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† Electronic Supplementary Information

Spontaneous Formation of Wrinkle-driven Tubular Structure as a Versatile Platform for Adaptive 3D Stretchable Electronics

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† Electronic supplementary information (ESI) available.

Material and Methods

Preparation of the wrinkle-driven 3D tubular structure. As shown in Figure S1a, †ESI, a poly(vinyl alcohol) (PVA) (KURARAY POVAL™ 28-99, M_w (weight average molecular weight) ~145,000) film with a thickness of ca. 3.25 μm was cast on a pre-cleaned polystyrene petri dish foundation (using a 10 mg/mL PVA aqueous solution) followed by the treatment of allyl isocyanate. Subsequently, a mixture of uncured Ecoflex® 00-30 precursors (all Ecoflex® used in this work contains Part A & Part B with w/w = 1:1, Smooth-On, Inc.) and red/white Silc-Pig™ pigment (mass ratio of red pigment to white pigment = 1.14:1, thickness = 0.14 mm, Smooth-On , Inc.) with a mass ratio of 26.7:1 was cast atop the allyl isocyanate treated PVA film followed by curing at 80 °C for 2 hours. Another similar layer of uncured Ecoflex® precursors and green/white Silc-Pig™ pigment with a mass ratio of 57.1:1 (mass ratio of green to white pigment = 1.3:1, thickness = 0.15 mm) was cast atop the cured red/white Ecoflex ® layer followed by curing at 80 °C for 2 hours. Note that the two colors are introduced to show the curve direction only. One layer of Ecoflex® is sufficient to form a tube structure. The PVA/ Ecoflex® bilayer sheet was then carefully peeled away from the foundation and cut into a size of 2.5 cm length × 5.8 mm width followed by mounting on a custom-made stretcher. A room temperature moisture mist from a humidifier was applied on the top surface for 40 s to fully plasticize the PVA film followed by immediately stretching the bilayer into 13.75 cm (450% strain) and then dried. Upon release, the bilayer automatically forms a 3D tubular structure.

Preparation of a tubular strain sensor/switch for finger motion monitoring. The preparation steps of the PVA-Ecoflex® bilayer are the same as above except for the total Ecoflex ® substrate having a thickness of 0.38mm. The resulting bilayer sheet was then carefully peeled from the foundation and cut into rectangle shape (2.7 cm length × 7.6 mm width) followed by mounting on a stretcher. A room temperature mist was applied on the PVA surface for 40 s followed by immediate stretching of the bilayer to 7.3 cm (170% strain) and then drying. The dried PVA surface was then treated by 5.26 μL of glutaraldehyde (GA)/hydrochloric acid (HCl) ethanol solution (GA: HCl mass ratio = 1.68:1, solution concentration: 10 mg/mL) followed by fully releasing to form a tubular structure. Here GA serves to crosslink PVA while HCl serves as the catalyst of the crosslinking reaction. A thickness of 3.5 μm of conductive carbon grease (MG Chemicals) was coated on the top and side of the tube's seam. The sample was then re-stretched to the tube-just-close state and then attached atop a 3M™ VHB™ 4910 substrate by a silicone adhesive. The resulting structure was cut down into a length of 5.8 mm. To sense the finger motion, the device was adhered on a dummy finger with silicone adhesive.

Preparation of an artificial *mimosa pudica*. The preparation of a tubular structure is the same as the tubular strain sensor/switch. As shown in Figure S5, †ESI, to prepare the pressure switch, a VHB™ 4910 double-sided adhesive tape was fixed on a stretcher followed by stretched to 185% strain. A flexible conductive thread spun from stainless steel fiber (diameter: ca. 0.12 mm, Sparkfun, Inc.) was adhered to the stretched VHB™ tape. A serpentine thread pattern was achieved as released, allowing the conductor to be re-stretchable within 140% strain. To reduce the VHB™ adhesion, a layer of silica/PVA composite (weight ratio = 95/5, concentration = 0.05 mg/cm^2, silica powders are AEROSIL® R202 from Evonik Inc.) was then spray coated on both of the VHB™ surfaces except for the conductive

thread surface. The conductive thread/VHB™ structure was then cut into a rectangle size of 2.7 cm × 2.45 cm and attached to a linear slider (CNBTR Linear Sliding Guideway Rail). One side of the linear slider was attached to a push pull type tubular solenoid (Uxcell, force: 20 N) (see Figure S5,†ESI). Thus, the displacement of the conductive thread/VHB™ structure is compliant with the slider movement that was controlled by the solenoid. Also, as shown in Figure S5 and Figure S6a, ,†ESI ,the conductive thread side connected to a power source was placed towards the metal sliding guide of the slider with a gap of 0.48 cm, and this metal sliding guide is electrically connected to the solenoid. Thus, the solenoid can be connected to the power source as the conductive thread/VHB™ is pressed to deform and contact the metal sliding guide, and this VHB™/conductive thread can be considered as a pressure switch to activate the solenoid motion. Without electrical bias applied, the spring on the solenoid will apply a stretching distance of 1.01 cm to the pressure switch. While with sufficient tactile pressure applied atop the pressure switch area (>10 kPa), the solenoid is on and will apply 0.5 cm releasing distance to the pressure switch as shown in Figure S6a ,†ESI. After the pressure switch was installed and the solenoid was off, the tubular structure with three light-weight green plastic leaves, attached on both sides, was stretched until the opening degree of the leaves was at 106°. The sample was then placed right atop the conductive thread of the pressure switch with the two ends were attached onto the slider as shown in Figure S6a, †ESI (the size of each leaf is 8.8 mm × 1.7mm). Thus, without bias applied, the pre-stretching strain will leave the tube and the green leaves open. With a sufficient tactile pressure (11 kPa was created as finger touch down in Figure 3b) applied atop the tubular structure, the solenoid will turn on. Right after the pressure is removed, the slow relaxation the of VHB™ tape will allow the tactile switch to keep contacting the metal sliding guide for ca. 7 s. Thus, after the pressure removed, the tubular structure keeps0 releasing with a distance of 0.5 cm for ca. 7s, with associated closing of the leaves due to the partial folding of the tube.

Preparation of the highly stretchable tubular tactile switch and the wearable tactile response electroluminescent device. The casting of a PVA film on the foundation and allyl isocyanate treatment is the same as the aforementioned sample. Subsequently, uncured pure Ecoflex® 00-30 precursors were cast atop the treated PVA film followed by curing at 80 °C for 2 hours to form a 0.6 mm thick Ecoflex® layer. The cured bilayer sheet was then carefully peeled away from the foundation and mounted on a custom-made stretcher with a size of 2.74 cm length ×10.5 mm width. A room temperature water mist was applied on the PVA surface for 40 s followed by immediately stretching the bilayer into 15 cm (450% strain) and then dried. A stencil mask was applied atop the PVA surface followed by successively spray coating of 4 layers of different materials: (1) 4.75 μm of flexible adhesive (AA-BOND 2170 Flexible Plastic Bonder Epoxy Adhesive, Atom Adhesives company) ; (2) 12.5 μm of silver epoxy (AA-DUCT 916 Flexible silver epoxy, Atom Adhesives company); (3) 1.8 μm of silver ink layer (CI-1036 highly conductive flexible silver ink, Engineered Materials Systems, Inc.) ; and (4) 1.125 μm of carbon ink layer (CI-2051 conductive carbon ink, Engineered Materials Systems, Inc.); and cured at ambient environment. The stencil mask was then removed to allow the formation of two opposing parallel electrodes. The sample was then released to form a tubular structure followed by sealing the seam with a silicone adhesive (Permatex 80050 Clear RTV Silicone Sealant). To characterize this device, the tubular sample was released from the stretcher and rotated 90 degrees around the *x* axis and then re-mounted on the stretcher for testing the tactile pressure response. The wearable tactile responsive

electroluminescent device was prepared by attaching the two ends of tactile switch atop a PDMS strip and an Ecoflex® strip (both strip sizes: 8 cm length × 7 mm width × 1 mm thickness). The device can be worn by expanding the gap between the PDMS and Ecoflex strip and put the hand/arm inside the space of two strips. And it was electrically connected to a wearable electroluminescent panel (Adafruit, Inc.).

Preparation of the dual-responsive stretchable tubular supercapacitor. As shown in Figure S9, †ESI, the casting of a PVA film on a foundation and allyl isocyanate treatment was the same as the aforementioned samples, and then a rectangle stencil mask (width = 2 mm) was placed in the middle of the sample, followed by the casting and curing of a 0.24 mm thick layer of Ecoflex/red thermochromic/normal orange dye (mass ratio = 80:3:1) (red thermochromic pigment was from Acumind Pigments, Inc. and normal non-thermochromic orange dye was from Mineral Makeup, Inc.) followed by a 20 min UVO treatment (Novascan PSD digital UV ozone system). A layer of mirror chrome (containing metal flakes, from Spaz Stix, Inc.; thickness ≈ 40 nm) were then spray coated atop the Ecoflex® layer by an airbrush style spray-gun (Master Airbrush G444-SET, equipped with a 0.5 mm needle nozzle and a Royal Mini Air Compressor, TC-20B). A layer of TiO_2 (99.9%, CR828, Tronox) /polyvinyl butyral (PVB) (Mowital® B 60 HH, Kuraray, mass ratio of PVB/TiO_2= 4:1, 10 mg/mL TiO_2/PVB ethanol suspension) composite with a thickness of ca. 890 nm was then spray coated atop the mirror chrome forming a light shield layer. A layer of pure Ecoflex® (thickness ≈ 6.6 μm, 100 mg/mL of Ecoflex®/hexane solution) was then spray coated atop the TiO_2/PVB layer and then cured at 80℃ for 30 min followed by a 20 min UVO treatment. Subsequently, the green thermochromic pigment layer (thickness ≈ 3.3 μm, from Acumind Pigments, Inc.) was spray coated atop the cured Ecoflex® layer. Upon the removal of the stencil mask and another UVO treatment, a layer of uncured Ecoflex® with a thickness of ca. 0.28 mm was cast atop the pigment layer and the middle empty area (see Figure S9,†ESI) that used to be covered by the stencil mask, followed by curing at 80 °C for 2 h. The bilayer sheet was then carefully peeled away from the foundation followed by mounted on a custom-made stretcher with a size of 2.74 cm × 10.6 mm. A room temperature mist from a humidifier was applied on the PVA surface for 40 s followed by immediately stretching the bilayer into 15 cm (450% strain) and then drying. A stencil mask was applied atop the PVA surface followed by spray coating of a same thickness of flexible adhesive, silver epoxy, silver ink, and carbon ink layers as that for tactile switch. Subsequently, the PEDOT: PSS and RuO_2 (mass ratio of PEDOT:PSS/RuO_2= 8/2) was cast atop the carbon ink layer. The preparation of RuO_2 nanoparticles is the same as the sol-gel process and low-temperature annealing method previous introduced[29]. The sample was then released to form a tubular structure and the seam was sealed by a silicone adhesive followed by injecting 115 μL of ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$, Fisher Scientific, Inc.) inside the tube as electrolyte with the two ends of tubes also sealed.

Characterization. The optical microscope images of all the top-view morphology of the tubular devices were recorded on an optical microscope (AmScope ME 520TA, company) under reflective mode. Electrical resistance test was done using a Keithley 2400 measurement set-up or a VA38 high accuracy digital multimeter with USB interface. The mechanical pressure and corresponding compression distance measurement was conducted on an Instron 5860 universal testing system. The electrochemical performance of the dual-responsive supercapacitor was done on a CHI

660A electrochemical workstation. All the digital photos and movies were captured by an iPhone 6 Plus smart phone.

Simulation Method for the wrinkle-driven tubular structure with 450% pre-stretching strain. The curved tube response is simulated through a nonlinear analysis using the commercial finite element software, ABAQUS (version 6.14-2). The bilayer material is modeled as a 3D solid shown in Figure S24,†ESI and meshed using the 8-node linear brick, hybrid, constant pressure element, C3D8H. The wrinkles are captured in the experiments once the bilayer system is released due to the compression developed in the PVA film. In the simulation, it is assumed that the wrinkled film cannot take any compression load along the *x*-direction shown in Figure S24,†ESI. Rebars are used to mimic the mechanical behavior of the wrinkled surface. The thickness of the rebar (t) is the same as that of the PVA film. The spacing and the area of the rebars are computed using Eq. (1) and (2), respectively. The spacing (s) between the rebars is equal to the wavelength of the wrinkles (λ). A is the area per bar.

$$s = \lambda = 2\pi t\left(\frac{\bar{E}_f}{3\bar{E}_s}\right)^{1/3} \qquad \text{Eq. (1)}$$

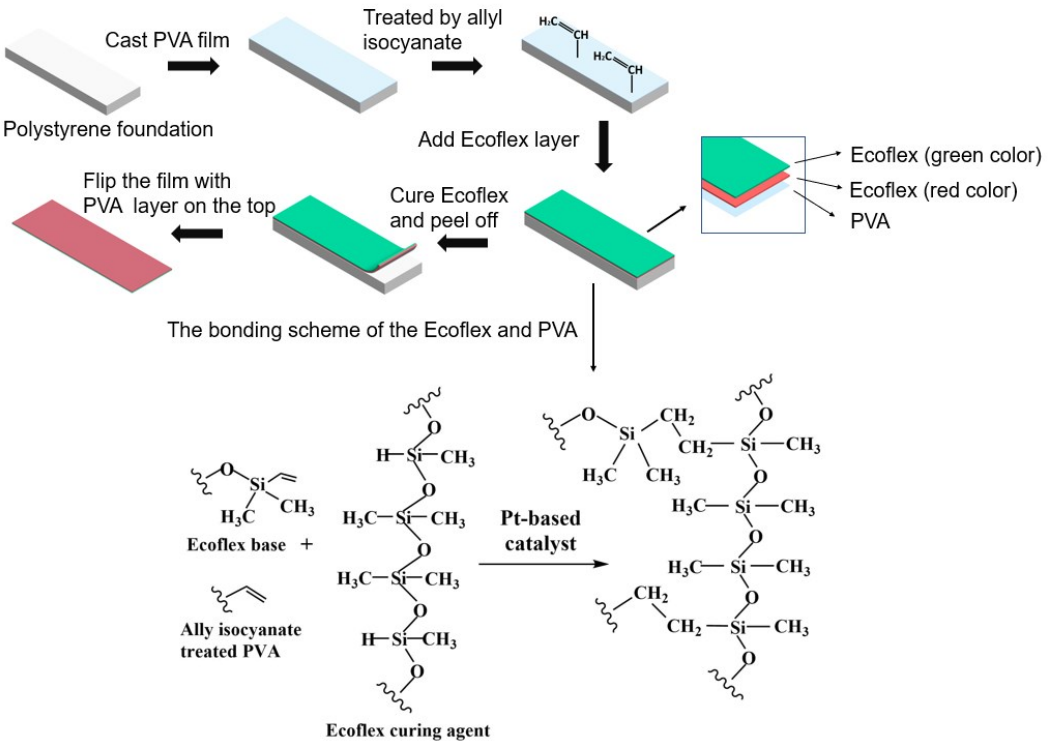
$$A = \lambda t \qquad \text{Eq. (2)}$$

The material properties for the rebars are the same as those of the PVA. The substrate is modeled as a hyperelastic material using the neo-Hookean model. The material constants used in the simulation are listed in the Table S1. The pre-stretching of the bilayer material system is modeled as a pre-defined stress field along the *x*-direction. The pre-defined stress is computed using Eq. (3) based on the uniaxial tension response of the neo-Hookean material.

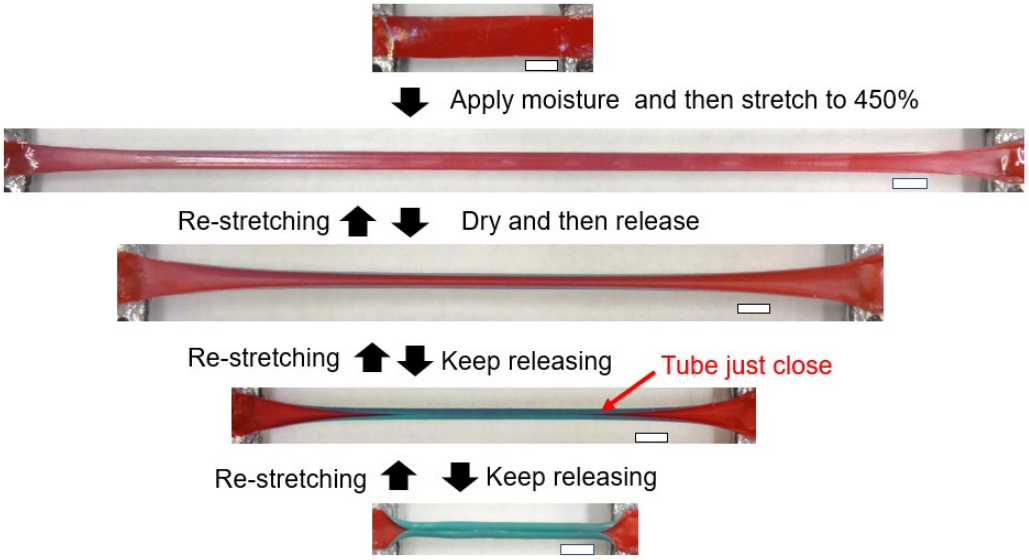
$$\sigma_{xx} = \frac{2C_1}{J^{5/3}}\left(\lambda^2 - \frac{J}{\lambda}\right) \qquad \text{Eq. (3)}$$

Here, σ_{xx} is the Cauchy stress serving as the pre-defined stress, λ is the pre-stretch ratio, and J is the volumetric change ratio which is solved based on Eq. (4).

$$D_1 J^{8/3} - D_1 J^{\frac{5}{3}} + \frac{C_1}{3\lambda} J - \frac{C_1 \lambda^2}{3} = 0 \qquad \text{Eq. (4)}$$



(a)



(b)

Figure S1 | Schematic and fabrication of tubular structure. (a) Schematic of the steps to prepare PVA-Ecoflex® bilayer with covalent bonding. (b) Digital photos of the fabrication of the wrinkle-driven tubular structure with only PVA-Ecoflex (450% strain of pre-stretching, scale bar = 5 mm)

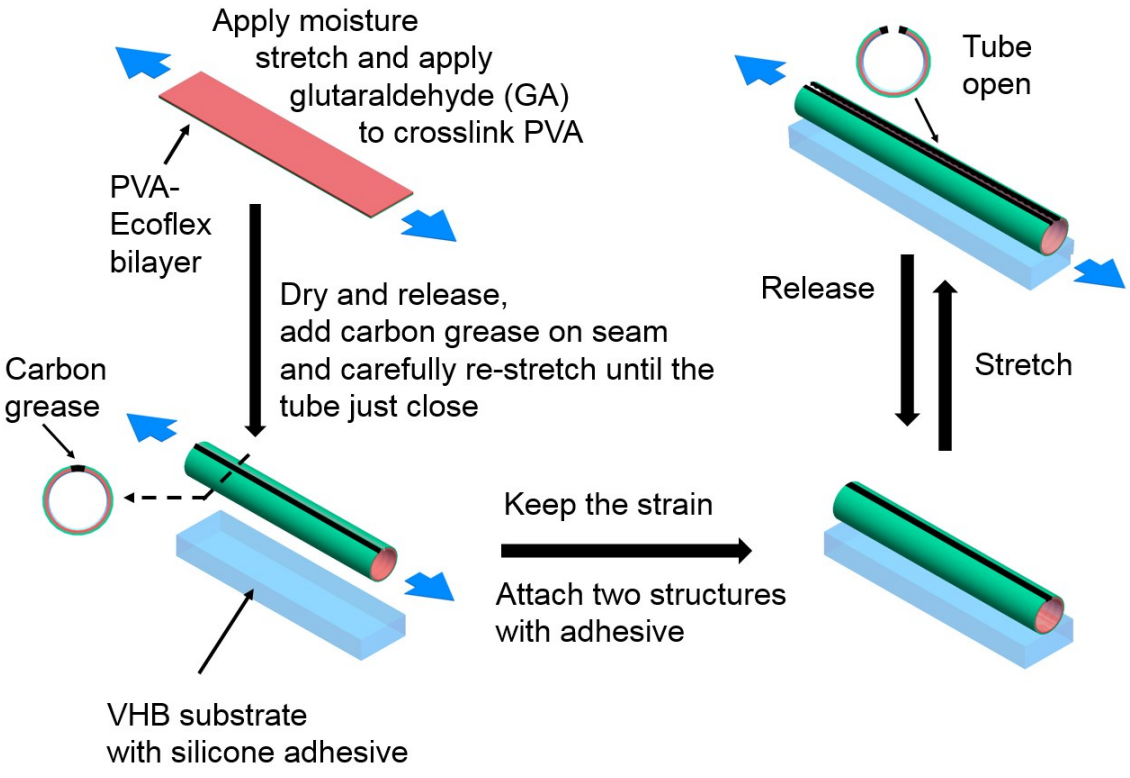


Figure S2 | Schematic of the preparation steps for the tubular strain sensor/switch.

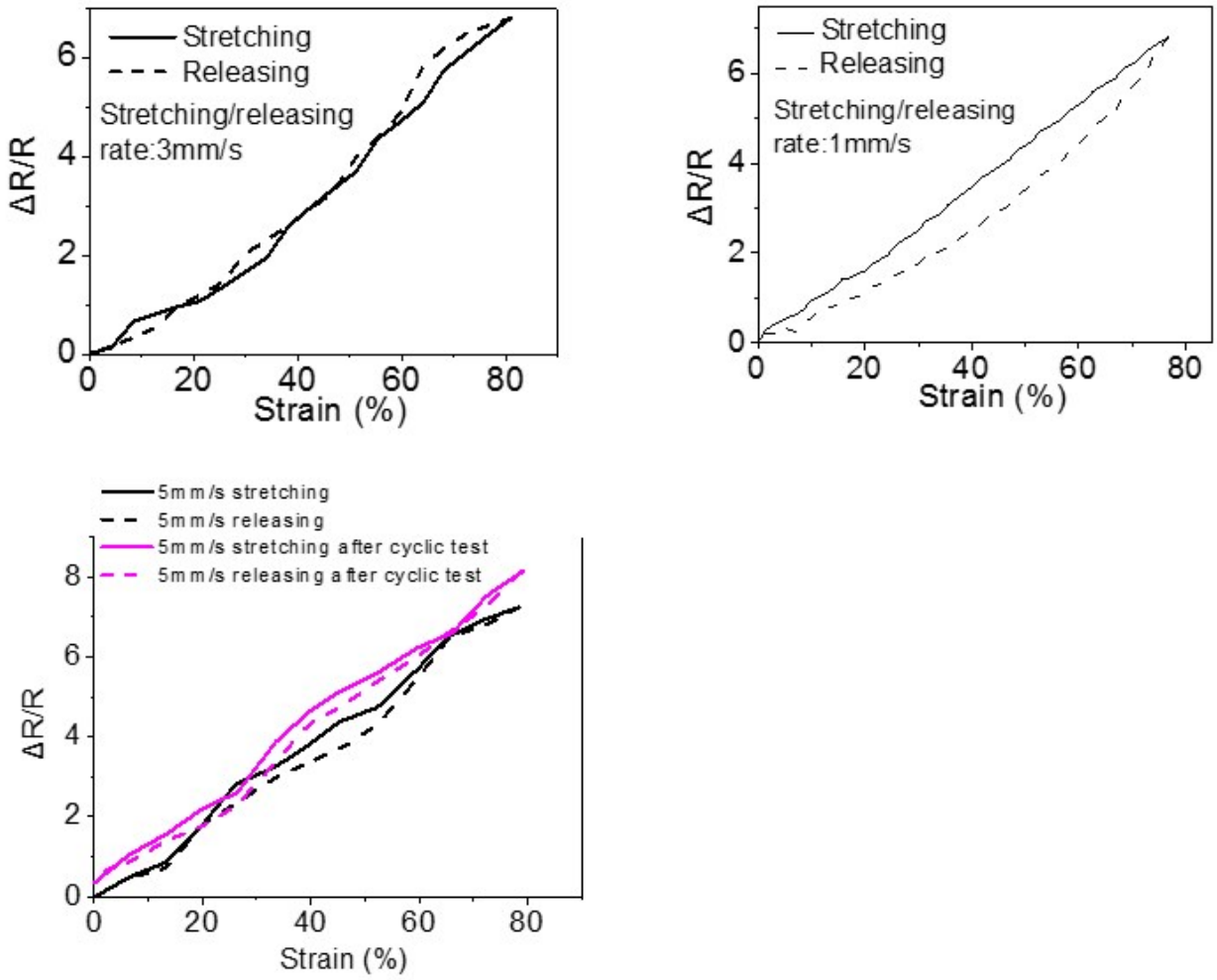
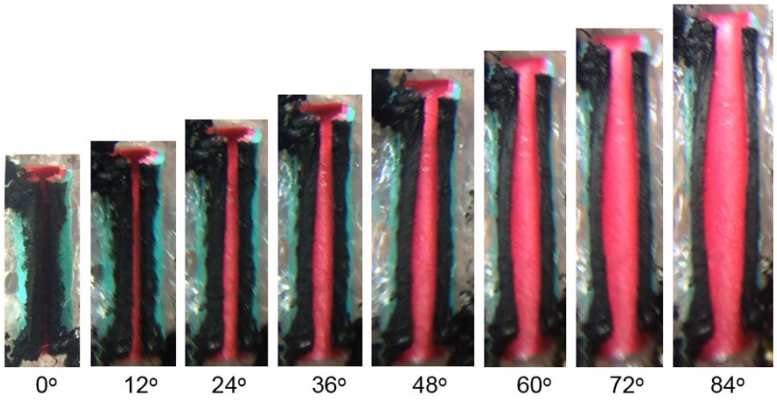
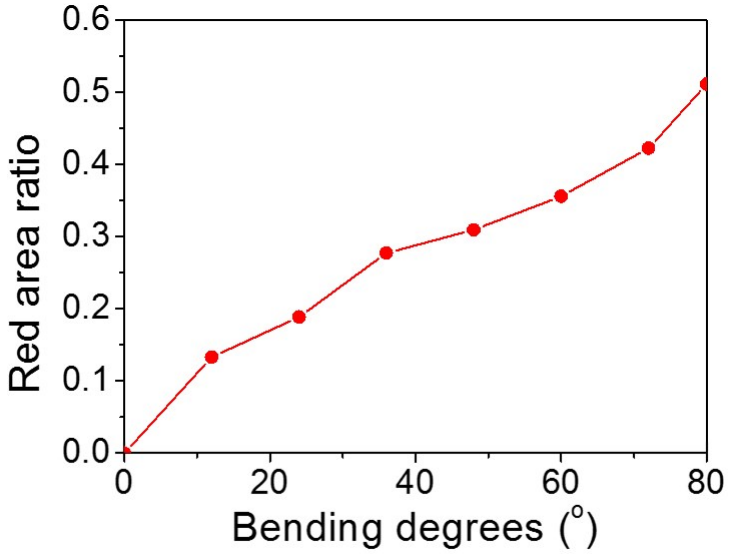


Figure S3 | Resistance of point 1 to point 3 piezoresistive performance with different stretching/releasing rates of the tubular strain sensor/switch (for the cyclic test, the sample was stretched/released between 0% and 80% strain for 1000 times).



(a)



(b)

Figure S4 | Mechanochromic effect of the dual channel piezoresistive tubular strain sensor/switch. (a) Digital photos of the mechanochromic effect because of tube opening as a function of finger bending degree (scale bar = 1 mm); and (b) ratio of the red color area to the total device top view area as a function of bending degree.

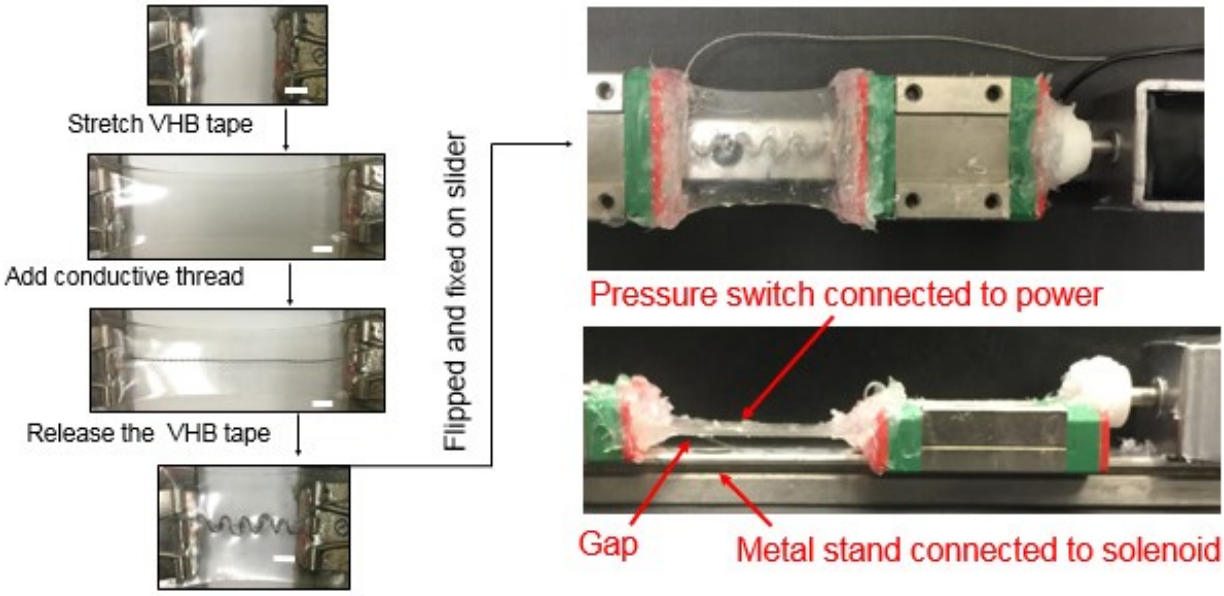
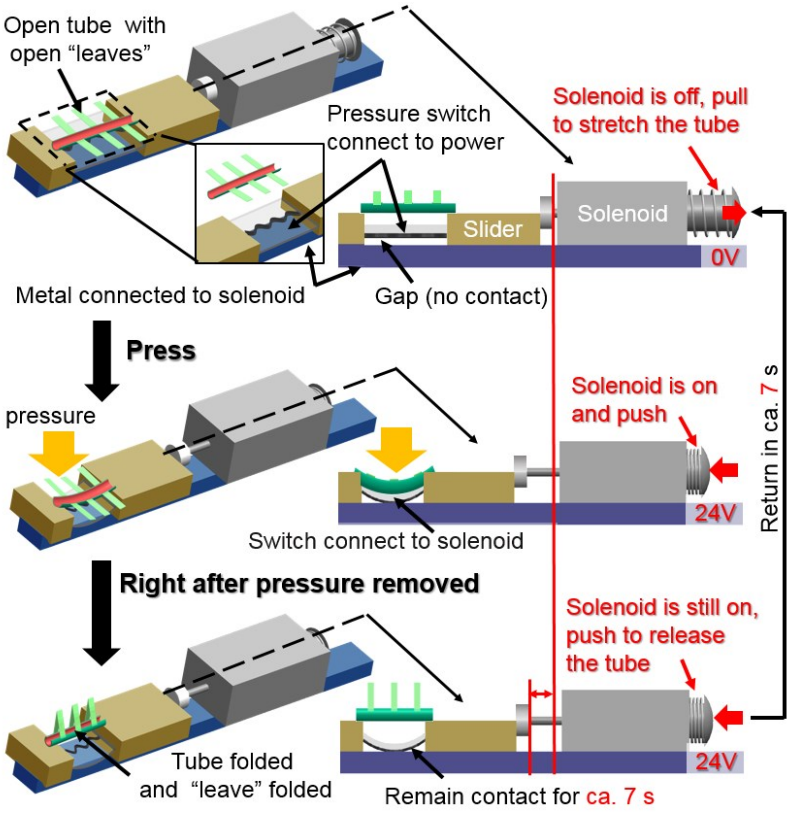
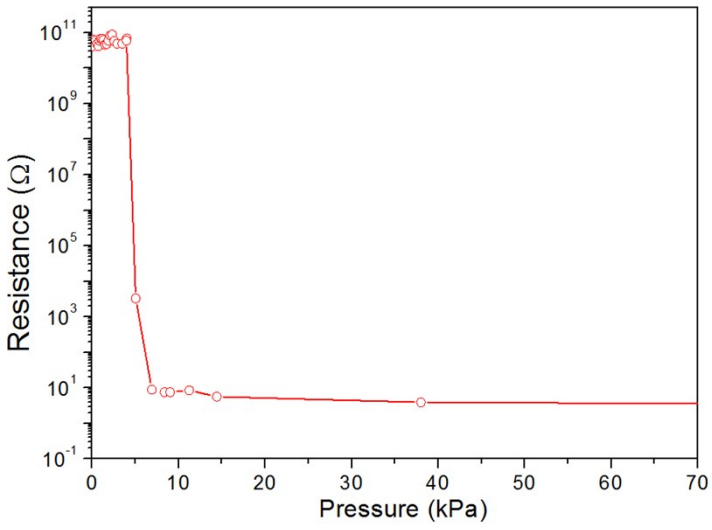


Figure S5 | Digital photos showing the preparation of the pressure switch and the installation of the pressure switch and solenoid on the slider (scale bar = 5 mm).



(a)



(b)

Figure S6 | Design and properties of artificial *mimosa pudica*. (a) Working mechanism of the artificial *mimosa pudica* and (b) resistance response to pressure of the pressure switch device applied on the artificial *mimosa pudica*.

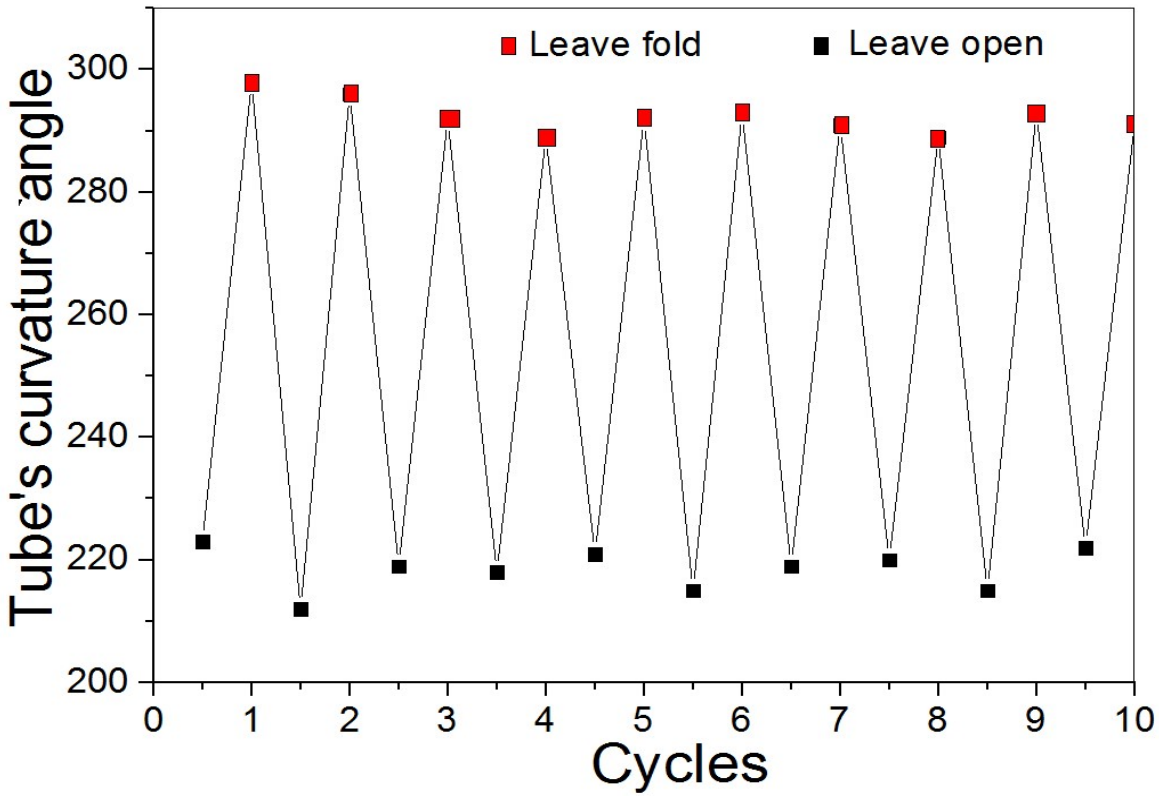
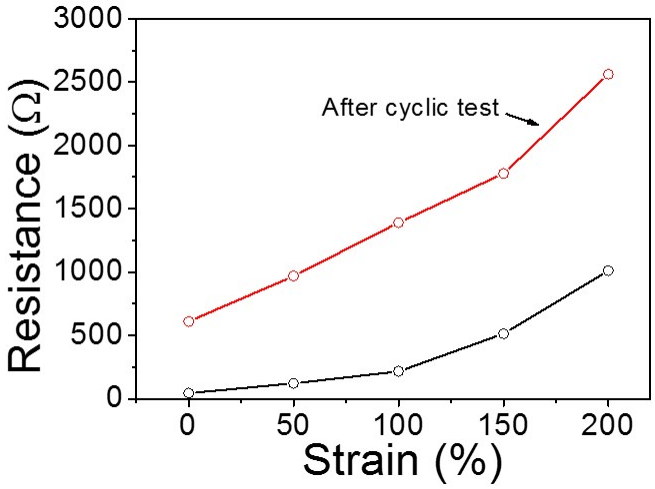
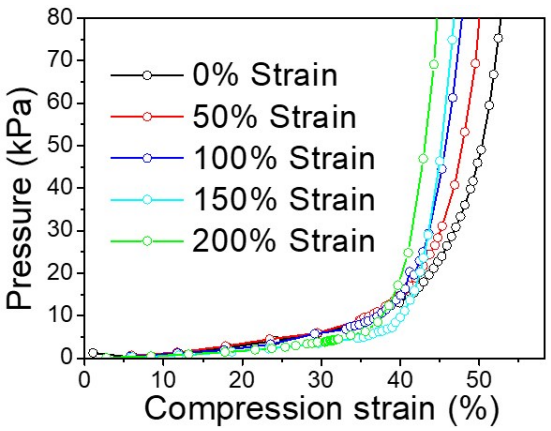


Figure S7 | Change of the curvature angle with multiple circles of leave folded and open in artificial *mimosa pudica*.



(a)



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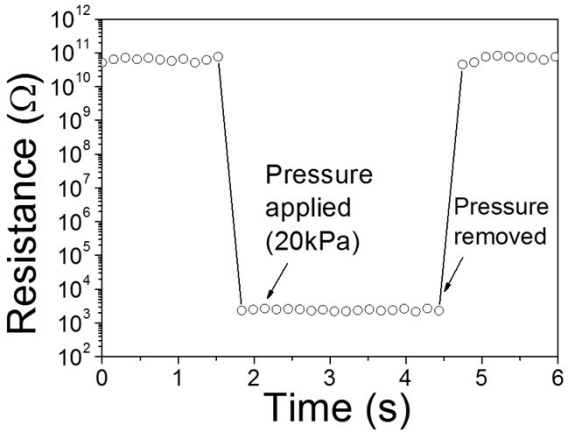

(c)

Figure S8 | Performance of highly stretchable tubular tactile switch. (a) Resistance of the silver and carbon electrode for the tactile switch as a function of strain and the performance after cyclic test (stretching/releasing between 0% to 100% strain for 1000 times). (b) Pressure as a function of compressing strain in the *z* direction for the tubular tactile switch. (c) Response time performance of the tactile switch.

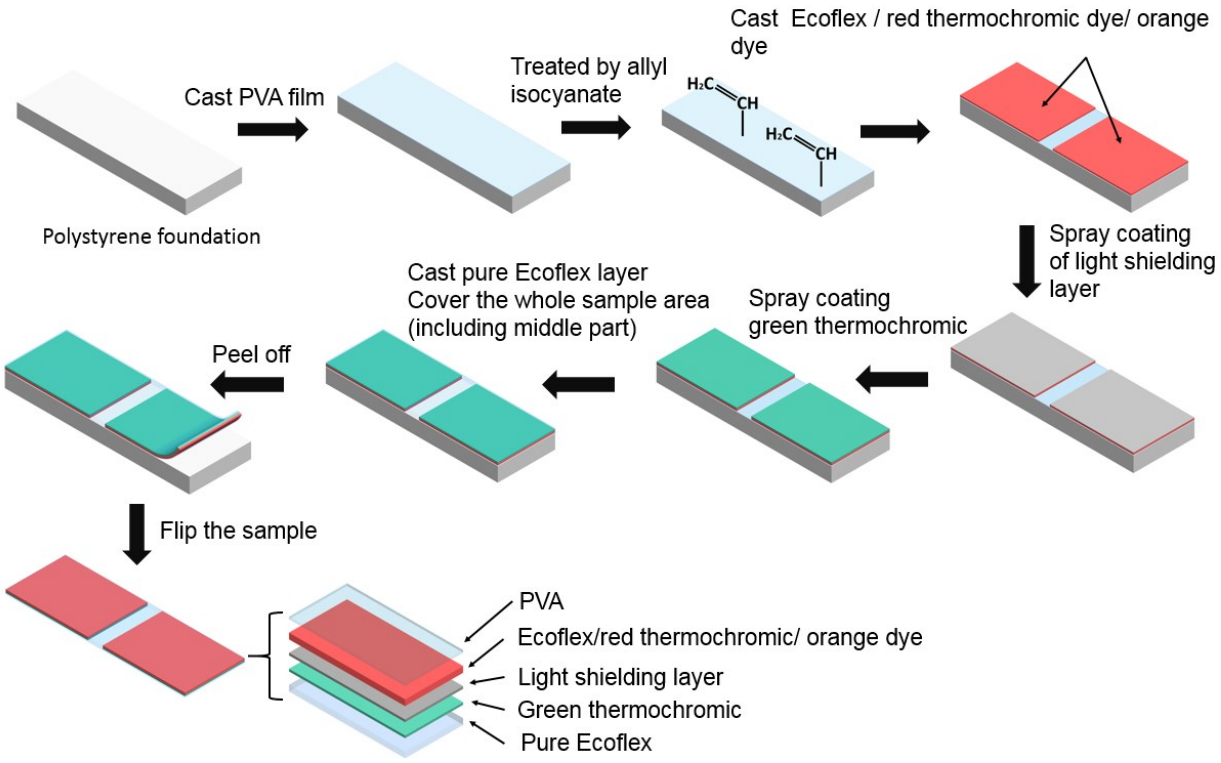

Figure S9. | Schematic of the steps to prepare PVA-Ecoflex film-substrate system with dual responsive chromic skin as the building block for the tubular supercapacitor.

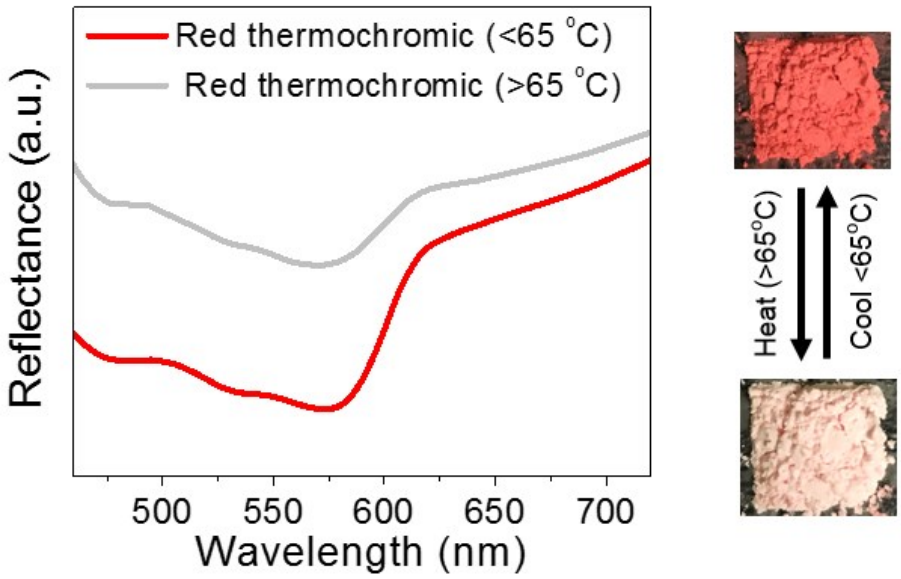

Figure S10. | Reflectance spectra and the digital photos of the thermal responsive behavior of the red thermochromic pigment.

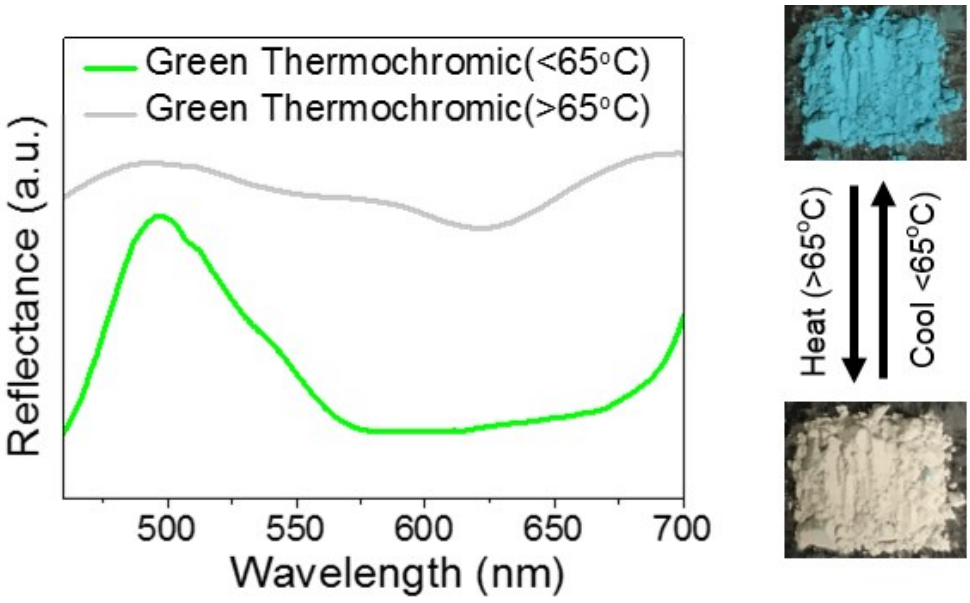

Figure S11. | Reflectance spectra and the digital photos of the thermal responsive behavior of the green thermochromic pigment.

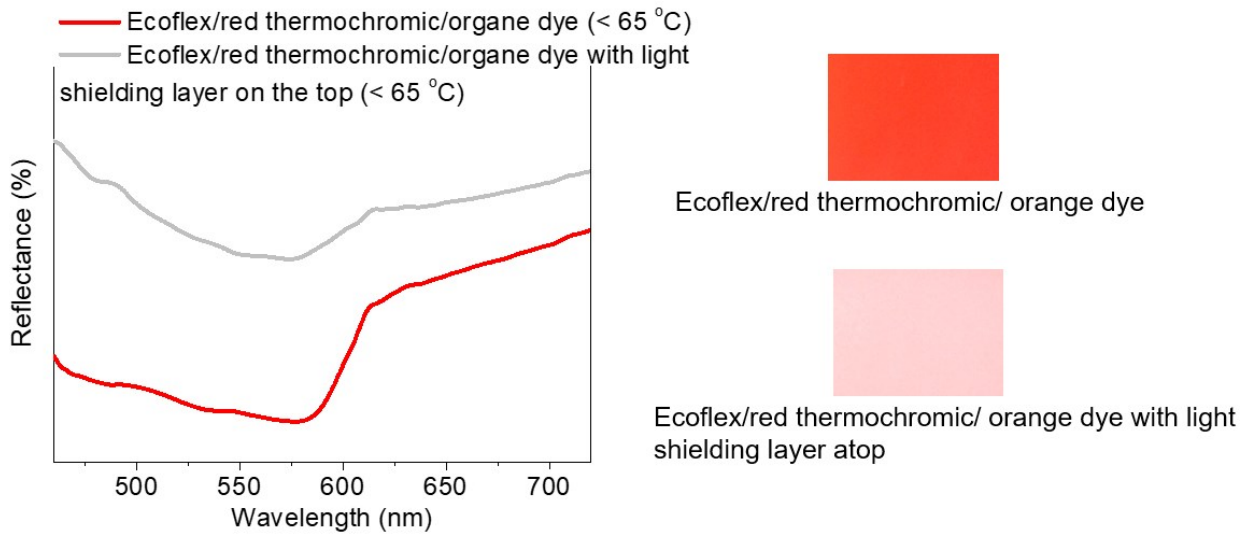

Figure S12. | Reflectance spectra and the digital photos of the light shielding effect as the light shielding layer spray coated atop the Ecoflex/red thermochromic/orange dye substrate.

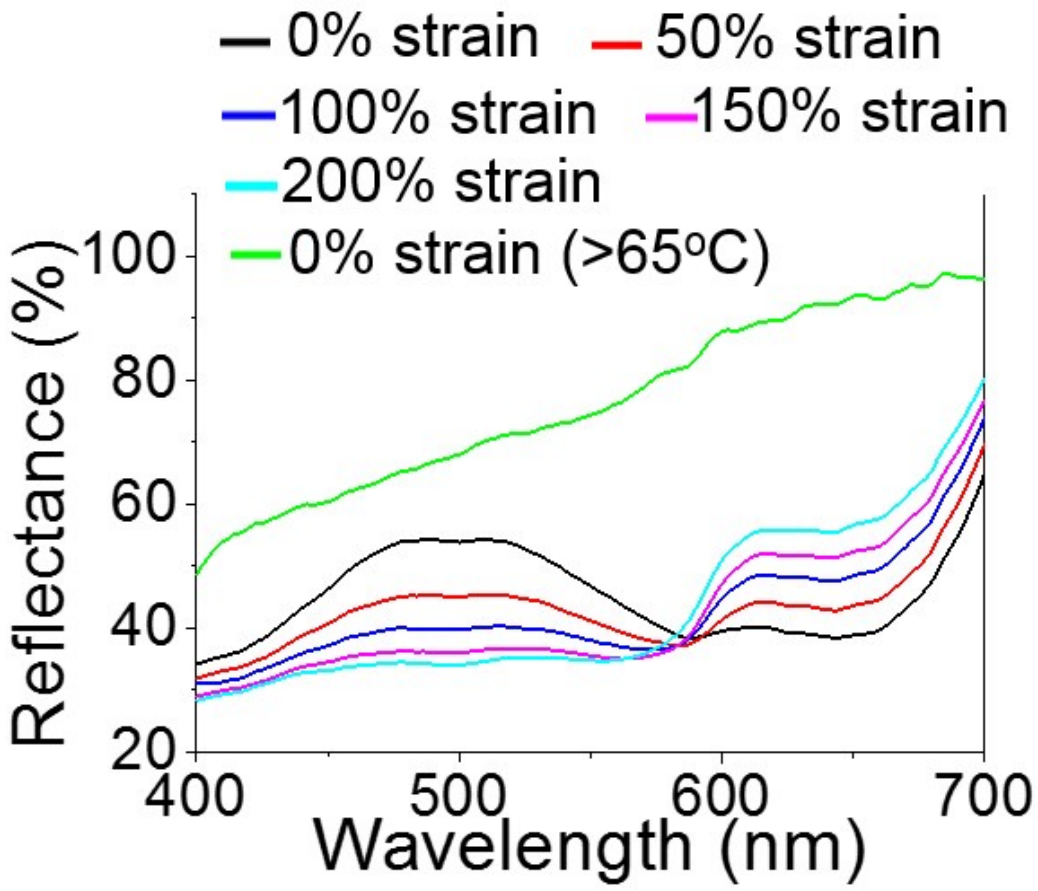

Figure S13. | Reflectance spectra of the dual stimuli responsive behavior of the chromic skin of the tubular supercapacitor

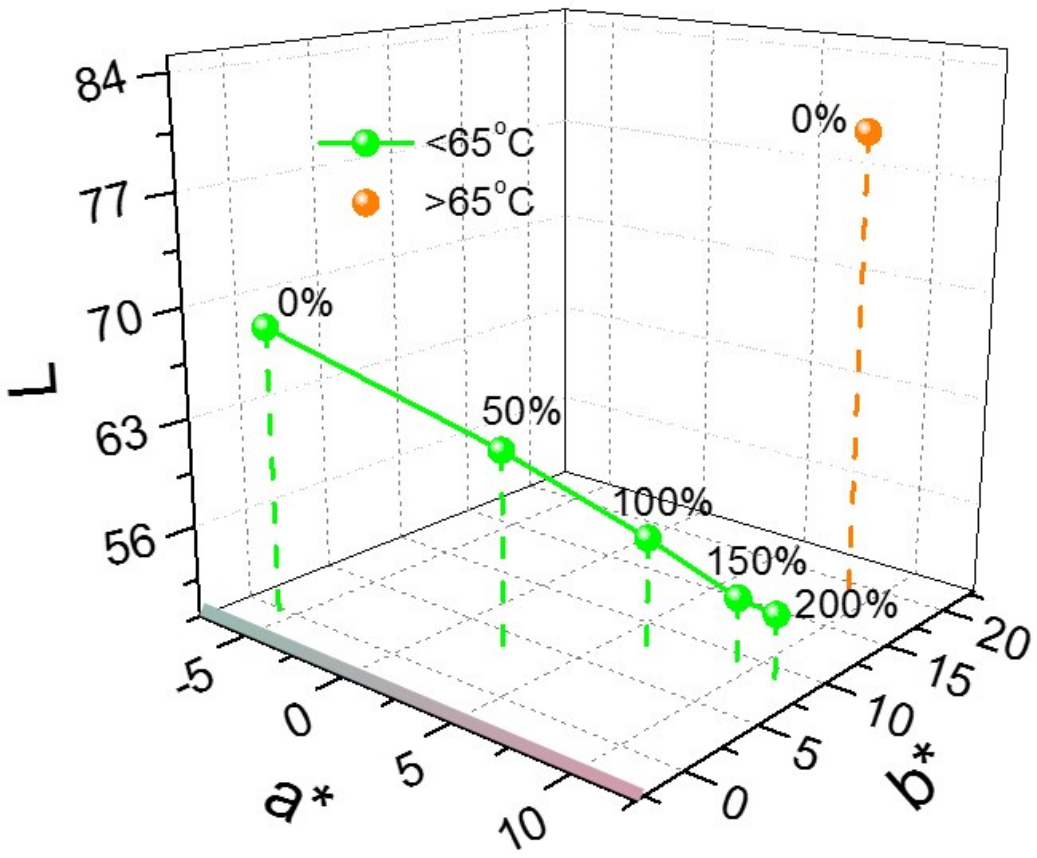

Figure S14. | La*b* color coordinate for the dual stimuli responsive behavior of the chromic skin of the tubular supercapacitor. The CIE La*b* color coordinate is a color space describing all the visible colors by a combination of L (lightness, value ranging from 0 to 100), a* channel (indicating the level of green to red, ranging from -128 to 127, a higher a* value exhibiting a higher red extent), b* channel (indicating the level of blue to yellow, ranging from -128 to 127).

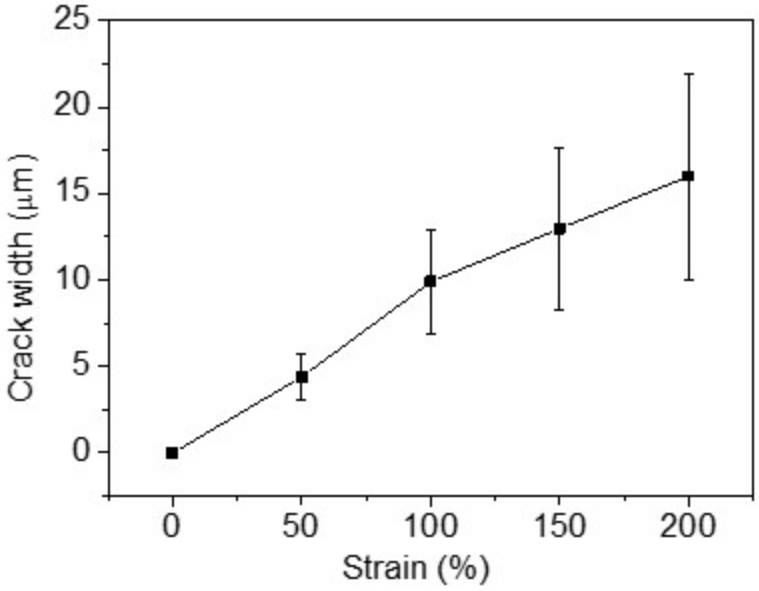

Figure S15. | Crack width of the light shielding layer as a function of stretching strain in the *x* direction.

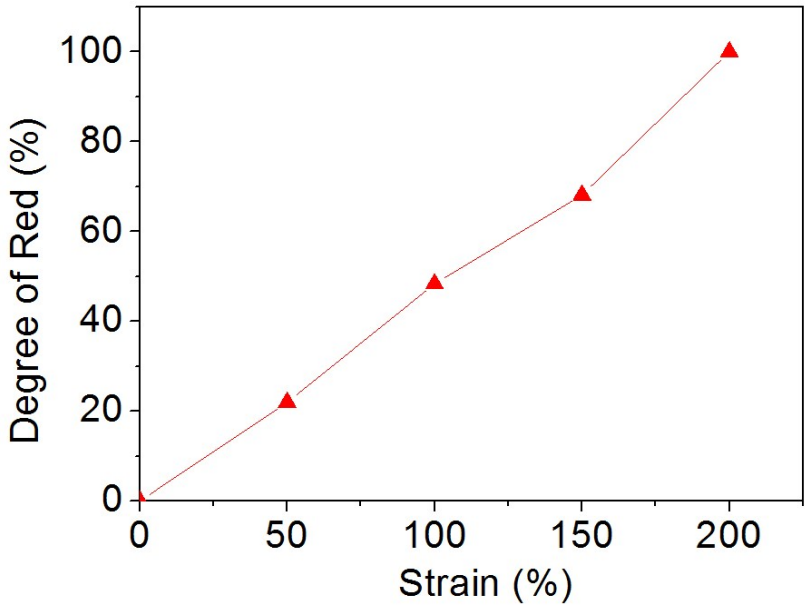

Figure S16. | Degree of red of the chromic skin as a function of stretching strain in the *x* direction. The degree of red (D_{red}) is defined as $D_{red} = 100\% * |a_{x\%} - a_{0\%}| / |a_{200\%} - a_{0\%}|$, where $a_{x\%}$, $a_{0\%}$, and $a_{200\%}$ is the a value of the La*b* color coordinate of the chromic skin at x% strain, 0% strain and 200% strain, respectively).

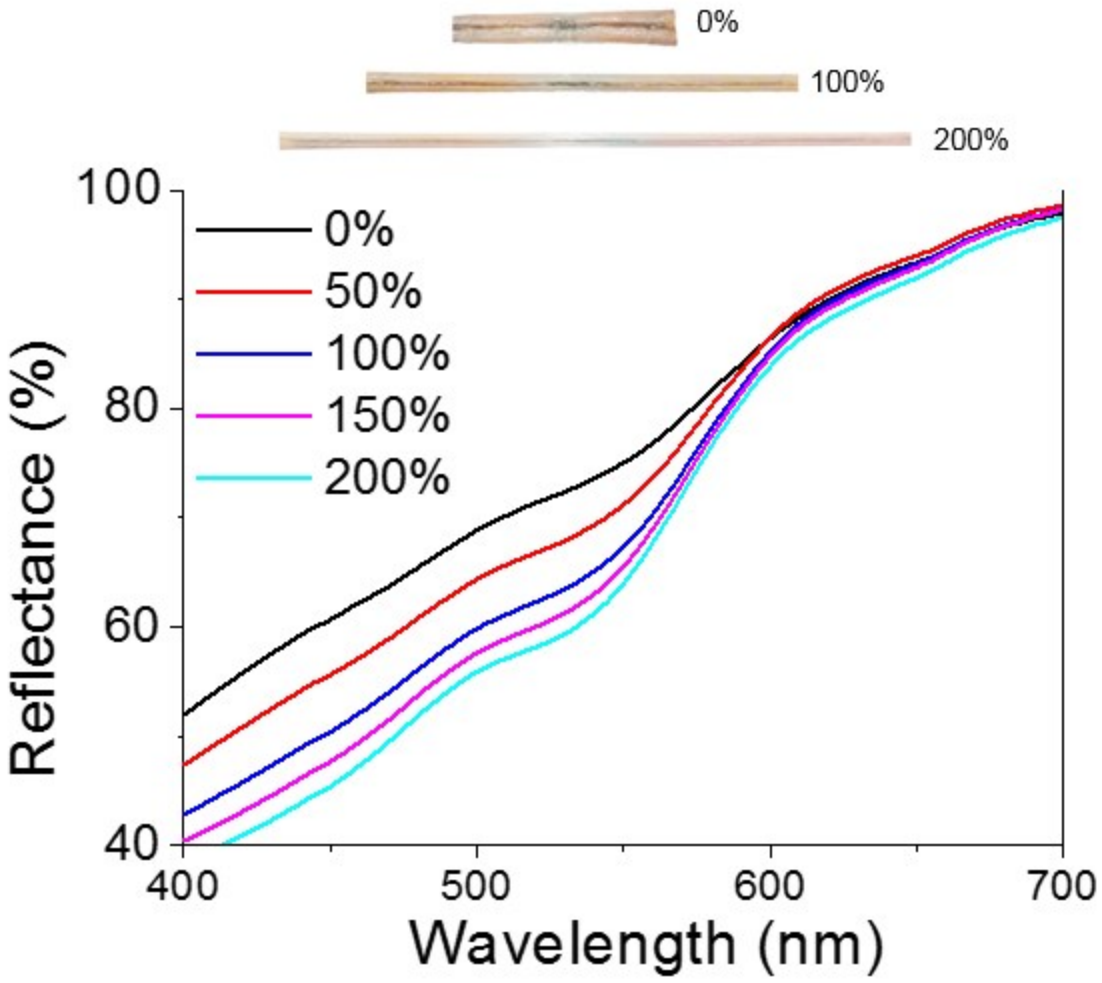

Figure S17. | Digital photos and reflectance spectra of the chromic skin of the tubular supercapacitor as stretched under T > 65℃ from 0% to 200% strain.

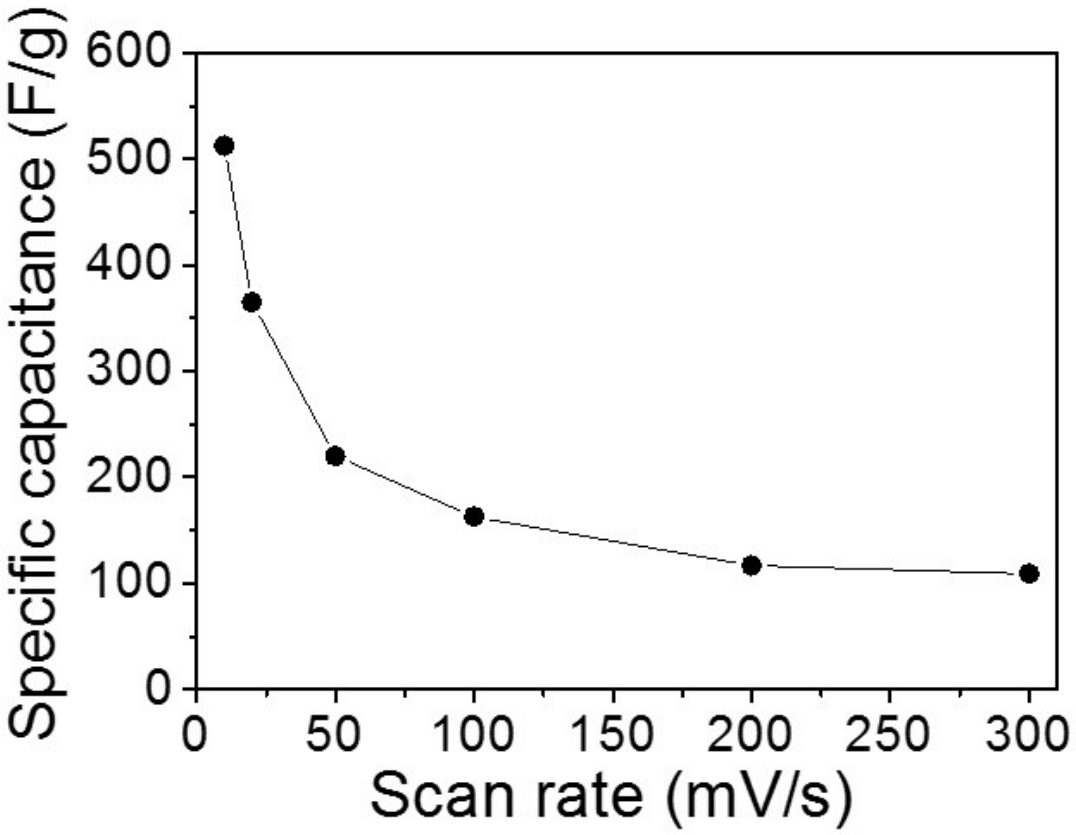

Figure S18. | Specific capacitance of the tubular supercapacitor (at 0% strain) as a function of different scan rates obtained from the cyclic voltammetry (CV) test.

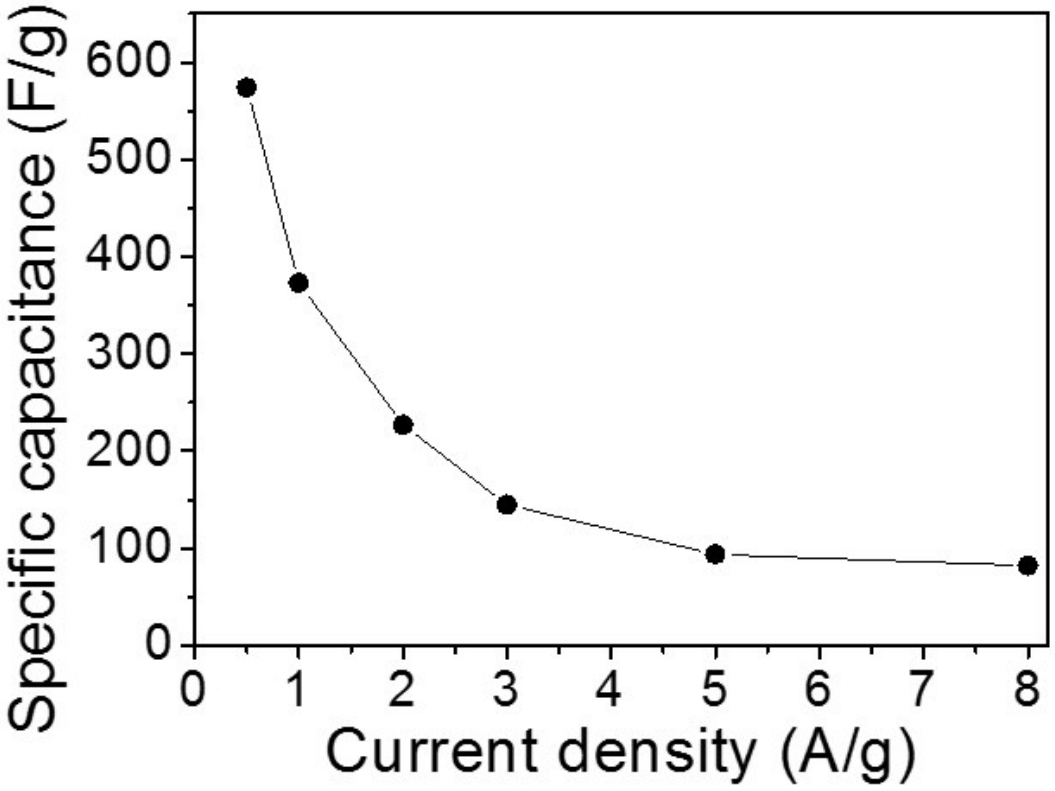

Figure S19. | Specific capacitance of the tubular supercapacitor (at 0% strain) as a function of current density obtained from the galvanostatic charge-discharge test.

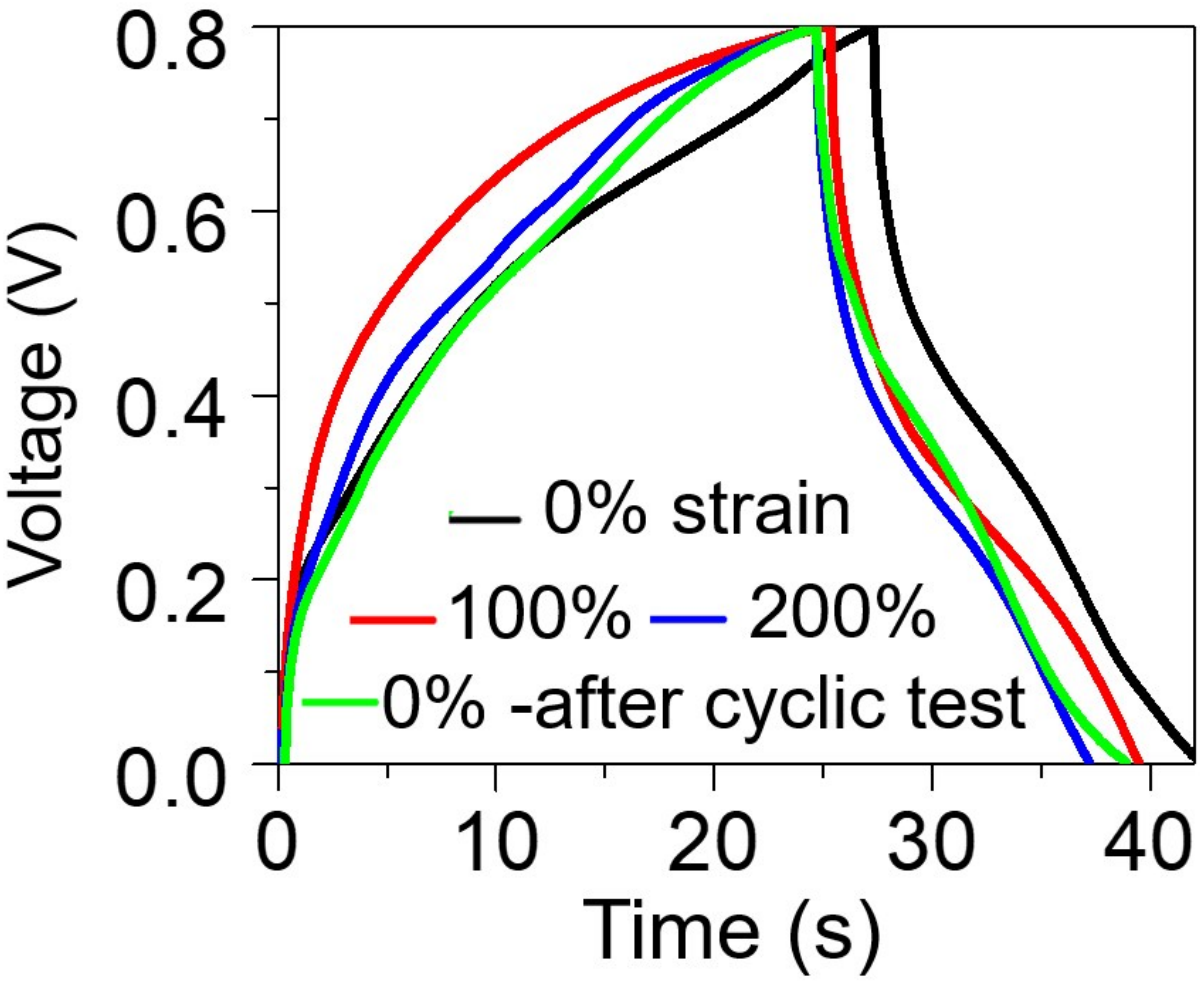

Figure S20. | Galvanostatic charge-discharge curves of the tubular supercapacitor at different stretching strains and the corresponding performance after cyclic test (stretching/releasing the tubular supercapacitor from between 0% to 100% strain for 1000 times).

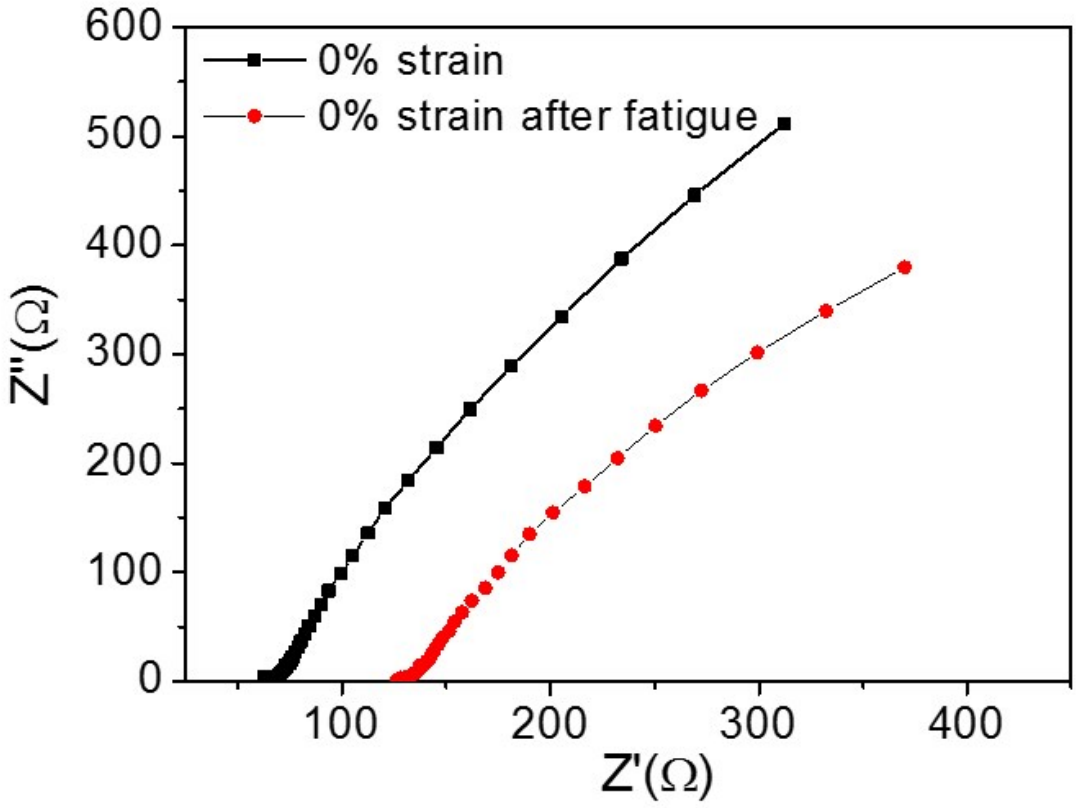

Figure S21. | Nyquist plots of the tubular supercapacitor at 0% strain before and after cyclic test (stretching/releasing the tubular supercapacitor between 0% to 100% strain for 1000 times).

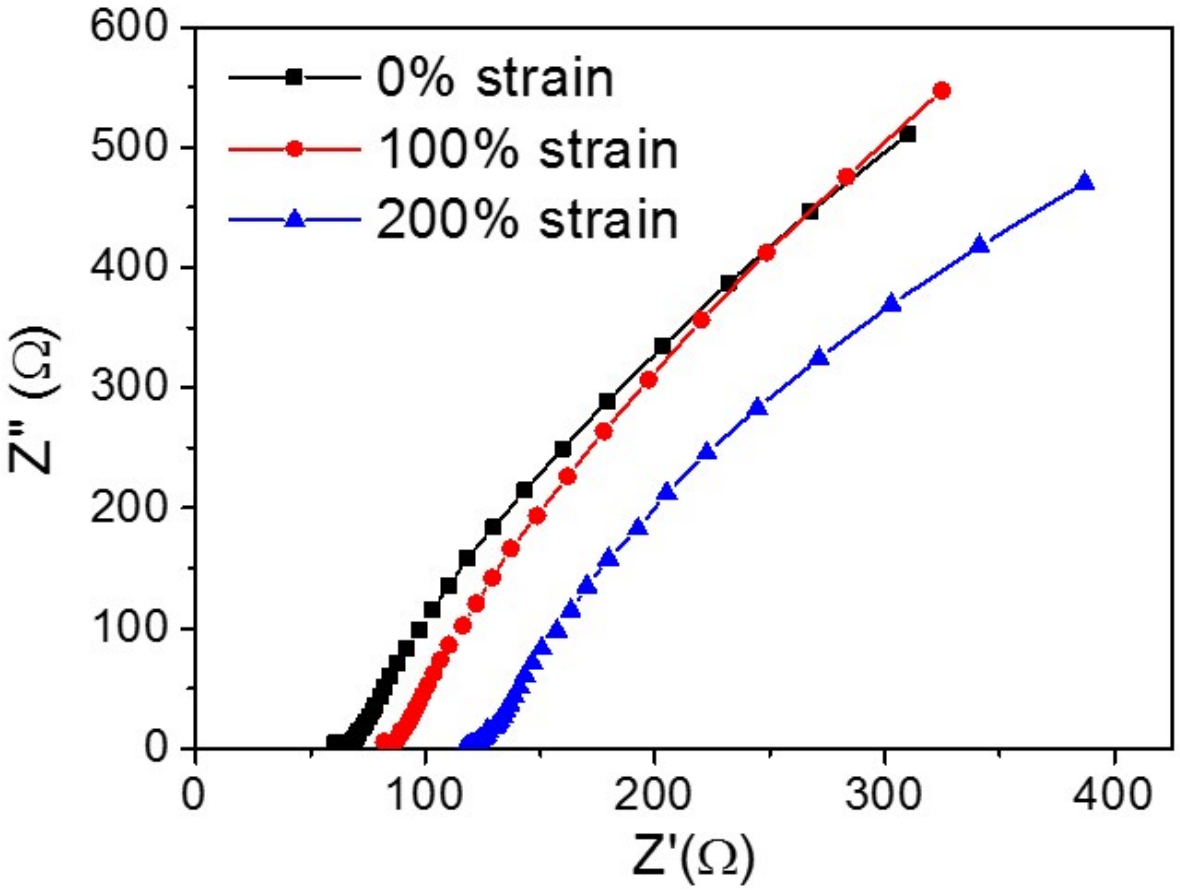

Figure S22. | Nyquist plots of the tubular supercapacitor at different stretching strains.

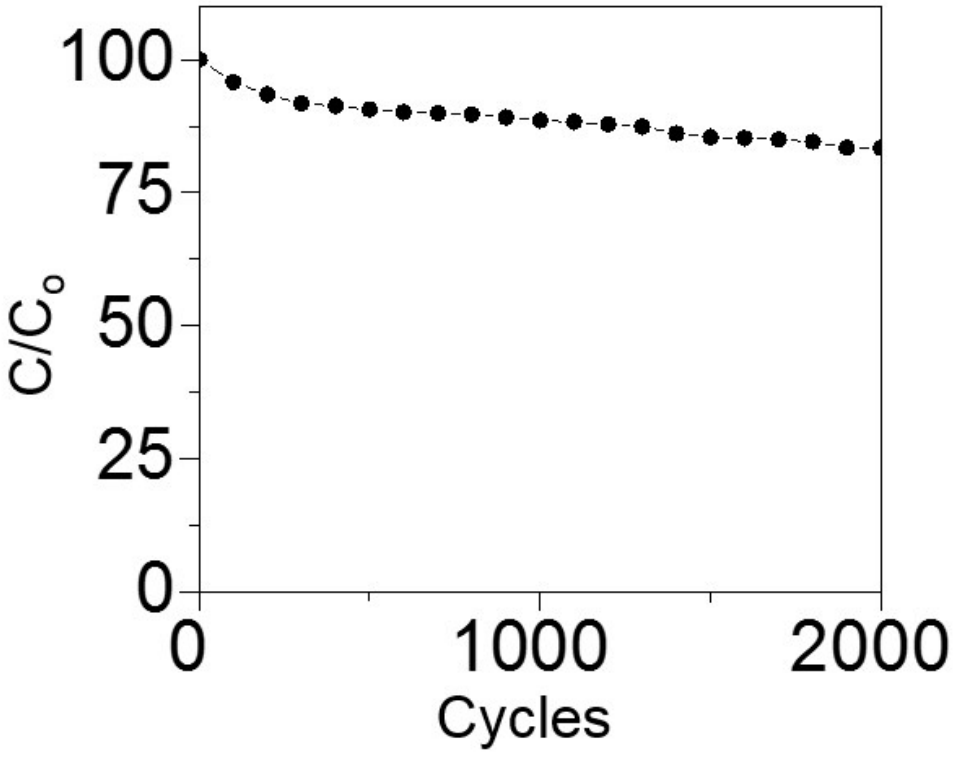

Figure S23. | Specific capacitance retention as a function of cycle number at a current density of 5 A/g.

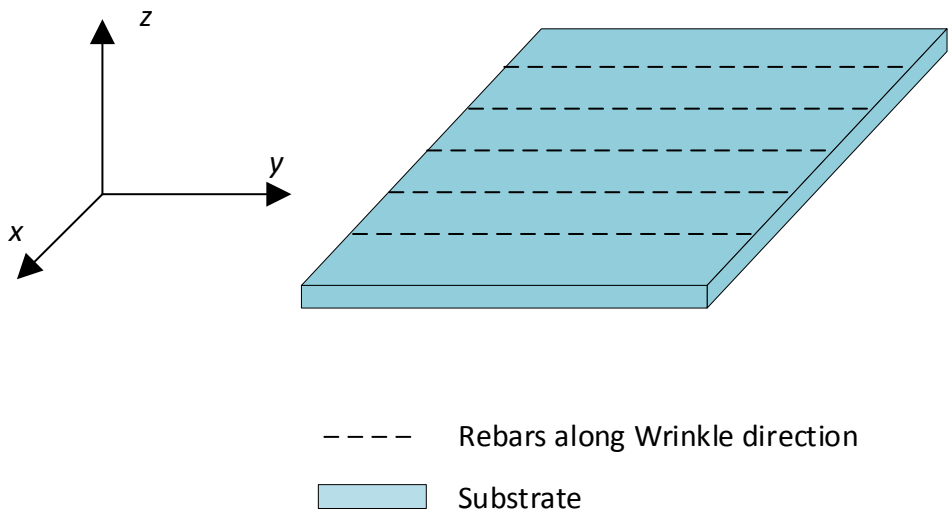

Figure S24 | Schematic for the FE model.

Table S1 | Material properties used in the simulation.

		Value	Unit
Rebars	Young's modulus	1000	MPa
	Poisson's ratio	0.3	-
Substrate	C_1	0.03	MPa
	D_1	0.0001	MPa^{-1}

Movie captions:

Movie S1. Formation of the wrinkle-driven tubular geometry from the strain relaxation (pre-stretching strain 450%) of the PVA- Ecoflex® bilayer structure.

Movie S2. Performance of the dual-channel piezoresistive tubular strain sensor/switch.

Movie S3. Performance of the artificial *mimosa pudica*.

Movie S4. Performance of the highly stretchable tubular tactile switch.

Movie S5. Performance of the dual responsive skin of the tubular stretchable supercapacitor.