Conductive liquid metal elastomer thin films with multifunctional electro-mechanical properties

A B M Tahidul Haque, Ravi Tutika, Meng Gao, Angel Martinez, Julie Mills, J Arul Clement, Junfeng Gao, Mohsen Tabrizi, M Ravi Shankar, Qibing Pei and Michael D Bartlett

1 Department of Materials Science and Engineering, Iowa State University of Science and Technology, Ames, IA 50010, United States of America
2 Current address: Mechanical Engineering, Soft Materials and Structures Lab, Virginia Tech, Blacksburg, VA 24061 USA
3 Department of Materials Science and Engineering, Soft Materials Research Laboratory, University of California, Los Angeles, Los Angeles, CA 90095, United States of America
4 Department of Industrial Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States of America
5 Current address: Macromolecules Innovation Institute, Virginia Tech, Blacksburg, VA 24061 USA

E-mail: mbartlett@vt.edu

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Abstract

Wearable electronics, conformable sensors, and soft/micro-robotics require conductive yet stretchable thin films. However, traditional free standing metallic thin films are often brittle, inextensible, and must be processed in strict environments. This limits implementation into soft technologies where high electrical conductivity must be achieved while maintaining high compliance and conformability. Here we show a liquid metal elastomeric thin film (LET) composite with elastomer-like compliance (modulus < 500 kPa) and stretchability (>700%) with metallic conductivity (sheet resistance < 0.1 Ω/□). These 30–70 µm thin films are highly conformable, free standing, and display a unique Janus microstructure, where a fully conductive activated side is accompanied with an opposite insulated face. LETs display exceptional electro-mechanical characteristics, with a highly linear strain-resistance relationship beyond 700% deformation while maintaining a low resistance. We demonstrate the multifunctionality of LETs for soft technologies by leveraging the unique combination of high compliance and electrical conductivity with transfer capabilities for strain sensing on soft materials, as compliant electrodes in a dielectric elastomeric actuator, and as resistive heaters for a liquid crystal elastomer.

1. Introduction

Soft electronics and machines simultaneously demand mechanical stretchability and compliance with high electrical conductivity [1–5]. Key to these technologies are stretchable and conductive thin films which can easily deform into complex shapes to enable actuation [6], sensing for electronic skins and smart clothing [7–10], and energy storage [11]. However, traditional metallic conductors (Au, Ag, Cu), semiconductors (Si, Ge), and metal oxides (indium tin oxide) thin films are not directly applicable in stretchable electronics due to their inherent stiffness and low elastic extensibility [4, 12]. One approach to overcome this limitation is to pattern curvy or buckled conductive traces on deformable substrates [13–15]. These materials can be easily bent and twisted, but their stretchability can be limited [12]. Additionally, rigid yet conductive micro/nanoparticles of carbon nanotubes (CNTs), graphene, or metal nanoparticles can be incorporated in elastomers as composites to improve stretchability, but electrical conductivity is often compromised, especially under large deformations [12]. Notably, conductive particles spread by spray coating [4], brush painting [16], inkjet printing [16], and drop casting [12] can be displaced during repetitive applications. Therefore, further development in multifunctional conductive and compliant thin-film material is required to enable soft and micro robotics, electronics, and actuators.

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Alternatively, intrinsically stretchable and conductive materials such as liquid metal (LM), ionic liquids, hydrogels, and conductive polymers can be utilized which display high compliance and stretchability [17]. For high electrical conductivity and low toxicity, LM based materials display advantages over ionic conductors (e.g. ionic liquids, hydrogels) for stretchable electrodes [18–20]. In contrast to solid, rigid conductors, the inherent fluidity and conductivity of LM has enabled inherently stretchable circuits and wirings [17, 21]. LM has further been embedded into elastomer to create composites with exceptional electrical [22–24] and thermal [25–29] properties. Creation of LM electronics has been demonstrated by pressure induced sintering of LM droplets [30–32], stretching enabled conductivity of polymerized LM networks [33], and LM micro-channels inside elastomers [34–36]. Patterned traces can also be developed by direct writing [18], printing and stencil approaches [37–39], inkjet-printing [40], and laser writing [41, 42] which are subsequently encapsulated by elastomers. Although, much progress has been made in patterning LM traces, they typically require a carrier substrate or are fabricated in composites which typically produce mm thick films. Despite these diverse fabrication approaches, the creation of homogeneous, thin LM films remains a challenge due to high surface tension, low viscosity, and solid gallium oxide coating of LM droplets [43, 44]. Particularly, the micron-sized thin films are conceptually different as they demand adaptable, surface mountable, and stretchable functionalities. Direct deposition of LM droplets to form conductive and adaptable thin film is difficult to develop [17]. Note that layers of metallic conductors including copper [45], chromium [42], and gold [46] are typically used to spray or print LM thin films. Biphasic (solid-liquid) metallization techniques are also used to impart stretchability of LM thin films [42, 43]. However, all of these approaches depend on a carrier substrate, and free standing LM based thin films without a carrier substrate of metal, elastomer, or a structural platform remains a challenge. Furthermore, adaptability of prominent thin-film fabrication techniques such as electrospinning [20], laser nanowelding [20], chemical vapor deposition [12], epitaxial growth [16], doctor-blading [4] to LM based thin-films remains unknown.

Here we introduce stretchable and conductive LM elastomeric thin films (LETs). This new class of highly stretchable yet free standing composite films has micron scale thickness and can be transferred onto diverse substrates and materials. LETs display a Janus microstructure where the same film has an electrically conductive and insulated surface on opposite sides (figure 1(a)). This is achieved through a rapid fabrication process where a LM-polymer solution is spin coated and then selectively electrical activated through contact pressure on one side. The films display a unique thin film microstructure consisting of LM droplets which protrude, yet are encased by a very thin elastomer. The soft and thin elastomeric shell can be delicately ruptured to spread the LM droplets to make a conductive surface without damaging the opposite insulated face and providing a means to intrinsically connect the LM and elastomeric phases to provide stable electrical performance. LETs have a high compliance (elastic modulus < 500 kPa) and extreme stretchability ($\varepsilon_{\text{max}} > 700\%$). Simultaneously, these films are highly conductive at both the unstrained state (conductivity, $G > 1\ S$), but also maintains electric connection (conductivity, $G \approx 0.2\ S$ at $\varepsilon_{\text{max}}$) at the stretching limit. Compared to other transferable, conductive thin-films remains a challenge due to high surface tension, low viscosity, and solid gallium oxide coating of LM droplets [43, 44]. However, much progress has been made in patterning LM traces, they typically require a carrier substrate or are fabricated in composites which typically produce mm thick films. Despite these diverse fabrication approaches, the creation of homogeneous, thin LM films remains a challenge due to high surface tension, low viscosity, and solid gallium oxide coating of LM droplets [43, 44]. Particularly, the micron-sized thin films are conceptually different as they demand adaptable, surface mountable, and stretchable functionalities. Direct deposition of LM droplets to form conductive and adaptable thin film is difficult to develop [17]. Note that layers of metallic conductors including copper [45], chromium [42], and gold [46] are typically used to spray or print LM thin films. Biphasic (solid-liquid) metallization techniques are also used to impart stretchability of LM thin films [42, 43]. However, all of these approaches depend on a carrier substrate, and free standing LM based thin films without a carrier substrate of metal, elastomer, or a structural platform remains a challenge. Furthermore, adaptability of prominent thin-film fabrication techniques such as electrospinning [20], laser nanowelding [20], chemical vapor deposition [12], epitaxial growth [16], doctor-blading [4] to LM based thin-films remains unknown.

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## 2. Results and discussion

### 2.1. Thin film development

The composite thin films are fabricated by dispersing LM (eutectic gallium and indium- EGaIn) droplets in a matrix of Styrene-Isoprene-Styrene (SIS) tri-block copolymer which is compounded with polybutadiene (PBD) plasticizer to enhance compliance of the composite. The thin matrix surface can be consistently ruptured by pressure induced electrical sintering without propagating defects in the bulk of the film. The first step of thin film fabrication is to dissolve solid SIS pellets in toluene solvent (25% vol in toluene) to achieve low viscosity for casting thin films. Then, PBD plasticizer is added to the solution at a volume concentration of $\delta = 30\%$ ($\delta = \text{PBD}/ (\text{PBD} + \text{SIS})$) to complete the polymer matrix phase. A high concentration of LM ($\phi = 50\%$) is added to this matrix phase and the whole mix is shear mixed to disperse the LM uniformly throughout the matrix. The shear mixing step shown in figure 2(a) is conducted in a dual asymmetric centrifugal (DAC) mixer which breaks-down LM into droplets and ensures a uniform emulsion [54]. The final suspension of LM, SIS/PDB, and toluene is immediately spin coated to preserve the dispersion. The solution is cast onto a circular glass disk which is subsequently spin coated (see figure 2(a) at
Figure 1. High stretchability and conductance of LETs. (a) Schematic of a twisted and bent conductive LET with micrographs showing the electrically conductive and insulated sides. (b) Property plot of stretchable conductors shows the unique combination of maximum conductance and strain limit of LETs compared to other conductive thin films [2, 5, 14, 42, 47–54]. (c) Continued functionality of a LED during extreme deformation of a LET circuit during stretching, bending, and twisting.

different speeds to vary the LET thickness. This process ensures a uniformly distributed LM microstructure throughout the composite as shown in the optical micrographs of figure 2(b) and S2. After solvent evaporation, the final film contains 50% LM, 35% SIS, and 15% PBD by volume. Note that a 2–3 nm thin layer of gallium oxide (Ga$_2$O$_3$) forms around EGaIn in the presence of oxygen [56]. The shear mixing technique used for fabrication efficiently breaks down the thin oxide coating and creates an emulsion of micron sized EGaIn droplets [55, 57]. This oxide is beneficial and acts as a surfactant to keep the droplets dispersed and prevent LM coalescence during fabrication. The resulting composite contains isolated EGaIn droplets with a thin oxide layer at the interface of the SIS matrix. The electrical activation of pristine film is performed by a simple yet reproducible sintering technique. Here, the polymeric coating on top of the LM droplets is ruptured by grazing a silicone elastomer block as shown in figure 2(a).

Unlike areal pressure based activation, just the thin edge of the cuboid shaped elastomer block comes in contact with the LET at an angle of ≈45°. The grazing is performed by hand without any additional test set-up. The activation pressure along the contact edge is measured to be approximately 25 kPa. We graze the LET film several times to uniformly spread the LM over the film surface. This technique also preserves the electrical insulation of the bottom surface of the LET film. Figure S1 shows electrically conductive thin films with uniform silver shining appearance. After removing them from the casting disk a small residual stress could develop in the free-standing film. Therefore, we anneal the film at 40 °C [29] to aid in handling and incorporation onto surfaces.

2.2. LM microstructure
We analyze the film morphology for both pristine and conductive conditions of thin films. Different spin coating speeds between 500 and 1500 rpm are used. We have also prepared thicker films by directly drop casting the liquid mix without any rotational spin to identify the effect of film thickness. Microscopic images of the encapsulated side of a LET are presented in figure 2(b), which shows closely packed, spherical shaped LM droplets encapsulated by the elastomeric matrix. Similar LM droplet sizes are observed in the micrographs for spin coating speed of 1500 rpm as well as the drop-casted film (see figure S2). In order to demonstrate the distinct surface morphology of encapsulated and exposed LM droplets in thin films, we also perform energy-dispersive x-ray spectroscopy (EDS) in scanning electron microscopy (SEM). The EDS images of figure 2(c) show element composition maps of pristine and conductive sides of films to track the gallium and indium of EGaIn and carbon of SIS. We find that the pristine surface is rich in carbon with scattered fragments of other elements. The conductive side is thoroughly coated by gallium with marked traces of indium. Such an insulated face is beneficial for facile bonding to a substrate and avoids short circuits which is difficult to achieve for traditional conductive films that often have through thickness and in-plane
conductivity. A SEM analysis of a thin-film surface in figure 2(d) distinctly shows the LM particles and polymer as dark and bright regions, respectively. The analysis indicates a unique thin film microstructure consisting of LM droplets which protrude, yet are encapsulated by very thin polymer matrix coating. Next, we determine the surface profile of LETs with a white light profilometer to obtain the surface profile and thickness at different spin speeds. The comparative summary of pristine and conductive film thickness is presented in figure 2(e). The analysis reveals a rapid drop in thickness for speeds over 500 rpm and negligible difference between pristine and conductive conditions. Particularly, we have calculated $66.7 \pm 4.2$, $32.1 \pm 1.1$, and $29.8 \pm 0.7 \mu m$ thickness for conductive films spin coated at 500, 1000, and 1500 rpm, respectively. Note that the films prepared by simply drop casting on a glass slide without spin coating only achieve thickness of 200 $\mu m$ or more.

The rapid decrease of film thickness with increased spin coating speed can significantly alter the encapsulated LM microstructure. Notably, we observe significant difference in surface waviness at the pristine condition (i.e. before activation) of films for different spin coating speeds (see contour plots in figure S3). However, the surface profile of conductive face presented in figure S4 demonstrates similar appearance for all films due to distributed network of LM coating. We also quantitatively determine the LM microstructure by measuring LM particle diameter. We have performed particle analysis of the thin film micrographs (shown in figure 2(b) and figure S2) and contour maps obtained by optical profiling to find LM droplet diameters. The summarized LM particle diameters in figure 2(f) show a similar value for all films in the range of 80–90 $\mu m$ irrespective of spin condition. The particle analysis from the drop casted film shows the same areal dimensions as the spin coated films.

The invariant LM diameter and rapid change of film thickness (as a function of spin coating speed) results in a unique 3D microstructure where the LM droplets protrude from the elastomeric matrix. We illustrate this LM reshaping as a function of film thickness using the stacked 3D view of spin coated ($30 \pm 1 \mu m$, $32 \pm 1 \mu m$, and $67 \pm 4 \mu m$) films in figure 2(g). Particularly, the plot illustrates surface elevation within a range of 0–20 $\mu m$ at the x–y plane of each film. The $67 \pm 4 \mu m$ (500 rpm) thick films have dimensions similar to the particle diameter which maintains LM droplets in a generally spherical shape with small impressions on the film surface. However, for thinner films of $30 \pm 1 \mu m$ (1500 rpm) thickness, the encapsulating elastomeric matrix tends to flatten the LM droplets which causes a distinct bulge of LM droplets on the film surface. As such, the LM droplets are reshaped into a disk or saucer shape during spin coating. The mono-layered LM dispersion sets apart the LETs from a wide variety of LM based composites and materials [25–29, 58] and circuit patterned sheets [32]. The thin layer of elastomer covering LM droplets can be ruptured with mechanical pressure during activation which then spreads LM on the conductive surface. A thin oxide layer immediately forms on the exposed LM coating. This oxide acts as a passivating layer to stabilize the coated surface and prevents the low viscosity LM from flowing [59]. Notably, the electrical conductivity of LM remains intact due to the small thickness of the oxide skin [59]. The Janus microstructure of LETs with protruding yet encapsulated LM droplets provides a means to intrinsically connect the LM and elastomeric phases to provide stable electrical performance. Janus refers to two distinct properties or facets of the same material. A Janus microstructure in thin films indicates a composite system with two different material features giving rise to distinct properties on opposite faces [60]. Specifically, LETs demonstrate a fully electrically conductive surface with an opposite insulated side. Contrasting to the mm-thickness LM films [28, 31, 32, 42, 58, 61], significantly thinner (<70 $\mu m$) LETs are more conformal to curvilinear profiles as a stretchable conductive medium.

### 2.3. Mechanical and electrical characterization

The mechanical behavior of standalone LETs is investigated through tensile testing of the free-standing thin films. The stress–strain relations from uniaxial tensile experiments of $67 \pm 4$, $32 \pm 1$, and $30 \pm 1 \mu m$ thin films are presented in figure 3(a). The summarized mechanical properties of tensile modulus and failure strain are shown in figure 3(b). We observe high compliance of the films, with tensile modulus values all less than 500 kPa which makes them suitable for soft devices. Similarly, the stretchability of these films is above 700% where some of the films have reached almost 1000% strain. Noticeably, we have found similar modulus and maximum strain for all the films which is indicative of consistent mechanical performance for thin composite films. Additionally, we conduct cyclic experiments of thin films to demonstrate their robustness for repeatable usage. We cyclically stretch $67 \pm 4 \mu m$ films to five different strain limits ranging between 100%–500% (figure 3(c)). The cyclic experiment demonstrates the same unloading and successive loading paths at each cyclic increment, which represents the conventional Mullins effect of polymers and composites. The electrical properties of the LETs are evaluated through the sheet resistance of the activated faces of LETs. This parameter represents the conductivity of the film surface instead of the bulk material. The sheet resistance is determined as a function of film thickness using a four-point probe test method. The tests are performed using a constant current supply between outer electrodes to determine the voltage drop between
Figure 2. Morphology of LETs. (a) Thin film fabrication performed by shear mixing, spin coating, and electrical activation. (b) Micrographs of LETs indicating uniform distribution of LM droplets. The inset shows closely packed LM droplets. (c) Particle mapping of films by EDS mode analysis showing carbon rich pristine side and gallium rich conductive side. (d) Secondary electron (SE) image of insulated LET surface from SEM analysis shows isolated dark regions of LM particles dispersed in light polymeric areas. (e) Thickness of pristine and conductive LETs as a function of spin coating speed. (f) LM particle diameter measurements from micrographs and surface profiles indicating constant values irrespective of spin coating condition. (g) 3D profiles for varying thickness of LETs to illustrate the influence of spin coating speeds on surface structure.

the inner electrodes. The current is gradually increased from 1 to 10 mA and corresponding voltage is measured. The corresponding sheet resistance is calculated as

\[ R_s = \frac{\Delta V}{I} \]

Here, \( \Delta V \) is the voltage drop due to applied current \( I \). The 67 \( \pm \) 4, 32 \( \pm \) 1, and 30 \( \pm \) 1 \( \mu \)m films all exhibit linearly increasing voltage and constant sheet resistance as a function of increasing current in figure 3(d). We observe significantly low sheet resistance of less than 0.1 \( \Omega / \square \) for all the films. High performing stretchable conductors are typically characterized by sheet resistance of \( > > 1 \Omega / \square \) [15, 16, 63, 64], which highlights the high electrical conductive of LETs.

The high stretchability (>700%) and conductivity (\( R_s < 0.1 \Omega / \square \)) LETs shows strong potential for stretchable conductors. Unlike most of the flexible conductive systems, this film is created in free-standing form which can sustain significant deformation by itself while maintaining electrical connection. Figures 3(e) and (f) demonstrate that under uniaxial strain, the resistance response of LETs is linear. Particularly, resistance proportionally increases to 6.2 \( \Omega \) during the tests which is a 12 \( \times \) increase at 700% strain. Note that, we have found linear resistance-strain relation for maximum strain of 930% for a free-standing film as shown in figure S5.

3. Implementation into soft technologies

The exceptional stretchability and electrical conductivity of LETs can enable multifunctional properties for emerging technologies such as flexible electronics and soft robotics. Here we incorporate the composite thin films for three distinct functionalities including a strain sensor, resistive heater for liquid crystal elastomer (LCE), and electrodes for dielectric elastomeric actuator (DEA).

3.1. Strain sensor

The linear electro-mechanical relation of LETs can enable thin film strain sensors which can remain functional at extreme stretching. As a representation of stretchable electronics, we use VHB tape (3 M 4910 VHB Double-Sided Tape) to attach the non-conductive face of the composite thin film. We sense the resistance change due to tensile strain in figure 4(a) for 700% strain of substrate. Both the resistance and normalized resistance responses (inset of figure 4(a)) illustrate the linear increase in resistance as a function of strain. Next, we perform strain and hold experiments by sequentially stretching a sample by 100%, then hold it in static condition for 100 s, then continue stretching to reach a maximum value of 500% strain. The experimental result in figure 4(b) provides resistance and strain measurements as a function of time, where the resistance output closely overlays on the applied strain. Further, the hold steps are not visible in the plot.
Figure 3. Electro-mechanical characterization of LETs. (a) Stress–strain curves of conductive films for different thicknesses. A set of representative images of the experiment showing initial ($\varepsilon = 0\%$) and highly stretched ($\varepsilon = 700\%$) state of a LET. (b) Mechanical behavior summary as a function of film thicknesses showing low tensile modulus and high ultimate strain. (c) Cyclic behavior of LETs for increase of strain in 100% steps up to 500% strain. (d) Sheet resistance values of conductive thin films of different thicknesses indicating constant sheet resistance as a function of current with an inset plot of liner voltage-current relation. (e) Electro-mechanical coupling of films under uni-axial tension showing a linear relationship of resistance as a function of applied strain. (f) The proportional increase of normalized resistance for highly stretchable films.

of normalized resistance and strain for this stepped experiment (figure 4(b) inset), showing the exceptional stability of the electrical response of the films under deformation even with non-uniform strain loading. In a cyclic resistance experiment, we increase the cyclic strain by 25% up to mid-range level of 100%. Then, subsequent cycles are increased by 100% to reach a final strain of 500%. The strain sensing performance of the sensor is presented in figure 4(c) for a total of eight cycles of various strain limits. The time-resistance relation in figure 4(c) exhibits a uniform rate of resistance change over time during loading and unloading of each cycle, overcoming the typical non-linear response of resistive sensors at large strain [9]. Figure 4(d) demonstrates that electrical response as a function of strain for all of the cycles overlay with minimal deviation even up to large strains. We also overcome the cracking and other common defects in stretchable conductors at high strains. For example, stretchable conductors that utilize metal nanoparticles integrated into elastomeric films [65] or LM doped elastomeric fibers [66] can suffer from wrinkling or buckling at the surface. In contrast, the LM coating at the LET surface is connected to a network of droplets embedded in the elastomeric matrix. The cyclic loading of LETs is not affected by residual strain and wrinkling dislocation and displays negligible hysteresis behavior in the resistance-strain relation and a linear resistance dependence on strain. These behaviors are critical advancements for stretchable conductors and LETs overcome common drawbacks of soft or stretchable resistive strain sensors. The initial and deformed shapes of the stretched LET sensor on an elastomeric substrate are presented in figure 4(e) for $\varepsilon = 0\%$ and 500%, respectively. The high compliance of the films provides minimal interference with the underlying substrate motion which makes them suitable candidates for deformation monitoring of stretchable electronics, smart clothing, and robotics.

3.2. Dielectric elastomeric actuator

We have also integrated electrically conductive LETs as electrodes in DEAs. DEA is a class of compliant parallel plate capacitors constructed by placing stretchable electrodes on two sides of a thin dielectric elastomeric film. The actuation of DEAs has enabled soft electronic technologies including sensors [67], actuators [68, 69], and energy harvesters [70]. Due to their high compliance, LETs are well suited to function as soft electrodes. We use VHB acrylic elastomer (1 mm thick) as high energy density dielectric elastomers (DE) which are prestrained to improve the breakdown strength, mechanical efficiency and response speed [68]. The VHB layer is equibiaxially stretched (see figure S6) and LET electrodes are attached on opposite faces of DE as shown by the schematic of figure 5(a). The DEA activation is controlled by a high voltage power supply and the results of figure 5(a) present areal strain as a function of gradually increasing voltage...
Figure 4. Demonstration of LETs for sensing functionality. (a) LETs sensor bonded onto VHB showing a linear increase of resistance as a function of applied strain. Inset of normalized resistance indicates the proportional relation with stretching. (b) Strain and hold test of LET using a stepped increase of 100% strain with 100 s holds to reach a final strain of 500% in five steps. The coincident response of strain and resistance is observed as a function of time. The inset presents liner electro-mechanical relation from relaxation test. (c) Performance evaluation of thin films as strain sensors by cyclically reaching 500% strain in eight steps. Strain sensing ability presented by uniform rate of resistance change during all loading-unloading instances. (d) Linear dependency between strain and resistance shown by coincidental results of all the cycles. (e) Deformed configuration of LETs showing function at a high strain of 500%.

(Video S2). The results illustrate that the DEAs can sustain a high voltage of 9.0 kV without breakdown with an areal stain of nearly 120%. Figure 5(b) demonstrates sequential DEA actuation by planar areal strain at different instances of supplied voltage in the range of 0–9.0 kV. The robust actuation of DEAs indicate rich functionality of LM composite film as compliant electrodes.

3.3. LCE Actuator

LCEs are stimuli responsive actuation materials with high work density, reversible actuation, and programmable control for use in sensors [58], artificial muscles [71], soft robotics [72], and smart surfaces [73]. Thermal stimuli induced nematic-isotropic phase transition is the prominent mode of mechanical actuation of LCE. However, the conventional heat generation techniques by incorporating rigid metal, ceramic nanoparticles, CNTs, SWNTs to develop LCE composites can reduce the actuation [71]. The lightweight, uniformly conductive, and transferable LM thin film can act as a resistive heater to enable facile actuation of LCE. The LCE used in this study is composed of nematic mesogen RM82 and thiol chain extender EDDT. The nematic–isotropic transition temperature is found to be 53 °C. The composite film is directly attached to a rectangular section of 1.0 cm × 0.5 cm LCE and connected to a power source using copper tapes as presented in the inset of figure 5(c). This demonstration is performed by applying Joule heating to the thin film at a constant voltage to enable efficient power consumption (<500 mW) during actuation. Figure 5(c) and Video S3 shows a 15% deformation of thermally stimulated LCE to pull a 1 g mass. Figure 5(d) includes images of the 15% shrinkage of LCE to pull the mass and the IR thermograph shows temperature raised to 150 °C by LET to cause nematic to isotropic transition. The strain-current and temperature-time plots in figure S7 show small change of current (∼20 mA) and rapid temperature change during actuation, respectively. Noticeably, LET enables LCE to reach transition temperature within 2 s and full actuation is achieved in 20 s. The large force-displacement of greater than 1 × 10^{-5} N.m of the actuator demonstrates the functionality of LM composite film for robust and flexible actuation.
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Figure 5. Demonstration of LETs for actuation of smart materials. (a) Integration of LETs as soft electrodes on opposite faces of dielectric elastomer (DE) shown using the schematic. The plot of DEA activation presented by biaxial areal strain as a function of applied voltage. (b) Images showing areal expansion of DEA for varying levels of voltage supply. (c) LET functioning as a resistive heater to actuate LCE. Schematic shows the material configuration. (d) Shrinkage of LCE through Joule heating of LET to lift a 1 g mass. The inset shows IR imaging of the resistive heating of LET to raise LCE temperature to 150 °C for actuation.

4. Conclusion

The LETs presented in this study demonstrate a new approach for elastic, conductive thin films. Through a systematic morphology investigation, we demonstrate a unique microstructure of LETs where LM protrudes above the film plane while being encapsulated by a thin elastomer layer. Initially, the droplets are intact and insulating, upon mechanical pressure they are ruptured to form a conductive surface while maintaining electrical insulation on the bottom surface. We report the flexible nature of the films marked by high compliance (modulus < 500 kPa) and ultimate strain (>700%) with accompanying metal-like conductivity (sheet resistance < 0.1 Ω/□). Furthermore, the films show unique electro-mechanical coupling with a highly linear resistance-strain relationship even at extreme deformation. The reliable and programmable performance of LETs allows for integration on films and surfaces for bending, twisting, and stretching deformations. The multifunctionality of LETs stemming from deformation sensitivity, thermal, and electrical conductivity are demonstrated by incorporating them as strain sensor, resistive heater, and electrodes, respectively. Such transferable and lightweight thin film systems can drive the progress of actuation of soft robotics and smart devices. At the same time, multifunctional performance of LETs can enhance a wide variety of stretchable electronics, flexible circuitry, and sensor technologies.

Experimental section

Composite thin film fabrication
The matrix of thin films consists of SIS (Polystyrene-block-polyisoprene- block-polystyrene) containing 14 wt% of styrene (Sigma-Aldrich Corp.) and PBD (Sigma-Aldrich Corp.). Eutectic Gallium Indium (EGaIn) is prepared by mixing 3:1 weight ratio (75% Ga:25% In) of gallium and indium at 200 °C for 24 h.
on a hot-plate. The matrix is developed by dissolving solid SIS pallets in toluene solvent by shear mixing technique in a DAC mixer (Flaktek Speedmixer™). Then the liquid PBD is added to the mix which is again run through the DAC mixer. After preparation of liquid phased matrix, required amount of LM is added to the mix which is shear mixed one more time to obtain the final liquid phase of composite. The complete liquid mix is then poured onto circular glass disks on a spin coater (Laurell WS-650). We use 500, 1000, 1500 rpm spin speeds for 30 s to fabricate different film thickness. The drop casted film is prepared from same mix by spreading the liquid composite on a glass slide. The composites are placed inside fume hood for 30 min to at room temperature. Sintering of thin films are performed on the glass disk using a wide silicon rubber block (Ex-Sil 100; Gelest Inc.) for electrical activation. The activation force across the full block length is measured by an analytical weighing balance (Radwag AXS2 PLUS) and contact area is imaged on a transparent glass slide and measured using Fiji image analysis software. LETs are then removed and placed on a separate glass slide and annealed at 40 °C in oven for 12 h. Finally, the standalone annealed film is secured in a paper frame made of masking tape for further usage.

SEManalysis
SEM analysis is performed using FEI Inspect F50. In secondary electron (SE) mode, the difference in surface topography of an insulated side is displayed by contrasting dark and bright regions. Specifically, the dark ridges represent isolated LM droplets and light flat regions indicate elastomer matrix respectively (see figure 1(b). Energy dispersive spectroscopy (EDS) are performed on conductive and insulated sides of thin film. The distinct Janus nature of the electrically conductive and insulated sides of the film are highlighted by tracing gallium (Ga) and carbon (C) elements.

Mechanical measurement
The mechanical measurement of LM composite thin films is carried out according to ASTM standard D882 of thin plastic sheet. A specimen dimension of 5 cm × 1 cm is determined by following the guideline. We precisely prepare dog-bone shaped film specimen using digital laser cutting machine (Epilog Laser Fusion M2, 75 watt). The specimens are attached to a PET poly(ethylene terephthalate) (W. W. Grainger, Inc.) frame for gripping the edges during experiments. We use a 10 N load cell to perform tension tests on the films in the Instron 5944 mechanical testing machine. Three LETs are experimented to obtained the mechanical properties. Both uniaxial tension and cyclic tests are conducted at a rate of 1 mm s⁻¹ where the tensile modulus is determined by post-processing the stress–strain data in MATLAB using a curve fitting algorithm for strain up to 5%.

Sheet resistance experiment
Sheet resistance of the thin films is measured using four-point probe tests. We use a multi-height adjustable probe (Jandel multi-height four-point probe model RM2) that uses a four-point linear probe technique (40 μm diameter tips at 1.0 mm spacing) to eliminate the contact resistance effect from the reading. A constant current is supplied between outer electrodes and the voltage drop is measured between the inner electrodes. The supply current is changed after each measurement of voltage. In this way the I–V curve is prepared for a thin film and the corresponding sheet resistance is determined using specimen and equipment parameters. Specifically, we use three samples for each case to determine sheet resistance for each thickness of LET.

Morphology analysis
Morphological characterization of the created LM composite films is conducted using an optical microscope (Leica DMi8 inverted microscope in dark field mode.) and white light profilometer (Zygo Profilometer 7100). We post-process the micrographs and surface profiles in Fiji image analysis software to determine diameter of a minimum of 30 LM droplets for each category of LM composite films. The optical profiling is also used to determine the thickness of the thin films. The profilometer scans the surfaces of thin film and glass near the intersection. Then we measure the thickness from difference in elevation of film surface and glass base using the MetroPro-X program. Figure S8 shows a three dimensional view of glass and thin film surface profiles obtained from the program.

Strain-resistance characterization
The free-standing tests are performed by attaching copper tape directly on LETs near the gripper for tensile tests. The electro-mechanical experiments of strain sensing thin films are performed by attaching them to a 1 mm thick VHB tape (3 M 4910 VHB Double-Sided Tape). The insulated side of the film is washed with isopropyl alcohol (IPA) and directly bonded to the tape. In order to establish electrical connection with the thin film, we attach copper tapes on two edges of the VHB bonded film. The copper connections of these
samples are completely clamped inside grippers to ensure that the measured resistance corresponds only to the stretched films. Thin films of dimensions 5 cm × 1 cm are mechanically stretched in Instron 5944 mechanical testing machine and resistance is measured using Keithley 2460 source meter. Both free-standing and strain sensing LETs are characterized for three specimens.

**LCE demonstration**

Preparation of LCE begins by mixing 1 mole of liquid crystal monomer RM82 (Wilshire Technologies Inc.) with 1.2 moles of thiol chain extender EDDT (Sigma-Aldrich Corp.) in a vial at 120 °C for 2 min. The vinyl cross-linker TATATO (Sigma-Aldrich Corp.), thermal inhibitor BHT (Sigma-Aldrich Corp.) and photoinitiator I-369 (Ciba Specialty Chemicals Inc.) are added before melting at 90 °C to mix for 2 more minutes. The final molar ratio of RM82 to TATATO is nearly 1:0.3. A base catalyst TEA (TCI Chemicals) is added to the compound to complete the composition which is then placed in thin cells to form films and then oligomerized for 30 min at 80 °C. While maintaining this temperature, we apply UV treatment for one min on each side of a LCE film and then cool it to room temperature. The micron sized (45 µm) LCE films recovered from the cell are inherently adhesive which enables direct attachment to the insulated side of LM composite thin films. The multilayered composite is stretched to about 60% in a frame to impose orientational order to LCE monomers and crosslinked under UV light for 10 min. We use conductive epoxy to bond a pair of copper strips on two opposite edges of the composite film. The multilayered composite is supported by a frame at the top and bottom with a small mass hanging from the bottom frame. Then, the metal strips are connected to a GW INSTEK GPS-4303 4CH power source to generate joule heating at constant voltage for thermal actuation of LCE. The actuation is recorded by a digital video camera (Digital Microscope camera from CELESTRON; 6 frames s⁻¹) which is processed by a tracking program Tracker (https://physlets.org/tracker/) to determine the strain. The temperature change is captured by FLIR 325A Infrared camera.

**DEA demonstration**

Preparation of the dielectric layer of DEA involves equibiaxial stretching (300% biaxial strain) of 1 mm thick acrylic elastomers (3 M 4910 VHB Double-Sided Tape) which is then fixed on a frame. LM composite films are cut into 1 cm diameter circular shape with a laser marker (Epilog Zing Laser) and treated in UV/Ozone for 15 min. UV/Ozone treatment ensures reliable bonding between LET electrodes and DE layer during actuation. In order to function as electrodes, the pristine side of the patterned film is attached on opposite sides of a stretched DE. The electrodes are connected to a custom-made voltage supplier through a thin metal wire for actuation. A digital video camcorder is used to record the actuation mechanism for different voltages. The areal actuation strain is calculated using Fiji software from the video frame-by-frame.

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**ORCID iDs**

A B M Tahidul Haque https://orcid.org/0000-0002-8684-281X
Junfeng Gao https://orcid.org/0000-0002-4564-0429
Mohsen Tabrizi https://orcid.org/0000-0003-1953-673X
Michael D Bartlett https://orcid.org/0000-0002-7391-5135

**References**

[1] Kim D-H et al 2011 Science 333 838–43
[2] Amjadi M Pichitpajongkit A Lee S Ryu S Park I 2014 ACS Nano 8 5154–63
[3] Rus D and Tolley M T 2015 Nature 521 467–75
[4] Zhao J Chi Z Yang Z Chen X Arnold M S Zhang Y Xu J Chi Z Aldred M P 2018 Nanoscale 10 5764–92
[5] Baëtens T Pallecchi E Thomy V Arscott S 2018 Sci. Rep. 8 1–17
[6] Shoji E Takagi S Araie H 2009 Polymers Adv. Technol. 20 425–6
[7] Benight S J Wang C Tolk J B Bao Z 2013 Prog. Polym. Sci. 38 1961–77
[8] Stoppa M and Chioriero A 2014 Sensors (Switzerland) 14 11957–92
[9] Amjadi M Kyung K U Park I Sitti M 2016 Adv. Funct. Mater. 26 1678–98
[10] Jin C et al 2020 Adv. Intelligent Syst. 2 1900162
[11] Lee T D and Ebong A U 2017 Renew. Sustainable Energy Rev. 70 1286–97
