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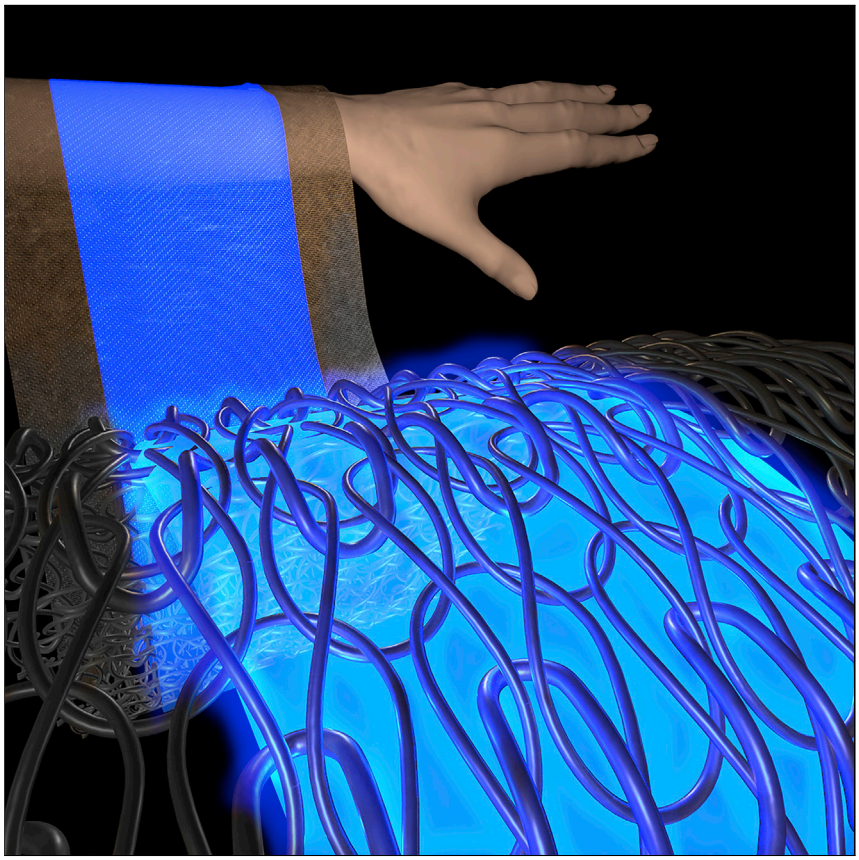

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HIGHLIGHTS

Ultrasheer knitted fabric forms the framework for transparent conductive electrodes

Solution-based electroless plating deposits a conformal gold coating on the fabric

Gold-coated ultrasheer fabrics produce highly stretchable light-emitting e-textiles

Soft-contact lamination produces e-textiles with changeable display patterns

Light-emitting textiles are an exciting emerging technology with a key challenge of achieving the seamless integration of light-emitting devices with textiles in a soft, stretchable, and wearable format. Here, we describe a new design approach to meet this challenge that uses the structural features of a knitted ultrasheer textile as a framework for a new textile-based transparent conductive electrode. Deposition of a conformal gold coating over the textile fiber surfaces using solution-based electroless deposition retains the intrinsic semitransparency and stretchability of the textile. Integration of this new electrode provides light-emitting e-textiles with unprecedented stretching performance.

Improvement
Enhanced performance with innovative design or material control

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Stretchable Ultrasheer Fabrics as Semitransparent Electrodes for Wearable Light-Emitting e-Textiles with Changeable Display Patterns

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SUMMARY

Despite the development throughout human history of a wealth of textile materials and structures, the porous structures and non-planar surfaces of textiles are often viewed as problematic for the fabrication of wearable e-textiles and smart clothing. Here, we demonstrate a new textile-centric design paradigm in which we use the textile structure as an integral part of wearable device design. We coat the open framework structure of an ultrasheer knitted textile with a conformal gold film using solution-based metallization to form gold-coated ultrasheer electrodes that are highly conductive (3.6 $\pm$ 0.9 Ω/sq) and retain conductivity to 200% strain with $R/R_0 < 2$. The ultrasheer electrodes produce wearable, highly stretchable light-emitting e-textiles that function to 200% strain. Stencil printing a wax resist provides patterned electrodes for patterned light emission; furthermore, incorporating soft-contact lamination produces light-emitting textiles that exhibit, for the first time, readily changeable patterns of illumination.

INTRODUCTION

Textiles have been a part of daily life since the beginning of human civilization itself, with centuries of development producing a seemingly endless variety of fabrics made from natural and synthetic materials that are knitted, woven, or braided to form a profusion of textile structures that vary in strength, porosity, durability, and stiffness.[1] The future of textiles is electronic, and will bring new wearable devices integrated into "smart clothing" systems, with sensors[2–5] to detect biometric data; supercapacitors,[6–9] batteries,[10] nanogenerators,[11] or solar cells[12–14] as power sources; and light-emitting devices to display data output.[15] Among these e-textile components, light-emitting e-textiles are an especially compelling emerging technology that will also inspire innovations in fashion design, interior design, visual merchandizing, and personal safety. At present, light-emitting textiles are mainly realized by sewing discrete, rigid elements such as light-emitting diodes (LEDs) or optical fibers into clothing, which reduces softness, stretchability, and wearability. Smart illuminated clothing that meets the demand for comfort and wearability will require light-emitting devices that are seamlessly integrated with the textile structure. Textiles, however, are difficult substrates for device fabrication. Conventional thin-film device fabrication methods are designed for planar substrates, whereas textiles present complex, three-dimensional (3D) structures with non-planar surfaces. This challenge has caused textiles to often be viewed as problematic for device integration. One approach has been to avoid fabrication on the rough textile surface by instead fabricating electroluminescent fibers that are then woven through existing

Progress and Potential

Light-emitting textiles will transform the very concept of fabric, leading to innovations in fashion, visual merchandizing, and personal safety. Wearability of these new fabrics is key, requiring the seamless integration of light-emitting devices with textiles while maintaining softness and stretchability. Sewing rigid elements such as light-emitting diodes into textiles diminishes softness, whereas fabricating thin-film light-emitting devices onto textiles presents challenges due to the porosity of textile structures. This article reports a new fabrication strategy that instead uses the structural features of an ultrasheer textile as an integral part of wearable device design. Coating the fabric fibers with gold produces a conductive, semitransparent e-textile used to generate highly stretchable light-emitting fabrics. With the countless varieties of textile structures available, this textile-centric design approach will inspire innovative e-textiles for a range of new applications.

textiles.[16,17] However, with the enormous variety of textile materials and physical structures that are available, reducing the textile element in wearable electronics to an inconvenient substrate is a missed opportunity to truly advance wearable electronics. Here, we present a new, textile-centric design paradigm for wearable electronics that uses a complex textile structure as a fundamental part of wearable device design. We seamlessly integrate new semitransparent and conductive e-textile electrodes with stretchable emissive materials for highly stretchable light-emitting e-textiles.

Previous research on developing light-emitting textiles has most often used flexible woven textiles as substrates, which consist of sets of yarns interlaced at right angles to each other. This fabric structure imparts flexibility, but stretchability is restricted due to the linearity of the yarns and occurs only to a small extent along the diagonal to the square weave pattern. Alternating current electroluminescent (ACEL) devices,[18–20] organic LEDs,[21–23] and light-emitting electrochemical cells[24,25] fabricated on flexible woven fabrics have all been reported. In contrast, knitted textiles present more complex 3D structures with yarns structured into interconnected loops separated by networks of voids, providing space for the yarns to unbend and move in response to stress for high omnidirectional stretchability. Despite numerous reports of conductive knitted textiles that retain conductivity to high elongations,[26] few examples of stretchable light-emitting devices based on knitted textiles have been reported. A central problem with the devices reported to date lies with the limited stretchability and wearability of the transparent electrode, a key component of all light-emitting devices. For example, ACEL light-emitting e-textiles fabricated using a gold-coated knitted textile as the bottom electrode and a thin film of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as the top transparent electrode retain functionality to only 40% strain due to cracking of the PEDOT:PSS electrode, despite the ability of the gold-coated textile electrode to remain conductive to 160% elongation.[27] Using a more stretchable transparent conductor to avoid this cracking problem can produce devices with greater stretchability; however, the essential requirement that new materials be durable enough for wearability can be a challenge. For example, ACEL light-emitting e-textiles fabricated on a conductive knitted bottom electrode that use a film of a stretchable ionic conductor as the transparent electrode produces devices that function to 100% strain,[28] but evaporation of the solvent/liquid component of the ionic conductor limits the durability and wearability of these devices.

Instead of seeking new transparent conductive films that are stretchable as well as wearable, we present a new textile-centric approach for the fabrication of e-textile light-emitting devices whereby we strategically use the open structure of an ultrasheer knitted textile as a framework for the fabrication of stretchable and semitransparent textile-based electrodes using solution-based metallization. Adhering these new textile-based semitransparent electrodes to a stretchable emissive material produces lightweight, wearable, light-emitting e-textiles that function to the strain limit of the textile (200%). Patterning the electrode and incorporating soft-contact lamination in the device fabrication produces light-emitting textiles that exhibit, for the first time, readily changeable patterns of illumination.

RESULTS AND DISCUSSION

In the textile industry, the denier is a unit of measurement used to express the thickness of individual fibers in a textile; low-denier fabrics are sheer and semitransparent

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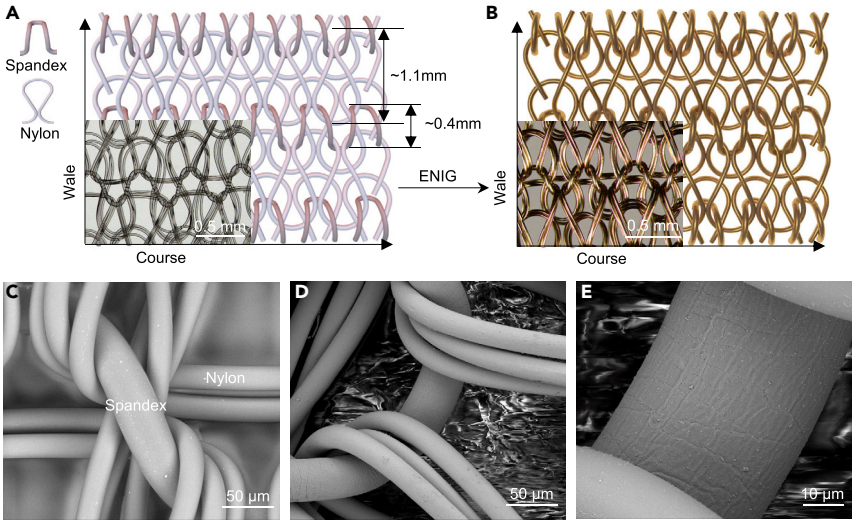

Figure 1. The Ultrasheer Knitted Fabric Coated with Gold

(A and B) Schematic and stereomicroscope images (inset) of the (A) uncoated ultrasheer fabric and (B) gold-coated ultrasheer fabric. Double arrows show the course height of nylon and spandex fibers.

(C–E) SEM images of (C) uncoated ultrasheer fabric, (D) gold-coated ultrasheer fabric. (E) Close-up image of gold-coated spandex fiber.

See also Figures S1–S5.

due to spaces between the fibers. We used a 10-denier ultrasheer knitted fabric to form stretchable and conductive e-textiles with optical transparency. The ultrasheer knitted fabric consists of 87% nylon and 13% spandex fibers knitted together to form interlinked course and wale loops, with nylon fibers of ~20 μm in diameter forming the knitted structure and spandex fibers of ~45 μm in diameter running along the course direction (Figures 1A and 1C). The open spaces between the fibers constituting the knitted structure permit the transmission of light through the textile (Figure S1A). The transmittance (*T*) of the ultrasheer fabric measured using UV-visible spectroscopy is 47% at 550 nm (Figure S1B). The absorption of the 200- to 230-nm wavelength is due to the peptide bond of the nylon and spandex fibers. The nylon fibers contribute to the strength of the ultrasheer fabric but are not intrinsically stretchable; instead, the knitted structure enables the nylon fibers to move and slip in response to stress, as well as unbending in the course direction. The intrinsically stretchable spandex fibers both unbend and elongate with stretching, providing resilience that returns the fabric to its original shape after stretching. The elastic limit of the fabric occurs at ~200% strain in both the course and wale directions (Figure S2).

We used electroless nickel-immersion gold (ENIG) metallization, a solution-based metal deposition technique commonly employed in printed circuit board fabrication, to produce an ultrasheer e-textile with high conductivity (Figure 1B). Electroless metallization is a promising technique for the preparation of conductive textiles because the aqueous plating solutions permeate the textile structure to conformally deposit metal on individual fibers, leaving the void structure intact and maintaining the softness and stretchability of the original textile.[27] We chose gold as the metal because it is biocompatible and chemically inert.[29] The ENIG process consists of two solution-based plating steps: electroless deposition (ELD) of nickel followed by an immersion gold process. The ELD nickel process involves first activating the textile by adsorbing a catalytic species onto its surface. We used a palladium-tin colloidal catalyst, which consists of a palladium-rich core protected from oxidation

by a hydrolyzed Sn^{2+}/Sn^{4+} shell, and an associated chloride layer that gives the colloids a negatively charged surface to enable electrostatic binding to positively charged surfaces. We prepared the ultrasheer fabric surface for electrostatic binding of the Pd/Sn colloids by briefly oxidizing the surface using air plasma and then chemisorbing 3-aminopropyltriethoxysilane (APTES) from solution. Immersing the resulting amine-functionalized textile in the acidic Pd/Sn colloidal solution protonates the amino groups of the bound APTES; the resulting positively charged ammonium groups electrostatically bind the Pd/Sn colloids. Subsequent etching in aqueous NaOH removes the Sn shell to expose the Pd core, which initiates ELD by catalyzing the reduction of Ni^{2+} ions in the ELD plating solution to nickel metal on the surface of the textile. Nickel deposition is autocatalytic thereafter, consuming the dimethylamine borane reducing agent in the nickel ELD solution. In the second ENIG plating step, immersing the nickel-coated textile in a solution of potassium gold cyanide deposits a gold film by galvanic displacement. Ni atoms in the film reduce Au^{+} ions from solution, releasing Ni^{2+} ions into the solution and depositing a gold metal film on the surface through molecular exchange.

Scanning electron microscopy (SEM) images show that the ENIG process produces uniform gold coatings on both nylon and spandex fibers, with a coating thickness of ~100 nm (Figures 1D, 1E, and S3). Small wrinkles and cracks on the surface of gold-coated spandex fibers, but not on the surface of gold-coated nylon fibers, likely originate from thermal expansion of spandex fibers due to the temperature (60°C) of the immersion gold process (Figure 1E). Energy-dispersive X-ray spectroscopy of the gold-coated ultrasheer fabric detected gold, but not nickel in the coating (Figure S4A). Analysis using X-ray diffraction shows diffraction peaks attributed to polycrystalline fcc gold (JCPDS No. 4-0784) (Figure S4B), with a primary (111) orientation at 38.2° accompanied by peaks at 44.4°, 64.6°, 77.5°, and 81.7°, corresponding to (200), (220), (311), and (222) orientations, respectively. This texture is typical of gold films fabricated by electroless deposition.[27,30] Mechanical adhesion testing using the tape test indicates robust adhesion between the gold coating and ultrasheer fabric, showing no visible gold on the tape surface after testing (Figure S5).

The thin, conformal gold coating on the fibers of the ultrasheer fabric provides electrical conductivity while preserving the softness and stretchability of the original uncoated fabric as well as open spaces in the fabric for optical transmittance. The gold-coated ultrasheer fabric exhibited an average sheet resistance of $3.6 \pm 0.9\ \Omega$/sq, which is slightly higher than the sheet resistance ($0.9 \pm 0.1\ \Omega$/sq) of a continuous, flat gold film of a similar thickness (100 nm) deposited by physical vapor deposition onto a glass substrate. The slightly higher sheet resistance of the gold-coated ultrasheer fabric can be attributed to contact resistances from interfiber contacts within the knitted fabric structure. The transmittance of the gold-coated ultrasheer fabric (37% at 550 nm) is 10% lower than that of the native ultrasheer fabric (Figure S1B). The lack of adsorption at 200–230 nm is due to the full coverage of the reflective gold coating on the fabric fibers (Figure S1B). Tensile testing of ultrasheer fabric before and after gold deposition shows that the ENIG process does not appreciably change the mechanical properties of the ultrasheer fabric, with a slight decrease in tensile strength and a slight increase in breaking load (Figure S2).

Stretching the gold-coated ultrasheer fabric changes the transmittance in ways that depend on the direction of stretching due to the anisotropic structure of the fabric. We measured the transmittance of the gold-coated ultrasheer fabric with stretching to the elastic limit in the wale direction and course direction. In the wale direction, the transmittance increases steadily with strain to a maximum value of 58% at 120% strain,

followed by a decrease to 47% at 200% strain (Figure 2A). In this direction, stretching initially causes the yarns to slip and move past each other, increasing the open space in the fabric as the wale and course loops eventually become interlocked due to the tension force in the loops. This process increases the transmittance as shown in the optical microscopy images of gold-coated ultrasheer fabric at 0% strain (Figure 2B) and 120% strain (Figure 2C). Further stretching causes yarns to move toward each other transverse to the stretching direction, due to the Poisson effect. This effect decreases the transmittance by decreasing the open area of the ultrasheer fabric, shown in optical microscopy images at 200% strain (Figure 2D). Stretching the gold-coated ultrasheer fabric in the course direction increases the transmittance initially to a maximum value of 60% at 160% strain, followed by a decrease to 58% at 200% strain (Figure 2E). In this direction, stretching initially unbends the nylon and spandex fibers, widening the course loops to open up the space in the fabric and increase the transmittance. Optical microscopy images at 0% (Figure 2F) and 160% (Figure 2G) strain show this process. As the strain increases, however, the loops straighten and interlock, and the Poisson effect causes them to move toward each other transverse to the stretching direction, which decreases the transmittance (Figure 2H).

To quantitatively validate the correlation between the observed structural changes in the fabric with the measured transmittance change under strain, we used a cover factor (CF) model to calculate a theoretical transmittance value based on optical microscopy images of the gold-coated ultrasheer fabric under strain. Calculated light transmittance values using the CF model are based on the assumption that the fibers completely block or absorb light transmission while the spaces between fibers allow complete light transmission:

$$\mathrm{CF} = \text{Area covered by fibers/total area of the fabric,} \qquad \text{(Equation 1)}$$

$$T = 1 - \mathrm{CF}. \qquad \text{(Equation 2)}$$

We calculated the CF and theoretical transmittance values using optical images of the gold-coated ultrasheer fabric at different strains in both directions (Supplemental Experimental Procedures; Figures S6 and S7). There is excellent agreement between the calculated transmittance values and those measured using UV-visible spectroscopy at 550 nm in both stretching directions (Figures 2A and 2E), supporting the idea that the observed opening of the loops with stretching, followed by compression due to the Poisson effect, are the source of the measured transmittance changes.

The resistance of the gold-coated ultrasheer fabric also changes with stretching, due to not only the anisotropic fabric structure but also the combination of gold-coated nylon and spandex fibers in the textile. Conductive knitted textiles made from fibers that are not intrinsically stretchable, such as polyester, typically exhibit an initial decrease, followed by stabilization, of the resistance with stretching. The knitted structure of these textiles causes the yarns to unbend with stretching and also increases the contact pressure between the yarn loops, reducing the contact resistance between adjacent conductive yarns and the overall resistance of the conductive e-textile.[27,31] In contrast, the resistance of the gold-coated ultrasheer fabric slightly increases with stretching in both the wale and course directions overall (Figure 3A), which we attribute to a combination of the resistance changes caused by stretching the gold-coated nylon yarns and the intrinsically stretchable gold-coated spandex fibers in the knitted fabric structure. Stretching the gold-coated ultrasheer fabric unbends the nylon yarns as shown in Figure 2 and thus increases the contact pressure between the loops, contributing to reducing the overall resistance of the e-textile. At the same time, however, the intrinsically stretchable spandex fibers in

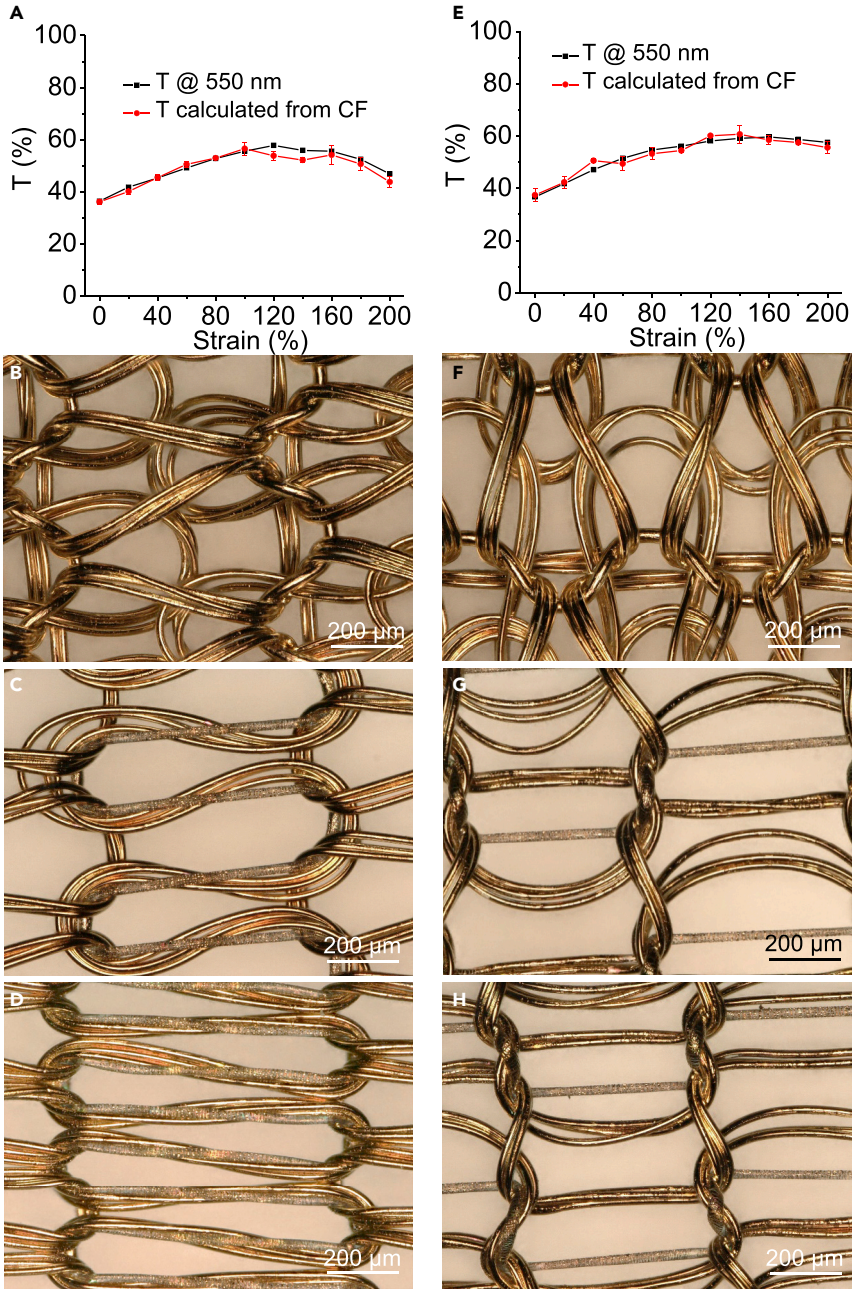

Figure 2. Transmittance of the Gold-Coated Ultrasheer Fabric with Strain

(A) Transmittance measured at 550 nm and transmittance calculated using the cover factor (CF) as a function of stretching strain in the wale direction. Error bars correspond to 1 standard deviation (SD) around the mean.

(B–D) Optical microscopy images of gold-coated ultrasheer fabric stretched in the wale direction at (B) 0%, (C) 120%, and (D) 200% strain.

(E) Transmittance measured at 550 nm and transmittance calculated using the cover factor (CF) as a function of stretching strain in the course direction. Error bars correspond to 1 SD around the mean.

(F–H) Optical microscopy images of gold-coated ultrasheer fabric stretched in the course direction at (F) 0%, (G) 160%, and (H) 200% strain.

See also Figures S6 and S7.

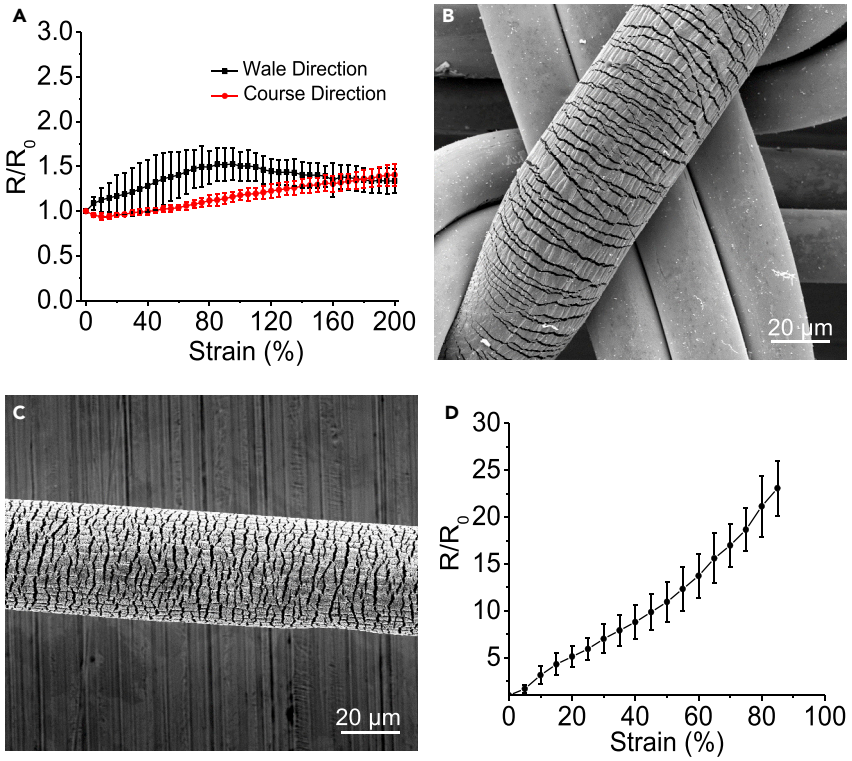

Figure 3. Resistance of the Gold-Coated Ultrasheer Fabric with Strain

(A) Normalized change in resistance as a function of stretching strain along the wale and course directions. Error bars correspond to 1 SD around the mean.

(B) SEM image of the gold-coated ultrasheer fabric stretched to 40% strain.

(C) SEM image of a gold-coated spandex fiber removed from ultrasheer fabric and stretched to 40% strain.

(D) Plot of normalized resistance of gold-coated spandex fibers as a function of stretching strain. Error bars correspond to 1 SD around the mean.

See also Figure S8.

the fabric structure elongate, causing cracks to form in the gold coating on these fibers due to the mechanical mismatch between the metal coating and spandex core (Figure 3B). These cracks increase the resistance of the gold coating on the spandex fibers and contribute to increasing the overall resistance of the e-textile. To confirm this effect, we pulled individual spandex fibers from the ultrasheer fabric and used the ENIG process to coat them with gold. Stretching gold-coated spandex fibers causes cracks to form in the gold coating (Figure 3C) that increase the resistance to 23.1-times the initial value at 85% strain; elongating the fiber further resulted in a loss of conductivity (Figure 3D). The total resistance of the gold-coated ultrasheer fabric with stretching is therefore determined by a combination of the resistance increase from the spandex fibers knitted into the fabric structure and the resistance decrease due to higher contact pressure between the gold-coated nylon fibers. In the wale direction, the resistance increases to 1.53-times the initial value from 0% to 95% strain. Here, the spandex fiber loops elongate perpendicular to the serpentine direction, causing cracks to form in the gold coating. The concomitant increase in resistance dominates the overall resistance of the e-textile. The resistance then gradually decreases to 1.34-times the initial value with further stretching from 95% to 200% strain, consistent with a higher contact pressure between the nylon fibers at these high strains. In the course direction, the resistance initially decreases slightly

with stretching from 0% to 15% strain and then gradually increases to 1.40-times the initial value from 15% to 200% strain. This behavior can be attributed to stretching along the serpentine direction of the spandex fibers, which run in the course direction. At low strains, these serpentines merely unbend, converting the stretching strain to bending strain by virtue of the serpentine structure and thus preserving conductivity. At higher strains, however, the serpentines flatten and elongate, forming cracks that increase the overall resistance of the e-textile.

Despite the intricacies of stretching the gold-coated textile due to the anisotropic structure and presence of spandex fibers, the conductivity of the fabric is, overall, remarkably stable to 200% strain in both directions with the change in the normalized resistance remaining within $\pm$2-times the initial value (Figure 3A). The conductivity also remains stable (within $\pm$2-times the initial resistance value) through 1,000 cycles of 50% strain; after the cycles of strain are complete, the resistance recovers to the initial value in both directions (Figure S8). The stable conductivity under strain makes gold-coated ultrasheer textiles suitable as wearable wiring and device interconnects; furthermore, the transparency of the e-textile makes this material suitable as a semitransparent electrode in stretchable and wearable light-emitting devices.

There are several important considerations for the fabrication of stretchable and wearable light-emitting devices using e-textiles, which must undergo repeated mechanical deformations and tolerate variable environmental conditions. The stretchability of individual functional layers, the adhesion between the electrodes and emissive layer, and the chemical stability of the emissive layer all contribute to the overall performance. We fabricated textile-based, highly stretchable ACEL devices using the gold-coated ultrasheer fabric as both top and bottom transparent electrodes with an elastomeric emissive layer sandwiched in between (Figure 4A). The choice of ACEL device for stretchable light-emitting e-textiles is motivated by previous reports of elastomer-based ACEL devices, which established that the simplicity of the device architecture, utility of elastomeric emissive composites, and insensitivity of these devices to the work function of the electrodes and uniformity of emissive layer are all significant advantages for stretchable devices.[32–34] Although a high operating voltage of >100 V is usually required for ACEL devices to reach practical brightness, the current through the devices is very low. Recent efforts have reduced the operating voltage of these devices by developing new high-permittivity, stretchable dielectric materials, opening the way to practical and safe wearable operation.[35] To fabricate the light-emitting e-textile, we prepared a ~200-μm-thick, uniform film of ZnS:Cu/Ecoflex composite by spin-coating the material onto a temporary carrier substrate. After curing the composite, we spin-coated a thin (~50 μm) layer of ZnS:Cu/Ecoflex composite on the top surface as an adhesive layer, applied the gold-coated ultrasheer fabric electrode, cured the adhesive layer, and repeated this process on the other side of the emissive layer to complete the device. The total thickness of the device is ~300 μm. This fabrication process partially embeds the gold-coated ultrasheer fabric into the elastomeric emissive layer (Figures 4B and 4C), ensuring good adhesion between the layers of the device, which is important for high stretchability and durability of the device. Device operation at 500 V AC and a frequency of 2 kHz produced uniform blue emission through both sides of the device (Figure 4D) that persisted to the 200% strain limit of the gold-coated ultrasheer fabric (Figure 4E), making this device the most stretchable light-emitting e-textile fabricated using a textile substrate reported to date and comparable with the stretching performance of light-emitting e-textiles fabricated by weaving stretchable electroluminescent fibers through textile substrates.[17] For practical wearable operation, we encapsulated both sides of the device with a thin (~300 μm) protective layer of Ecoflex to prevent possible current leakage when devices are adhered to human skin. After encapsulation,

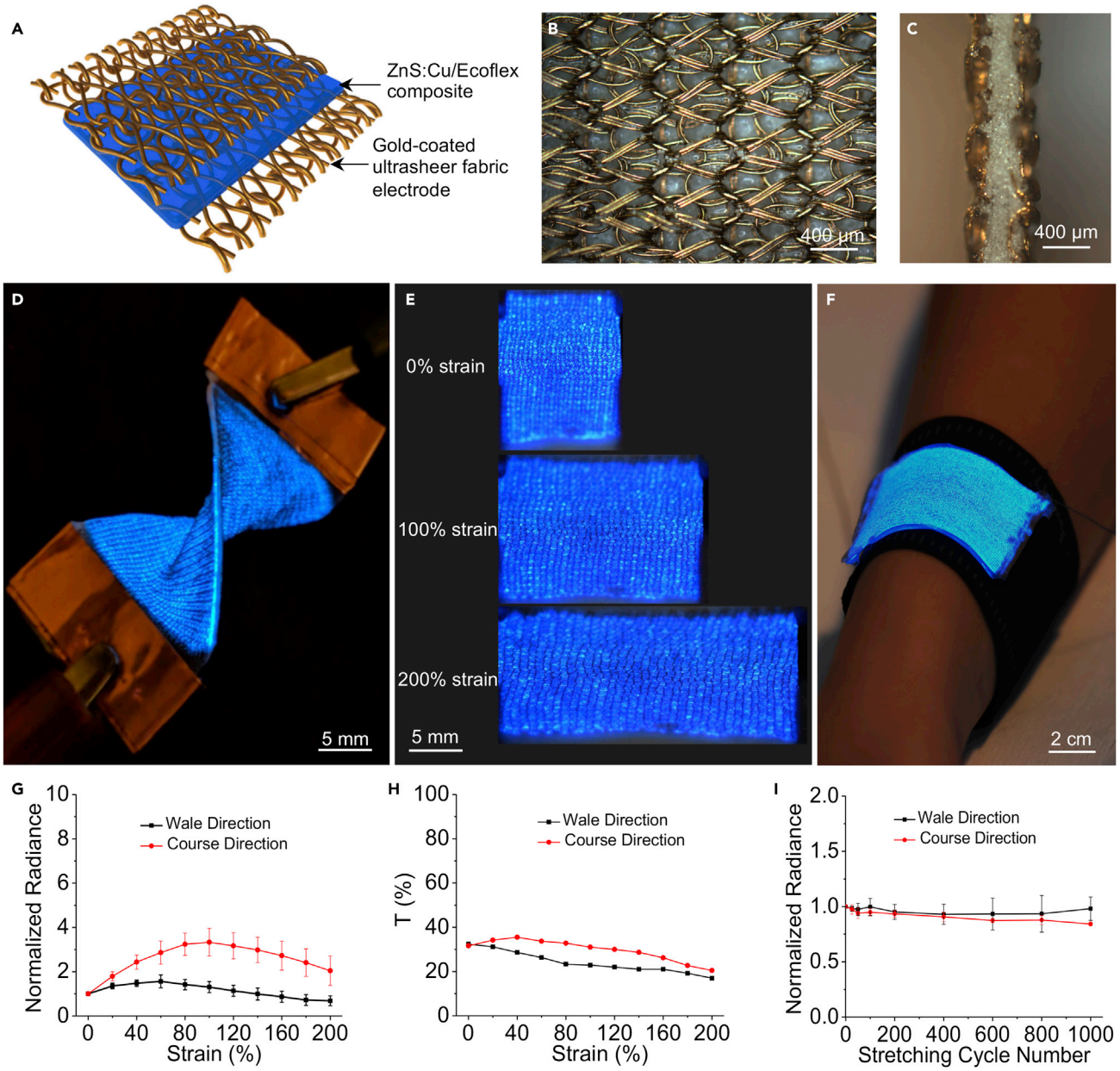

Figure 4. Light-Emitting e-Textiles Fabricated Using Gold-Coated Ultrasheer Fabric Electrodes

(A) Diagram of the device structure.

(B and C) Optical microscopy images of (B) top-view and (C) cross-section of the device.

(D–F) Photographs of light-emitting e-textiles (D) at twisted state; (E) at 0%, 100%, and 200% strain; (F) with large area (3 cm × 5 cm) conformal to human arm.

(G) Normalized change in radiance as a function of stretching strain in wale and course directions. Error bars correspond to 1 SD around the mean.

(H) Transmittance measured at 550 nm of encapsulated gold-coated ultrasheer fabric as a function of stretching in the wale and course directions. Error bars correspond to 1 SD around the mean.

(I) Normalized change in radiance as a function of cycles of 0%–50% strain in wale and course directions. Error bars correspond to 1 SD around the mean.

See also Figure S9 and Video S1.

the light-emitting e-textile remains soft (Figure S9A) and lightweight with a total thickness of 900 μm, a density of ~0.01 g/cm^3, and a mass per unit area of ~0.1 g/cm^2. A large-area device (3 cm × 5 cm) easily conforms to the human body (Figure 4F). The

hydrophobicity of the Ecoflex encapsulation layer and chemical stability of inorganic ZnS particles enable the light-emitting e-textiles to function during immersion in water (Figure S9B and Video S1) as well as after ten cycles of stirring in an aqueous solution of laundry detergent, rinsing with water, and drying in an oven at 60°C (Figure S9C). While these experiments show proof of concept of the stability of the light-emitting e-textiles to these aqueous conditions, future work will conduct more extensive washability testing using standard washing conditions such as the ISO 105-C06 standard established in textile research to show the practical washability of these wearable light-emitting e-textiles.

The emission brightness of the light-emitting e-textile varies with strain, initially increasing in brightness followed by a decrease with additional strain. We quantified the emission performance by measuring the device radiance with stretching in both the wale and course directions and plotting normalized values as a function of strain (Figure 4G). There are mainly two factors that both contribute to these brightness changes: first, stretching reduces the thickness of the emissive layer, increasing the electric field and contributing to higher brightness; second, the light transmittance of the gold-coated ultrasheer electrodes varies depending on the strain as well as the direction of stretching, thus regulating the emission brightness. Since the gold-coated ultrasheer fabric electrodes are partially embedded into the elastomeric emissive layer of the devices, we created a model electrode by embedding the gold-coated ultrasheer fabric in Ecoflex. The model Ecoflex-embedded electrode exhibits slightly different transmittance values with stretching in the wale and course directions (Figure 4H) than those of the unembedded gold-coated fabric (Figures 2A and 2E), which we attribute to Ecoflex restricting the free slippage of the fabric loops with stretching. The changes in resistance of the gold-coated ultrasheer electrodes with strain, on the other hand, do not play a major role in changing the emission brightness, since ACEL devices are voltage driven and the resistance changes of the gold-coated electrodes with strain are relatively small compared with the resistance of the emissive layer.[36]

In the wale direction, the emission brightness increases as the strain increases from 0% to 60%, ultimately reaching a maximum value of 156%. Since the transmittance of the Ecoflex-embedded e-textile electrode decreases throughout this range, this performance is consistent with the increase in electric field dominating the emission response. At strains >60%, the decrease in transmittance outweighs increases in the electric field, resulting in a decrease in emission brightness that reaches 68% at 200% strain. In the course direction, the transmittance of the Ecoflex-embedded e-textile electrodes initially increases and remains higher than the initial transmittance to 100% strain. This increased transmittance, coupled with the higher electric field in the emissive layer, leads to a rapid increase in emission brightness that reaches a maximum of value of 333% at 100% strain. At strains >100% the transmittance of the e-textile electrodes decreases below its initial value, dominating the emission response and decreasing the emission brightness to 204% at 200% strain. Along with conformability and stretchability, the light-emitting e-textiles are also highly durable, making them well suited to applications in wearable electronics. The e-textiles exhibited consistent light emission through 1,000 stretch-release cycles of 50% strain (Figure 4I).

Patterned light emission is important for wearable light-emitting e-textiles to enable information displays and graphics. We used a low-cost stencil-printing method to fabricate patterned e-textile electrodes for patterned light-emitting displays. The patterning process in Figure 5A is based on stencil printing of cold-wax medium, a soft, viscous, beeswax-based paste. Applying the cold-wax medium though a stencil mask onto plasma-oxidized ultrasheer fabric produces a patterned hydrophobic

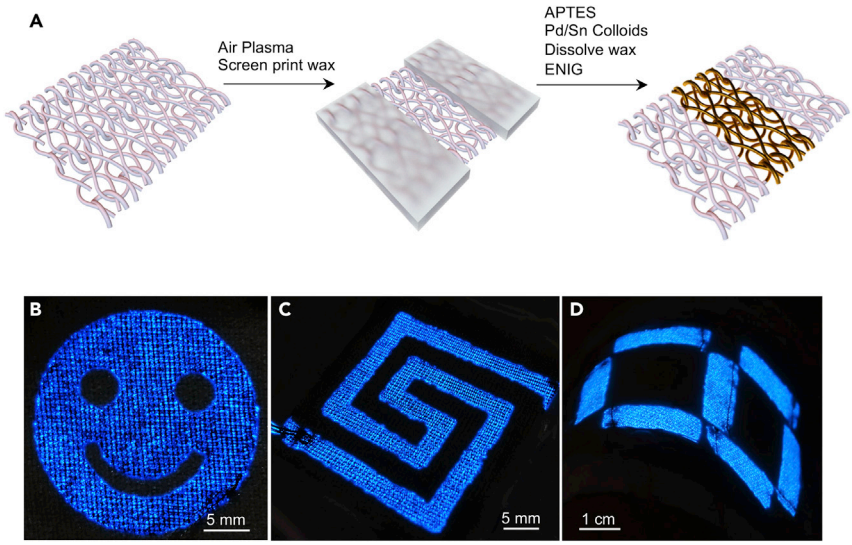

Figure 5. Patterned Light-Emitting e-Textiles

(A) Schematic of the patterning process.

(B–D) Photographs of light-emitting textiles displaying (B) the "smiling face" emoji, (C) a rectangular spiral, and (D) the number 8.

See also Figure S10.

barrier due to penetration of the cold-wax medium into the fabric structure. Immersion of the patterned ultrasheer fabric in an aqueous Pd/Sn colloidal dispersion then results in selective uptake of colloids in the regions without wax resist; regions coated in wax resist do not adsorb Pd/Sn colloids and thus remain inactive to ENIG. Dissolving the wax resist using hexane leaves a pattern of Pd/Sn catalyst on the fabric; subsequent ENIG processing deposits metal only in these catalyzed regions. We fabricated patterned light-emitting e-textiles by replacing one of the unpatterned gold-coated ultrasheer textile electrodes in the device with a patterned gold-coated ultrasheer textile electrode. In this way, we fabricated light-emitting textiles displaying the "smiling face" emoji (Figure 5B) and a rectangular spiral (Figure 5C). We also used the patterning technique to fabricate a dynamic seven-segment textile display by patterning seven rectangular segments on the ultrasheer fabric (Figure S10A) and then selectively operating the segments in different combinations to display the numbers from 0 to 9 (Figures 5D and S10B).

Soft and wearable electroluminescent clothing has applications in safety apparel, marketing, and fashion. In these domains, the ability to change the illuminated image to suit different situations is more advantageous than requiring the user to change the article of clothing to display a new image. We modified the light-emitting e-textile fabrication process to create multipurpose light-emitting e-textiles by incorporating soft-contact lamination between two e-textile electrodes coated with the emissive material (Figure 6A). The fabrication process uses two e-textile electrodes: The base electrode, which is integrated into the article of clothing itself, is an unpatterned rectangular ENIG coating. The changeable electrode, which is the top electrode for the light-emitting device, is printed with a desired ENIG pattern. We adhered a thin (~150 μm) layer of the Ecoflex/ZnS:Cu emissive composite to each surface using the process described previously. Simply laminating the emissive surface of the changeable electrode onto the emissive surface of the base electrode adheres the two Ecoflex/ZnS:Cu surfaces together by van der Waals forces, completing the device. Figure 6B shows a demonstration of this approach, using a base electrode integrated into the leg of a pair of

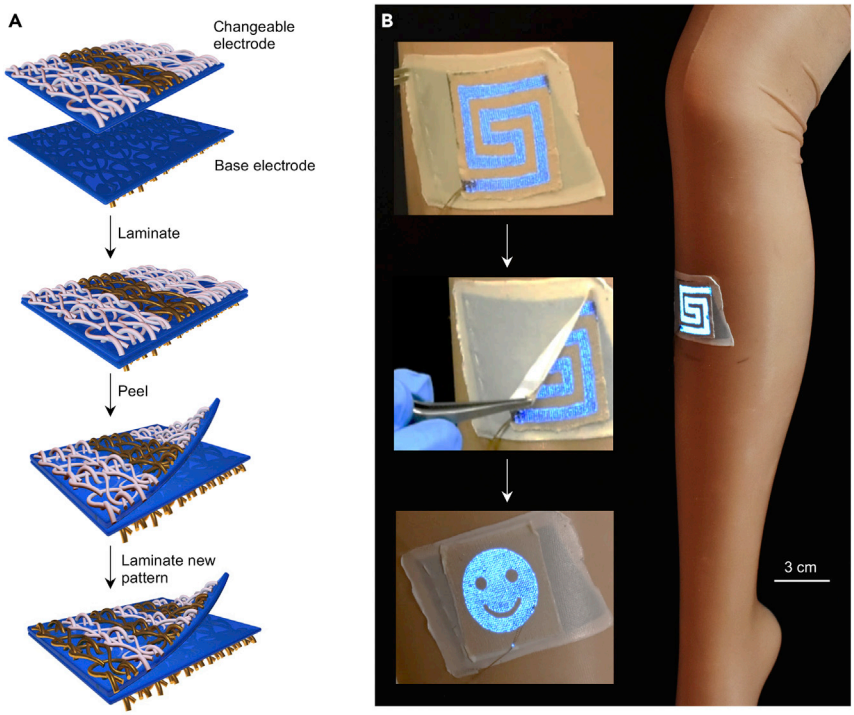

Figure 6. Patterned Light-Emitting e-Textiles with Changeable Patterns of Light Emission
(A) Schematic of the pattern-changing process.
(B) Photographs of changeable patterned e-textile worn on a mannequin leg.
See also Videos S2, S3, and S4.

ultrasheer pantyhose and a changeable electrode laminated over the top. The patterned changeable electrode can be easily peeled off and replaced with an electrode bearing a different pattern, allowing the user to express, for example, different emotional states (Videos S2, S3, and S4).

Conclusions

We have demonstrated that the complex 3D structures of textiles, often viewed as problematic substrates for e-textile fabrication, can instead form the basis for a new design approach whereby the textile structure is a fundamental design component to enable wearable devices. Here, we have shown that the open framework structure of ultrasheer textiles provides a unique way to address the challenging problem of stretchable and wearable transparent electrodes for light-emitting e-textiles. This new textile-centric approach to wearable electronics has enormous potential beyond this present work, especially considering the incredibly wide range of textiles available for study: natural and synthetic materials that are knitted, woven, tufted, and braided into a variety of structures, all of which vary in fiber density, composition, structure, stiffness, elasticity, weight, water absorbency, water repellence, strength, and durability.

EXPERIMENTAL PROCEDURES

All chemicals were purchased commercially and used as received.

ENIG Metallization of Knitted Ultrasheer Fabric

Ten-denier knitted ultrasheer fabric (87% nylon and 13% spandex) was sonicated in deionized water and isopropyl alcohol for 15 min each, then exposed to air plasma for 10 min. The oxidized fabric was immersed in a 1% (v/v) solution of APTES in deionized

water for 30 min, a Pd/Sn solution (prepared from Cataposit 44 and Cataprep 404 [Shipley], as directed by manufacturer) for 2 min, and aqueous 1 M NaOH for 1 min. Samples were rinsed with water in between steps. The fabric was then metallized in a nickel ELD solution (0.08 M $NiSO_4 \cdot 6H_2O$, 0.14 M $Na_4P_2O_7 \cdot 10\ H_2O$, and 0.07 M dimethylamine borane in water) for 10 min with sonication. After rinsing with water, the Ni-coated fabric was immersed in an Au ELD bath (Gobright TAM-55, Uyemura) for 30 min.

Patterning of Knitted Ultrasheer Fabric

The ultrasheer fabric was sonicated in deionized water and isopropyl alcohol for 15 min each, then exposed to air plasma for 10 min. A 0.15-mm-thick stainless-steel stencil mask with the desired pattern was placed on top of the fabric, cold-wax medium (Gamblin) was applied to cover the metal stencil, and a glass microscope slide was used as a squeegee to remove the excess. The ENIG metallization procedure was then performed.

Electroluminescent Device Fabrication

The emissive layer was formed by mixing ZnS:Cu phosphor powder (KPT) with Ecoflex 30 prepolymer (Smooth-on) in 1:1 (w/w) ratio. This mixture was spin-coated at 500 rpm for 1 min onto a carrier surface comprising a glass substrate covered with a layer of tape, then curing on a 70°C hotplate for 5 min. a second layer of ZnS:Cu/Ecoflex was then spin-coated on the cured layer at 1,000 rpm for 1 min as an adhesive layer, and the gold-coated ultrasheer textile brought into contact with the surface. Curing the adhesive layer at 70°C for 5 min adhered the gold-coated textile to the surface. The structure was peeled away from the tape-covered glass, flipped over, and the process was repeated by spin-coating a second adhesive layer of ZnS:Cu/Ecoflex blend, adhering the second gold-coated ultrasheer textile electrode, and curing.

Washing Durability

ACEL devices were soaked in 1 wt % solution of Tide Original Liquid Laundry Detergent in deionized water with stirring for 1 h, followed by rinsing with water and drying in an oven at 60°C for 1 h.

DATA AND CODE AVAILABILITY

The authors did not deposit any data associated with this paper.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.matt.2020.01.017.

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AUTHOR CONTRIBUTIONS

Conceptualization, Y.W. and T.B.C.; Methodology, Y.W., S.S.M., and T.B.C.; Investigation, Y.W., C.L., S.S.M., and R.S.C.; Writing, Y.W., T.B.C., and R.S.C.; Funding Acquisition, T.B.C.; Supervision, T.B.C.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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REFERENCES

1. Barber, E.J.W. (1992). Prehistoric Textiles: The Development of Cloth in the Neolithic and Bronze Ages with Special Reference to the Aegean (Princeton University Press).
2. Liu, M., Pu, X., Jiang, C., Liu, T., Huang, X., Chen, L., Du, C., Sun, J., Hu, W., and Wang, Z. (2017). Large-area all-textile pressure sensors for monitoring human motion and physiological signals. Adv. Mater. *29*, 1703700.
3. Atalay, A., Sanchez, V., Atalay, O., Vogt, D., Haufe, F., Wood, R., and Walsh, C. (2017). Batch fabrication of customizable silicone-textile composite capacitive strain sensors for human motion tracking. Adv. Mater. Technol. *2*, 1700136.
4. Coppedè, N., Tarabella, G., Villani, M., Calestani, D., Iannotta, S., and Zappettini, A. (2014). Human stress monitoring through an organic cotton-fiber biosensor. J. Mater. Chem. B *2*, 5620–5626.
5. Zhao, Y., Zhai, Q., Dong, D., An, T., Gong, S., Shi, Q., and Cheng, W. (2019). Highly stretchable and strain-insensitive fiber-based wearable electrochemical biosensor to monitor glucose in the sweat. Anal. Chem. *91*, 6569–6576.
6. Pu, X., Liu, M., Li, L., Han, S., Li, X., Jiang, C., Du, C., Luo, J., Hu, W., and Wang, Z. (2016). Wearable textile-based in-plane microsupercapacitors. Adv. Energy Mater. *6*, 1601254.
7. Yang, Y., Huang, Q., Niu, L., Wang, D., Yan, C., She, Y., and Zheng, Z. (2017). Waterproof, ultrahigh areal-capacitance, wearable supercapacitor fabrics. Adv. Mater. *29*, 1606679.
8. Lee, S., Choi, K., Kim, S., and Lee, S. (2018). Wearable supercapacitors printed on garments. Adv. Funct. Mater. *28*, 1705571.
9. Hu, L., Pasta, M., Mantia, F., Cui, L., Jeong, S., Deshazer, H., Choi, J., Han, S., and Cui, Y. (2010). Stretchable, porous, and conductive energy textiles. Nano Lett. *10*, 708–714.
10. Gaikwad, A., Zamarayeva, A., Rousseau, J., Chu, H., Derin, I., and Steingart, D. (2012). Highly stretchable alkaline batteries based on an embedded conductive fabric. Adv. Mater. *24*, 5071–5076.
11. Xiong, J., and Lee, P. (2019). Progress on wearable triboelectric nanogenerators in shapes of fiber, yarn, and textile. Sci. Technol. Adv. Mater. *20*, 837–857.
12. Pan, S., Yang, Z., Chen, P., Deng, J., Li, H., and Peng, H. (2014). Wearable solar cells by stacking textile electrodes. Angew. Chem. Int. Ed. *53*, 6110–6114.
13. Lee, S., Lee, Y., Park, J., and Choi, D. (2014). Stitchable organic photovoltaic cells with textile electrodes. Nano Energy *9*, 88–93.
14. Li, R., Xiang, X., Tong, X., Zou, J., and Li, Q. (2015). Wearable double-twisted fibrous perovskite solar cell. Adv. Mater. *27*, 3831–3835.
15. Cherenack, K., Zysset, C., Kinkeldei, T., Münzenrieder, N., and Tröster, G. (2010). Woven electronic fibers with sensing and display functions for smart textiles. Adv. Mater. *22*, 5178–5182.
16. Kwon, S., Kim, H., Choi, S., Jeong, E., Kim, D., Lee, S., Lee, H., Seo, Y., and Choi, K. (2017). Weavable and highly efficient organic light-emitting fibers for wearable electronics: a scalable, low-temperature process. Nano Lett. *18*, 347–356.
17. Zhang, Z., Cui, L., Shi, X., Tian, X., Wang, D., Gu, C., Chen, E., Cheng, X., Xu, Y., Hu, Y., et al. (2018). Textile display for electronic and brain-interfaced communications. Adv. Mater. *30*, 1800323.
18. Hu, B., Li, D., Ala, O., Manandhar, P., Fan, Q., Kasilingam, D., and Calvert, P. (2011). Textile-based flexible electroluminescent devices. Adv. Funct. Mater. *21*, 305–311.
19. Hu, B., Li, D., Manandharm, P., Fan, Q., Kasilingam, D., and Calvert, P. (2011). CNT/conducting polymer composite conductors impart high flexibility to textile electroluminescent devices. J. Mater. Chem. *22*, 1598–1605.
20. Vos, M., Torah, R., and Tudor, J. (2016). Dispenser printed electroluminescent lamps on textiles for smart fabric applications. Smart Mater. Struct. *25*, 045016.
21. Kim, W., Kwon, S., Lee, S.-M., Kim, J., Han, Y., Kim, E., Choi, K., Park, S., and Park, B.-C. (2013). Soft fabric-based flexible organic light-emitting diodes. Org. Electron. *14*, 3007–3013.
22. Kim, W., Kwon, S., Han, Y., Kim, E., Choi, K., Kang, S., and Park, B. (2016). Reliable actual fabric-based organic light-emitting diodes: toward a wearable display. Adv. Electron. Mater. *2*, 1600220.
23. Choi, S., Kwon, S., Kim, H., Kim, W., Kwon, J., Lim, M., Lee, H., and Choi, K. (2017). Highly flexible and efficient fabric-based organic light-emitting devices for clothing-shaped wearable displays. Sci. Rep. *7*, 6424.
24. Kim, H., Kwon, S., Choi, S., and Choi, K.C. (2015). Solution-processed bottom-emitting polymer light-emitting diodes on a textile substrate towards a wearable display. J. Inf. Disp. *16*, 179–184.
25. Lanz, T., Sandström, A., Tang, S., Chabrecek, P., Sonderegger, U., and Edman, L. (2016). A light–emission textile device: conformal spray-sintering of a woven fabric electrode. Flex. Print. Electron. *1*, 025004.
26. Wang, B., and Facchetti, A. (2019). Mechanically flexible conductors for stretchable and wearable e-skin and e-textile devices. Adv. Mater. *31*, 1901408.
27. Wu, Y., Mechael, S., Chen, Y., and Carmichael, T. (2018). Solution deposition of conformal gold coatings on knitted fabric for e-textiles and electroluminescent clothing. Adv. Mater. Technol. *3*, 1700292.
28. Zhang, Z., Shi, X., Lou, H., Xu, Y., Zhang, J., Li, Y., Cheng, X., and Peng, H. (2017). A stretchable and sensitive light-emitting fabric. J. Mater. Chem. C *5*, 4139–4144.
29. Zhu, B., Gong, S., and Cheng, W. (2018). Softening gold for elastronics. Chem. Soc. Rev. *48*, 1668–1711.
30. Chen, Y., Wu, Y., Mechael, S., and Carmichael, T. (2019). Heterogeneous surface orientation of solution-deposited gold films enables retention of conductivity with high strain – a new strategy for stretchable electronics. Chem. Mater. *31*, 1920–1927.
31. Zhang, H. (2015). Flexible textile-based strain sensor induced by contacts. Meas. Sci. Technol. *26*, 105102.
32. Shin, H., Sharma, B., Lee, S., Lee, J.-B., Choi, M., Hu, L., Park, C., Choi, J., Kim, T., and Ahn, J.-H. (2019). Stretchable electroluminescent display enabled by graphene-based hybrid electrode. ACS Appl. Mater. Interfaces *11*, 14222–14228.
33. Wang, J., Yan, C., Cai, G., Cui, M., Eh, A., and Lee, P. (2016). Extremely stretchable electroluminescent devices with ionic conductors. Adv. Mater. *28*, 4490–4496.
34. Wang, J., Yan, C., Chee, K., and Lee, P. (2015). Highly stretchable and self-deformable alternating current electroluminescent devices. Adv. Mater. *27*, 2876–2882.
35. Zhou, Y., Zhao, C., Wang, J., Li, Y., Li, C., Zhu, H., Feng, S., Cao, S., and Kong, D. (2019). Stretchable high-permittivity nanocomposites for epidermal alternating-current electroluminescent displays. ACS Mater. Lett. *1*, 511–518.
36. Wang, Z., Chen, Y., Li, P., Hao, X., Liu, J., Huang, R., and Li, Y. (2011). Flexible graphene-based electroluminescent devices. ACS Nano *5*, 7149–7154.