage of 7 V. The AgNW networks are broken at a voltage of 9 V. The corresponding temperature distributions are shown in Figure 5(b). Figure 5(c) shows infrared (IR) images of AgNWs/chitosan heaters under various tensile strains at a constant voltage. The AgNW/chitosan heaters stretched up to 40% exhibit the outstanding stretchability with uniform temperature distributions. Heater applications on the wrist and the finger are demonstrated in Figure 5(d). The homogeneous temperature distributions on various bending conditions are observed. The AgNW/chitosan heaters are easily attached on human skins, showing the excellent conformal performance with various form factor. The stretchable AgNW/chitosan transparent conductors could be valuable for the use in biocompatible wearable electronics on human body.

4. Conclusion

In summary, we demonstrate highly robust and stretchable transparent conductive electrodes based on the AgNWs/chitosan biopolymer. The organic surface modifier 11-AA induces a strong chemical bond between nanowires and chitosan films, which greatly improves adhesion properties. The surface functionalized AgNW/chitosan thin-films show a low sheet resistance of 12.2 ohm/sq with a high transmittance of 88.9%. The introduction of 11-AA achieves the reduction of sheet resistance by two orders of magnitude with the simultaneously enhanced electrical, mechanical properties as well as the chemical stability of stretchable AgNW/chitosan films. In addition, stretchable ACEL and heater devices are successfully constructed with the chemically modified-AgNW/chitosan films. The devices can be cut, stretched, bent, and twisted without performance degradation, showing outstanding elastic behaviors. The outstanding stretchability and biocompatibility of AgNW/chitosan films enable to form robust contact with the skin, thus, skin-mounted displays and heater devices can be readily realized. We believe that the mechanically robust, stretchable AgNW/chitosan transparent conductors can be a key step towards future biocompatible wearable electronics on the human body.

Disclosure statement

No potential conflict of interest was reported by the authors.

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