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Abstract

Advanced flexible, stretchable and sensitive strain sensors are essential components of wearable electronic devices and technologies. Here, we illustrate our patented technology for creating ultra-stretchable and conductive materials applicable for stretchable electronic technologies. A simplified, two-step manufacturing process exploits the hierarchical self-assembly of a functionalized, commercially available triblock copolymer in a protic ionic liquid, followed by photo-induced chemical crosslinking to create an iono-elastomer with remarkable mechanical and electrical properties. The synthesis is very robust with nearly 100% conversion and 90% yield. The resulted materials exhibit an unprecedented combination of high stretchability (elongation at break is 3000% and tensile strength is 200 MPa), tunable ionic conductivity and mechano-electrical response. The stretchability is about one order of magnitude higher than a typical crosslinked rubber. Importantly, the material's conductivity *increases* with extension, a unique and non-trivial material response, whose origin derives from the nanoscale microstructural rearrangements under stretching deformation. Building upon this novel iono-elastomer, we created the "Motion Strain Patch" (MSP), which is the first, high strain amplitude stretchable resistive strain sensor patch. As the MSP can be easily mounted on clothing or adhesively attached to body to measure the local displacement of specific body parts under motion, potential applications include: biomechanical motion capturing, sports performance tracking and rehabilitation monitoring. This article will also outline the potential benefits and impacts provided by our invention to the economy, the environment and the society. MSP is not a replacement to existing wearable products in the market, but a superior complement to existing performance optimizing wearable technology.

Key words: wearable electronics, iono-elastomer, ionic liquid, block copolymer, stretchable strain sensor

Introduction

Recently, numerous efforts have been made on research and development of wearable, flexible, stretchable and sensitive strain sensors, due to their applications in monitoring personal health[1] and structural health[2] monitoring, rehabilitation monitoring,[3,4] sports performance monitoring,[5,6] human motion capturing for entertainment systems (e.g., motion capture for games and animation),[7–10] robot control and robotic skin (or electronic skin),[11–13] etc. In particular, highly stretchable and sensitive strain sensors are required in biomechanics, physiology, and kinesiology applications where very large strain should be accommodated by the sensors.[9]

Motion capture, especially, can be commonly found in surveillance, military, entertainment, sports and medical applications.[14,15] Conventional human motion capture is primarily based on optical systems, inertial sensors, magnetic systems or mechanical systems. Optical systems, which are intensively studied and widely used, typically come in two categories: systems with markers and systems without markers. Marker systems require very complex equipment, special environment, and are financially and spatiotemporally expensive. Markerless systems, while more convenient and more broadly applicable, have many drawbacks, such as requiring further digital processing using complex algorithms and sensitivity to the environment of use, and are generally not as accurate as marker systems. A review of these and other prevalent methods provides an overview of the advantages and drawbacks of the current methods.[16] Improvements that can reduce cost, shrink the size/volume of the device, and minimize the influence on performers while maintaining accuracy are highly desired. As body motion can often involve relatively large strains ($\geqslant$

55%),[17,18] a possible solution is the creation of new ***wearable, flexible and highly extensible strain sensors.***

The design criteria for high-performance wearable, flexible and stretchable strain sensors including high sensitivity (i.e., large gauge factor (GF) for measuring small human motions), high flexibility and high extensibility (capable of accommodating elongational strains of ⩾ 55%), good stability (capable of measuring repetitive deformations with low hysteresis), fast response speed (fast signal acquisition), low material and fabrication cost and technical simplicity, lightweight and small size, and biocompatibility for skin-mountable applications and comfortable to wear.[19,20] Although conventional strain sensors have advantages in low fabrication cost, they typically have poor stretchability and sensitivity (maximum strain of 5% and GF ~ 2). Recent advances on creating advanced strain sensors have focused on nanomaterials, e.g., graphene,[18,21,22] carbon nanotubes,[17,19,23] nanoparticles[24] and nanowires.[8] Among them, carbon nanomaterial based sensors have shown outstanding performance as highly sensitive strain sensors.[10,18,25] For example, a recently reported carbon nanotube–silicone rubber based strain sensors can be stretched to maximum strain of 500% with a good reversible response.[26]

Herein, we describe the invention of a simplified, two-step manufacturing process to create ultra-stretchable materials with tunable conductivity that are particularly applicable for wearable electronics and associated technologies. At the heart of the fabrication of this novel iono-elastomer is the nanoscale, hierarchical self-assembly of functionalized, commercially available, polymers in a protic ionic liquid, followed by chemical crosslinking. The invention uses this novel iono-elastomer to create a transparent, lightweight, customizable and skin mountable strain sensor patch. The potential for commercialization, including market size and competitive landscape, and potential benefits to society of this invention are presented and discussed.

Description of ultra-stretchable conductive iono-elastomer invention

The raw materials were down selected for creating the highly stretchable, conductive material spontaneously self-assemble at the nanoscale to form a hierarchically-microstructured iono-elastomer. A commercial triblock copolymer (Pluronic F127)[27], which is macromolecule with linear and/or radial arrangements of two or more different blocks of varying monomer compositions is selected for the mechanical building block.[28] Block copolymers can impart mechanical strength to the system via self-assembly in suitable self-assembly media, as shown in Figure 1 (a).[29] Conductivity is provided by ethylammonium nitrate (EAN)[30], which is a room temperature, protic ionic liquid. An ionic liquid is chosen for its remarkable physio-chemical properties: high ion conductivity (up to 100 mS/cm) with wide electrochemical windows (up to 5.8 V), and high electrochemical and thermal stability.[31] Furthermore, it has negligible vapor pressure, which implies that it does not evaporate at any service temperature.[32,33] Importantly, EAN can also act as an effective self-assembly media for the block copolymer.[34] In addition, both block copolymers and ionic liquids are two representative classes of "designer compounds", meaning that specific combinations selected from the related classes of block copolymers and ionic liquids can be used to tune the iono-elastomer's physical and chemical properties. The variety and variability of raw materials will not only cultivate diversity in our product and prototype invention, but also leads to manifold commercialization streams.

Utilizing the selected raw materials, we have successfully demonstrated a simplified manufacturing process to create stretchable conductive materials applicable for stretchable electronic technologies by self-assembly of concentrated solutions of end-functionalized commercially available, inexpensive triblock copolymer, Pluronic F127, in a protic ionic liquid, EAN, followed by micelle corona crosslinking to generate elastomeric ion gels, termed "iono-elastomers".[35,36] The chemical structures of Pluronic F127 and EAN are presented in Figure 2 (a) and (b), and a schematic of the synthesis and fabrication of the Pluronic F127 diacrylate, iono-elastomer are shown in Figure 2 (c), (d), and (e). As shown in Figure 2 (e), the resulted material is an optically clear, free-standing elastomer, which is our "iono-elastomer". This particular iono-elastomer exhibits an unprecedented combination of high stretchability, tunable ionic conductivity and mechano-electrical response.[36] Figure 3 demonstrates the stretchability of iono-elastomer by stretching, twisting, and bending the material. To quantify the stretchability, we tested the elongational properties of our iono-elastomer using a Sentmanat Extensional Rheometer, shown in Figure 4 (a).[36] The mechanical response shown in Figure 4 (b) indicates that our iono-elastomer breaks at 3000% elongation and has an ultimate tensile strength of 200 MPa.[36] Compared to a regular rubber band shown in Figure 4 (b), our iono-elastomer has about one order of magnitude higher extensibility. Remarkably, the conductivity of our iono-elastomer *increases* with extension,[36] which is a response opposite to that of most conductive materials, such as the calculation for the comparable extension of a copper wire, as shown in Figure 5 (a). This is a unique and non-trivial material response because, for instance, the electrical resistance of a constant volume copper wire increases as it is (irreversibly) extended into longer and thinner wire (as depicted in Figure 5 (b)). The calculated, normalized electrical resistance as a function of elongation strain is also plotted on Figure 5 (a), which shows the opposite response of our iono-elastomer. This novel mechano-electrical material property plays a significant role in strain sensor device design because, as resistance *decreases* under extension, the device is anticipated to require less energy, and thus, longer battery life. The origin of this novel electromechanical response is the nonlinear microstructural rearrangement of the hierarchically assembled micelles under uniaxial extension.[36] To summarize this microstructural rearrangement, when stress is applied to the elastomer, as depicted in Figure 6 (a), the formation of hexagonally close packed (HCP) layers of crosslinked micelles produces ion channels between layers. This configuration reduces the tortuosity for ion transport in the stretching direction (1) as compared to the initial configuration of randomly oriented face centered cubic (FCC) micelles; therefore, electrical resistance *decreases* upon stretching. When stress is released, as shown in Figure 6 (b), the bridging polymers that were extended now retract to random coil conformation and thereby, pull the micelles are back to their original configuration. This explains the increase in electric resistance upon unloading stress as a consequence of the increase in ion transport tortuosity when the randomly oriented FCC grain morphology is recovered. A detailed elucidation of the scientific basis of this novel mechano-electrical response for this self-assembled material is presented in a recent publication in *ACS Macro Letters*.[36] A baseline study of the hierarchically self-assembled material without crosslinking and its behavior under flow is published in *Macromolecules*.[35] The provisional patent for this material invention has been filed with University of Delaware (UD), U.S. Patent Serial No. 62/393,133 with priority date September 12, 2016,[37] and the international patent has been filed on April 7, 2017.[38]

Description of motion strain sensor invention

Strain sensors respond to mechanical deformations typically by the change in electrical characteristics, such as resistance or capacitance. Due to simple device structures and easy read-out transduction mechanisms, ***resistive strain sensors*** have attracted significant attention and impressive progress has been achieved in their development. Building upon the iono-elastomer materials described here, we envision our product to be a DIY (do it yourself) reusable flexible biometric motion strain sensor kit, named “MSP Kit” (Motion Strain Patch Kit). This would be the first large strain amplitude, stretchable resistive strain sensor patch that can be easily mounted on clothing or directly attached to the body to measure the local displacement under workload and/or motion. The MSP Kit enables customers (e.g., athletes, patients undergoing physical therapy, physical trainers, biomechanicians, etc.) to accurately track motion and performance of specific joints and/or muscles on their smart phone, tablet or computer via Bluetooth wireless communication, with applications in motion capturing, sports performance tracking and rehabilitation monitoring.

As shown in Figure 7 (a), our envisioned Motion Strain Patch is a transparent sensor comprised of a soft (disposable) iono-elastomer integrated into the Smart Plug and the electronics in the Smart Outlet. The Smart Plug is constructed as sandwiched structure. Our iono-elastomer (in red) is sandwiched in between two waterproof and adhesive encapsulant films (in yellow) on the top and bottom, which is connected to the electronics via a Plug (in green) attached to one end. The waterproofing provides additional water and sweat resistance, shielding the iono-elastomer from the environment. The adhesive property enables attaching directly to clothing, devices, or the skin. The Smart Outlet is a lightweight Bluetooth energy system embed with Bluetooth wireless system and coin battery, which transmits data from the patch to a desktop, tablet or phone. Figure 7 (a) illustrates the working procedures of our Motion Strain Patch. End users, such as athletes, rehabilitation patients or anyone who would like to track their motion, attach the Motion Strain Patch onto the targeted body parts and the strain sensor will measure the strain motion and send the strain signal in real-time to a computer, tablet or phone. The computer app provides real-time, quantitative performance measures to the end users, allowing them to monitor, track and potentially improve their motion performance. It is envisioned that the app can be integrated with a mirage of existing data analysis software incorporating data analytics.

We designed and fabricated our 1st generation Motion Strain Patch minimal viable product prototype and its photo is in Figure 7 (b). As shown in the figure, one piece of our iono-elastomer is taped to laboratory glove at finger joint position, and the change in finger strain is measured via Bluetooth system. Finally, the result could be directly read out from the pre-calibrated and custom programmed phone app, where 0% elongation strain is read out when finger is not bended (see left photo of Figure 7 (b)), and 38% elongation strain is read out when finger is rotated along the joint (see the right photo of Figure 7 (b)). The lifetime of our device is approximately 13 hours. Work is progressing to dramatically reduce the footprint of the electronics to a postage-stamp size, such that it can be directly integrated with the polymeric component without wires.

Analysis of market and industry need

A global market size report (Figure 8 (a)) predicts that stretchable conductive material will rapidly become a billion-dollar market. The global market size is predicted to reach $1.7 billion for flexible conductive materials by 2026,[39] $2 billion for flexible electronics by 2018,[40] $34 billion for wearable technology by 2020[41] and $87 billion for smart textiles/fabrics by 2024.[42] In addition, the wearable technology market is expected to grow from USD 15.74 Billion in 2015 to reach USD 51.60 Billion by 2022, at a CAGR of 15.51% between 2016 and 2022.[43]

Our motion strain sensor addresses customer needs for wearable electronics in sports, which has an even bigger market potential; as shown in Figure 8 (b). Predictions for global market size of $8.2 billion for sport devices is anticipated by 2019,[44] $184.5 billion for sport apparel industry by 2020,[45] and $1.5 trillion for the global sports industry.[46]

Potential for commercialization

Three favorable aspects of our invention are: (1) All the raw materials are commercially available and comparatively inexpensive. (2) The synthesis is easy and robust, with nearly 100% conversion and 90% yield.[36,37] (3) The manufacturing is simple (liquid molding) and entire manufacturing process is commercially scalable; namely, photo-polymerization is an established, commercially available process. In summary, the manufacturing of iono-elastomer is technically feasible, financially efficient and spatiotemporally effective.

The commercialization potential of the MSP kit benefits from five key aspects of the invention: (1) All the required raw materials and electronics parts are low-cost, commercially available and technically feasible. (2) The Motion Strain Patch is optically transparent, removable, reusable and tailorable for different body parts and applications; thus, it satisfies customer needs for wide range of consumers and end users. (3) It provides different levels of comfort to consumers and end users by providing the options of attachment to the body or integration into clothing, orthotics, prosthetics, or other devices. (4) The MSP kit will provide numerous customization capabilities to consumers on the shape, dimension, color and other aspects of the strain sensor. (5) The MSP kit offers hands-on experience and allows the customers to DIY their own health monitoring strain sensor at home. In summary, the motion strain sensor fabrication is technically feasible, cost efficient and user-friendly.

The potential for commercialization for our intended product has been validated via two valuable activities that included gathering significant voice of the customer information. We participated in a local, National Science Foundation (NSF) I-Corps UD site Delaware Startup Launchpad Program, from October 2016 to December 2016.[47] The NSF I-Corps UD site Delaware Startup Launchpad Program is funded by the Horn Program in Entrepreneurship and Delaware Founders Initiative and

Alfred Lerner College of Business and Economics at UD.[47] This program offers intense hands-on business and commercialization training based on Lean Startup method, with a focus on business canvas construction, falsifiable hypotheses testing, customer discovery/solution interviews, scientific data analysis, evidence-based decision making, minimum viable product design, and unique value proposition validation spreading in 7 weeks' period of time. Based on the Lean Startup Method, we conducted customer discovery interviews and defined our customer segments. Through the interviews, we not only validated that there is urgent market and industry demand for our material and device, but also confirmed competitive pricing for our invention. These interviews will be discussed in greater details in the "Customer discovery interviews" section. Our team won 2nd place in the final business pitch competition, which was highlighted in the local news.[48] The second event is the Blue Hen Proof of Concept Program (BH-POC Program)[49] organized by UD Horn Program in Entrepreneurship and College of Engineering.

Customer discovery interview

To develop an understanding of the customer needs, we conducted 105 customer discovery interviews within three potential markets: advanced materials, wearable electronics and sensor for sports and rehabilitation. The interviewees cover three main customer segments: material suppliers, (both technical and business sectors in global chemical companies including Dow, DuPont, and Gore); business partners (both technical and business sectors in global sports apparel companies including Nike and Under Armour); end users (University of Delaware College of Health Sciences and Delaware Blue Hens Basketball team).

Our interviewees in the advanced material field are technical and business experts, or the early adapters, from global chemical companies, including DuPont, Gore, and Dow. One of the commercial stretchable conductive material in the market is the stretchable conductive ink from

DuPont, with limited stretchability. In addition, the quantitative analyses on the customer discovery interview data, shown in Figure 9, revealing that conductivity and stretchability are two most important challenges. A direct quote from one of the interviewees incisively summarizes this: “the challenge for stretchable conductive material lies in how to reach high stretchability without compromising conductivity.” Therefore, we concluded that there are market and industry needs for our stretchable conductive material.

The interviewees in wearable electronics are technical and business experts in global sports apparel companies, including Nike, Under Armor, Reebok and Adidas. The interview results could be summarized into two main conclusions. Firstly, current wearable electronics requires form factor, such as watch band, shirt, or chest band shown in the right figure. Often times these form factors are rigid and uncomfortable to wear, so form-factor free wearable electronics is the rising star in next generation wearable electronics. Secondly, most of the performance tracking products can only measure global body response, such as heart rate, acceleration. There is a demand for product that could quantify local body performance, such as range of motion which is critical for basketball jump shots, soccer kicks and baseball pitches, for example.

The interviewees in sensors for sports and rehabilitation are technical experts in the rehabilitation field, and end users, such as basketball players in sports field. The main takeaway messages of the interviews are twofold. Firstly, data provided from current rehabilitation diagnosis tool are convoluted with many signals and difficult to interpret. Secondly, most of the sensors in those fields can only be used indoor. It follows that a more accurate and location independent sensor is required, which suggests that our device is a solution of the three, major un-resolved problems raised by the customers.

From the customer discovery interview, we also defined two potential commercialization value chains shown in Figure 10. The preferred route is to form a startup and seek venture capital for toll manufacturing and direct marketing to customers. The alternative path is to license our technology to an existing company, such as those already interviewed in our customer discovery work (i.e., Reebok, Nike, Under Armour) for incorporation into their emerging product lines of performance wearable technologies.

In summary, we used both literature and customer discovery interviews to confirm that there are both market and industry demands for our invented stretchable conductive materials and motion strain sensor.

Potential economic, environmental and societal benefits

The broader impacts of our material and device inventions are multifold, including societal, environmental and economic benefits. Sports clothing, military, police, firefighter and industrial uniforms will benefit from integration of our patented highly extensible, flexible conductive materials for use as sensors and electrical connectors for communication and other added functionalities. Aside from this potential society benefit, our stretchable conductive material is made of environmentally friendly raw materials which will help reduce the waste and assist in the global sustainable development. Last but not the least, the raw material cost for our stretchable conductive material is comparatively low. This suggests uncompetitive advantages in commercialization by both unique capabilities as well as competitive price points as compared to existing products. While stretchable, skin-mountable and wearable strain sensors have tremendous potential economic, environmental and societal benefits, challenges still remained to be overcome, for which we refer to a recent review[50] and publication.[51]

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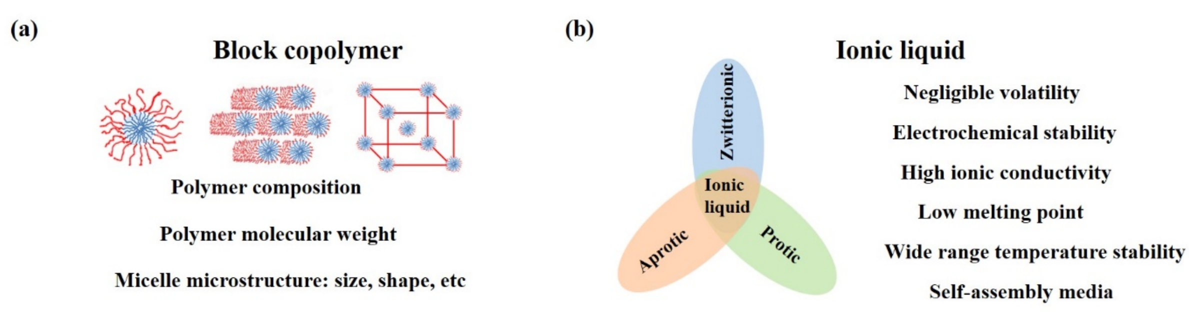

Figure 1: (a) Schematic showing the hierarchically self-assembled microstructures formed from block copolymers in ionic liquid and a list of the tunable parameters for reaching desired properties. (b) Left panel: three ionic liquid categories, aprotic, protic and zwitterionic ionic liquids. Right panel: Desirable properties of ionic liquids have.

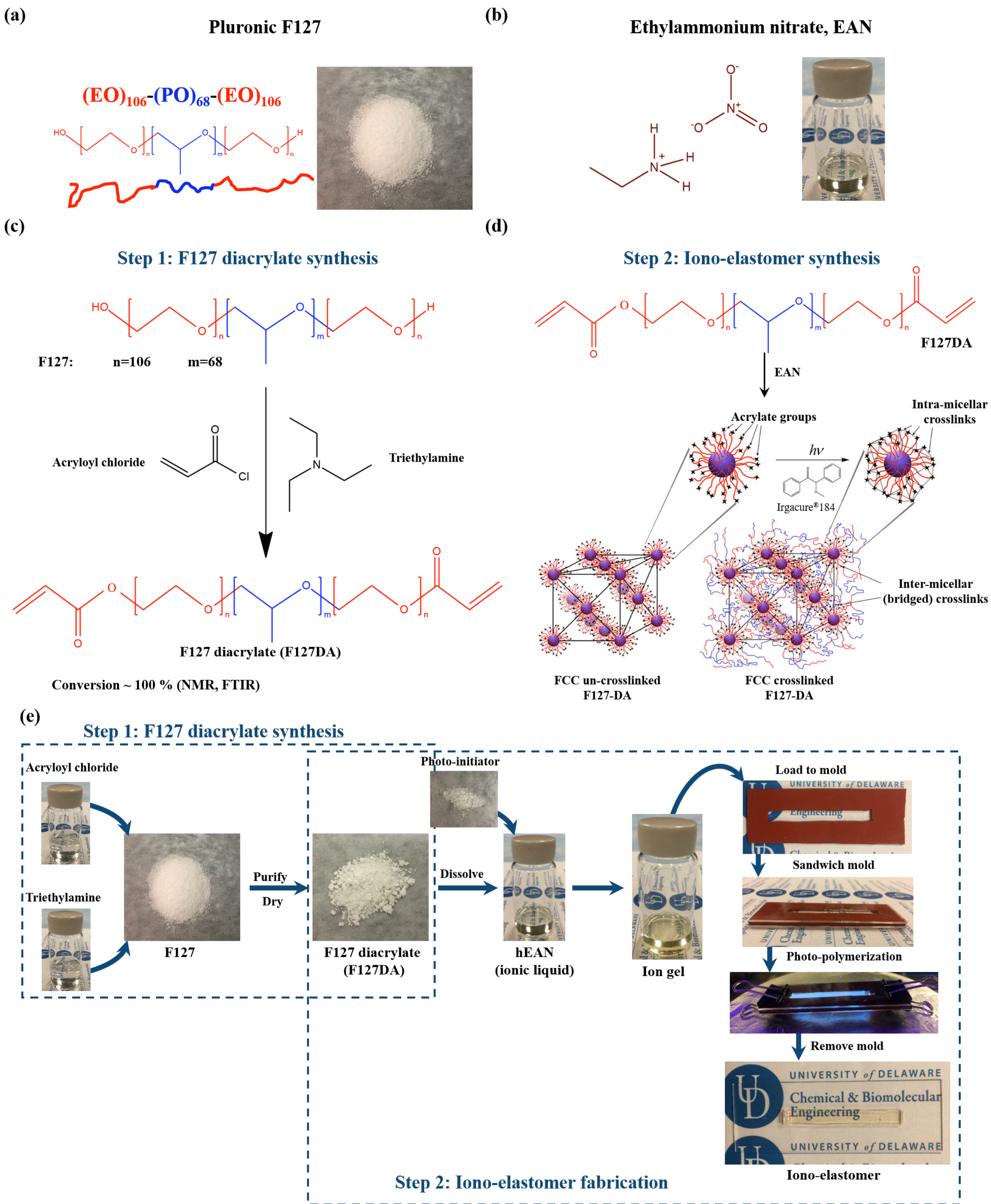

Figure 2: Synthesis and manufacturing of the iono-elastomer: (a) Pluronic F127: left, chemical

structure; right, image of neat polymer. (b) Ethylammonium nitrate: left, chemical structure; right, image of neat EAN. (c) Acrylation of Pluronic F127 to diacrylate. (d) Iono-elastomer synthesis. Reprinted (adapted) with permission from López-Barrón, C. R.; Chen, R.; Wagner, N. J. Ultrastretchable Iono-Elastomers with Mechanoelectrical Response. *ACS Macro Lett.* **2016**, *5* (12), 1332–1338. Copyright 2016 American Chemical Society. (e) Step-wise demonstration of Pluronic F127 diacrylate synthesis steps. (f) Step-wise demonstration of iono-elastomer fabrication.

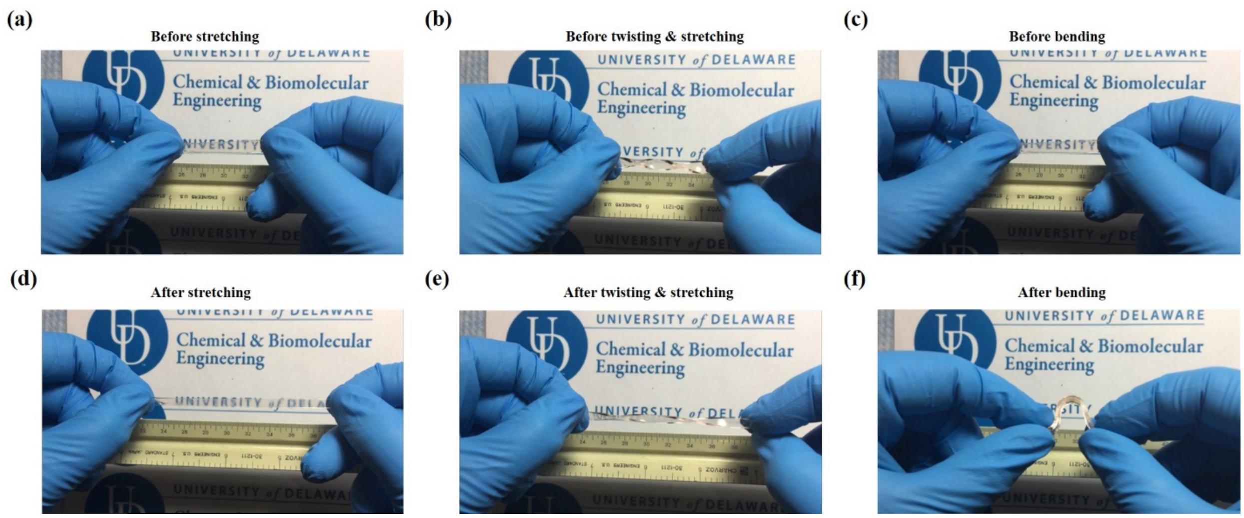

Figure 3: Demonstration of high flexibility of the iono-elastomer via (a, d) stretching, (b, e) twisting then stretching, (c, f) bending. (a), (b) and (c) are photos before course of action, (d), (e) and (f) are photos post each corresponding course of action.

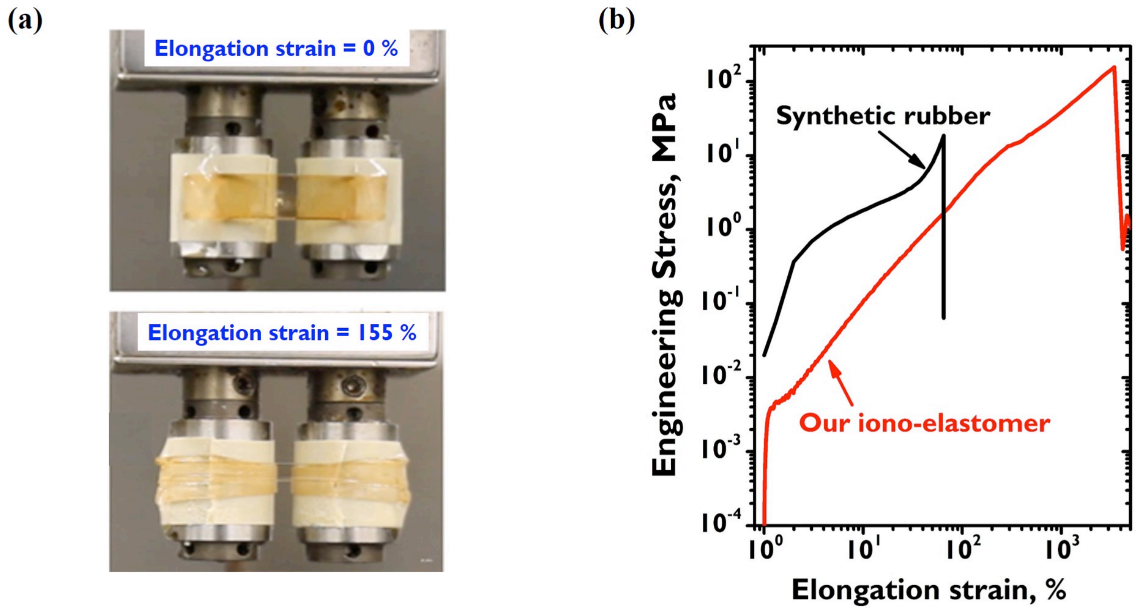

Figure 4: (a) Images showing how the iono-elastomer's extensional properties are measured using a Sentmanat Extensional Rheometer taken at indicated elongation strain values. (b) Engineering stress as a function for elongation strain is plotted for the iono-elastomer as compared to a standard, commercial rubber band. Reprinted (adapted) with permission from López-Barrón, C. R.; Chen, R.; Wagner, N. J. Ultrastretchable Iono-Elastomers with Mechanoelectrical Response. *ACS Macro Lett.* **2016**, *5*(12), 1332–1338. Copyright 2016 American Chemical Society.

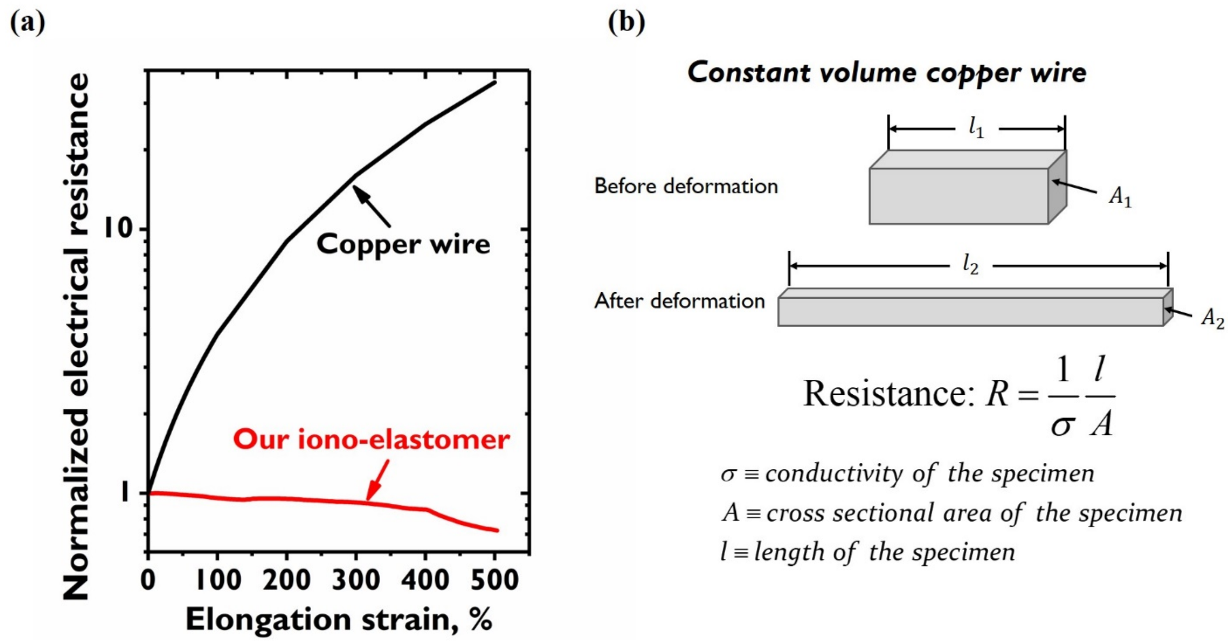

Figure 5: (a) Normalized electrical resistance as a function of elongation strain for our iono-elastomer and calculated for a copper wire under the same hypothetical strain. Notice the unexpected behavior showing a *decrease* in resistance with elongation. (b) Schematic illustrating how resistance increases with extension for a normal material, such as the copper wire.

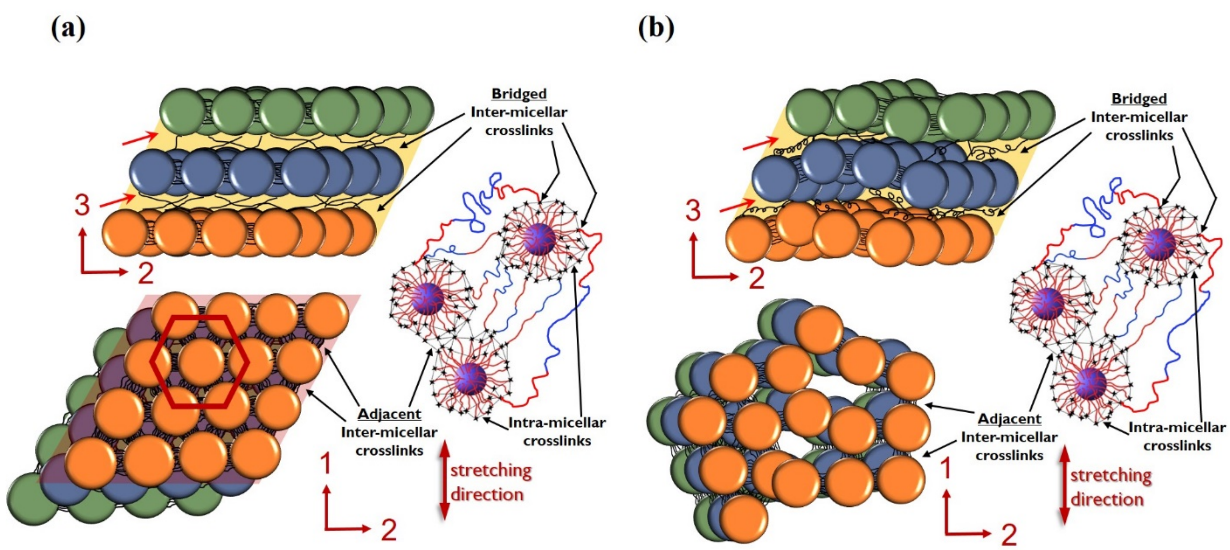

Figure 6: The microstructural rearrangement (a) when the iono-elastomer is stretched. (b) when

the iono-elastomer is not stretched. Reprinted (adapted) with permission from López-Barrón, C. R.; Chen, R.; Wagner, N. J. Ultrastretchable Iono-Elastomers with Mechanoelectrical Response. *ACS Macro Lett.* **2016**, *5*(12), 1332–1338. Copyright 2016 American Chemical Society.

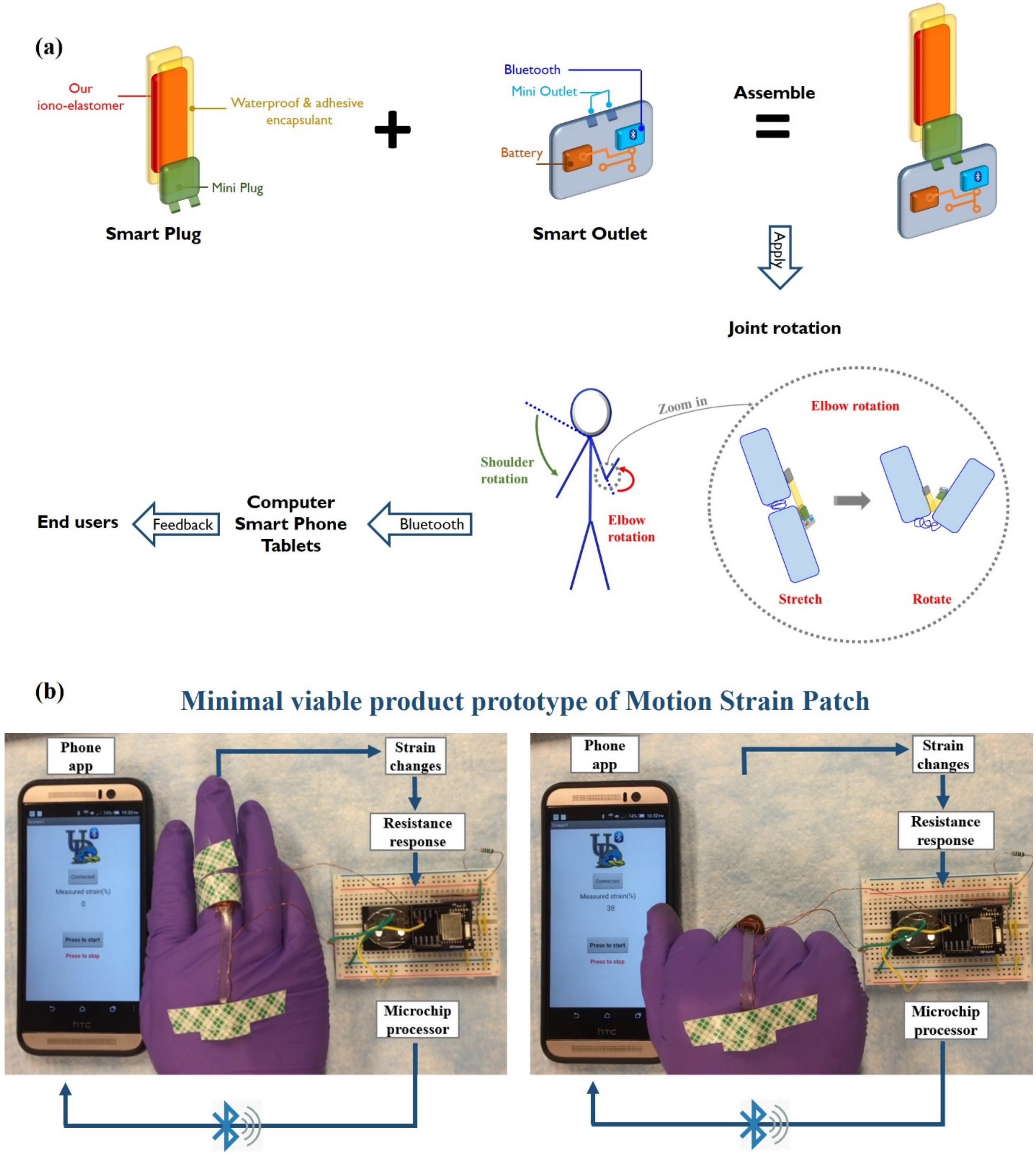

Figure 7: (a) The schematic illustration of envisioned Motion Strain Patch and the operating map of Motion Strain Patch. (b) Real image minimal viable product prototype of Motion Strain Patch at 0% elongation strain (left) and 38% elongation strain (right).

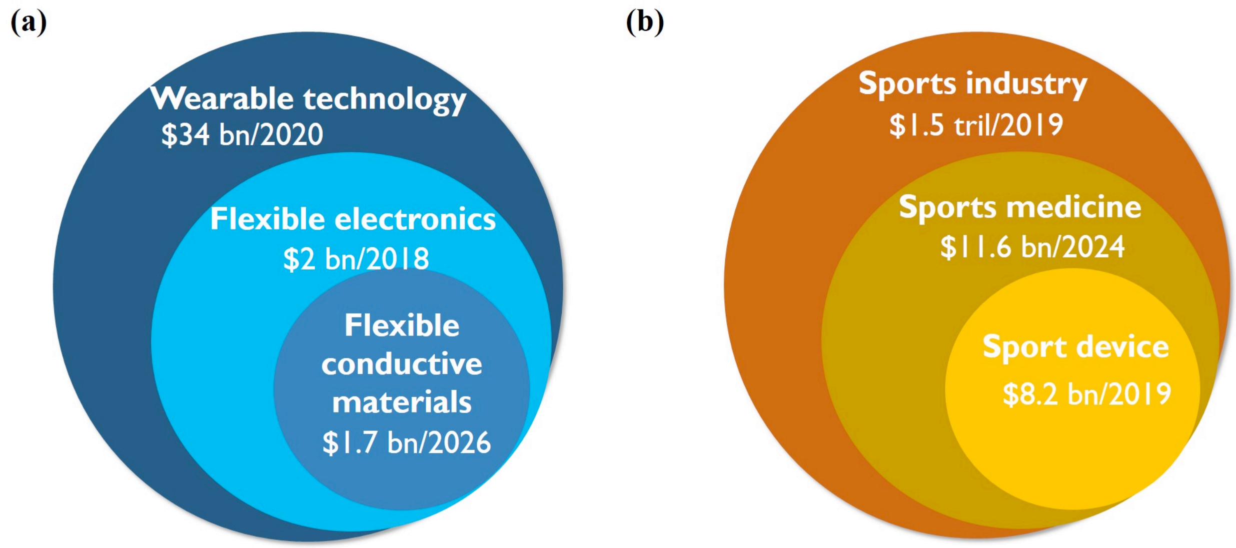

Figure 8: Predicted global market size for (a) wearable technology, flexible electronics and flexible conductive materials; (b) sports industry, sports medicine and sport device.

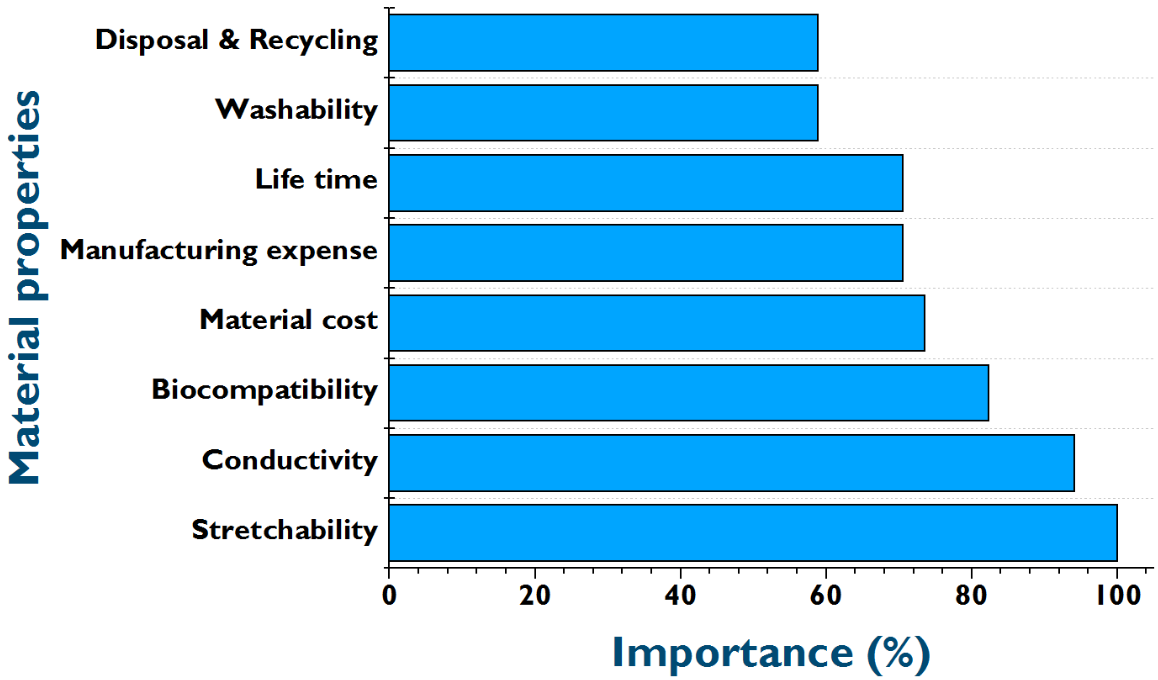

Figure 9: The ranking of priority of current challenges in stretchable conductive materials as determined from customer interviews.

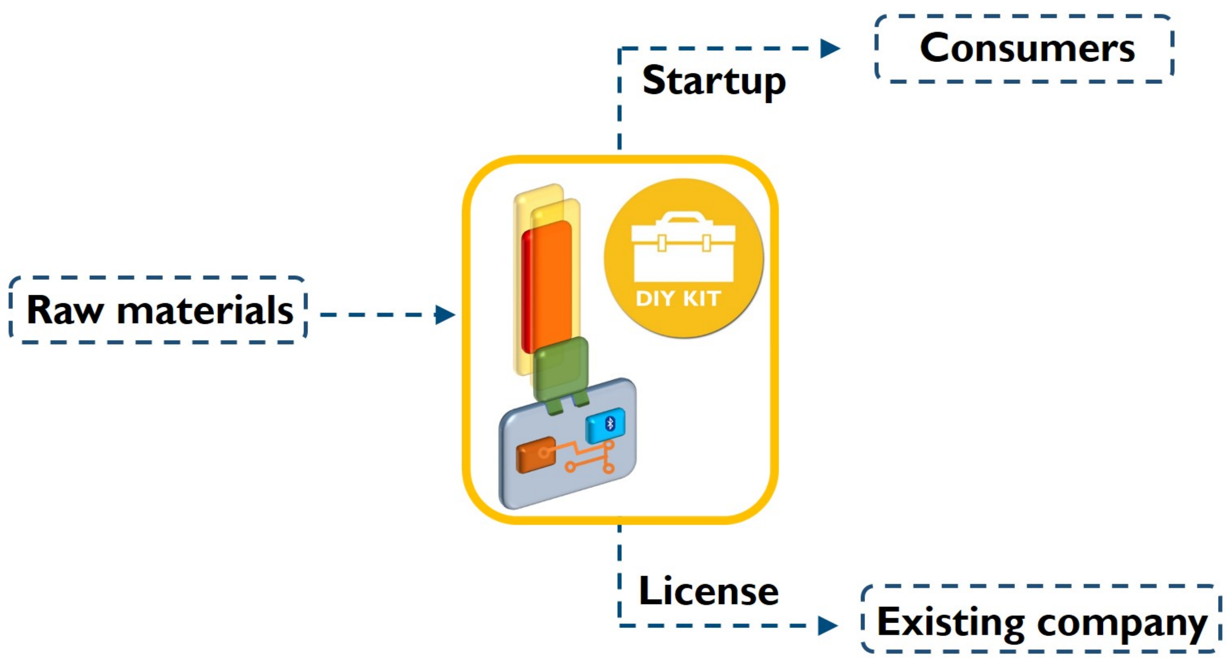

Figure 10: Proposed commercialization value chains: licensing or start-up.