Mechanical sensors

Supercapacitive Strain Sensor With Ultrahigh Sensitivity and Range

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Manuscript received December 9, 2018; revised January 3, 2019; accepted January 10, 2019. Date of publication January 16, 2019; date of current version February 6, 2019.

Abstract—This article develops a novel strain sensor with ultrahigh sensitivity and range that can be easily fabricated using a paper-based electrolyte and two metal pins bought from a local hardware store. No cleanroom facilities are needed. The sensor utilizes a new sensing principle consisting of a paper-based solid-state electrolyte, which deforms in response to strain and changes its contact area with a pair of electrodes. This results in a highly sensitive capacitance change in a double-layer supercapacitor. The new sensor is shown to have a monotonically increasing response for strains as large as 25%, while at the same time providing a high measurement resolution of 0.025% strain. The new sensor could enable a new generation of ubiquitous monitoring applications by replacing more expensive traditional strain sensors.

Index Terms—Mechanical sensors, solid electrolyte, strain sensors, supercapacitors.

I. INTRODUCTION

Strain sensors that measure size and deformation are of significant practical importance in wearable devices and biomedical skin applications. As evidenced by recent publications, there is significant current research interest in development of strain sensors that are flexible and highly stretchable [1]–[4]. For example, flexible transducers consisting of piezoresistive sensors made from metallic glass thin films [1], resistive strain sensors made using metallic nanoparticles [2], highly stretchable piezoelectric strain sensors designed using Kirigami [3], and resistive strain sensors made from carbon nanotube elastomers [4] have been reported. All of these devices use sophisticated fabrication technologies that typically require the use of clean rooms.

On the other hand, sensors made using paper as a substrate, with/without the use of cleanrooms, have been reported for applications such as microfluidics [5], [6], biosensing of analytes [7], [8], and printed microelectronics [9]. Paper offers advantages of being inexpensive, lightweight, environmentally friendly, and easy to use [10]. Mechanical strain sensors have also been previously fabricated using paper-based substrates. In these previous sensors, functional resistive materials, such as patterned carbon or graphite, are added on top of paper substrates. As the paper is bent or stretched to generate a strain, a change in the resistance of the functional materials is experienced. However, currently available paper-based strain sensors suffer from inadequate range and sensitivity. For example, a flexible and degradable resistive strain sensor on a paper substrate was reported in 2017 [11] that can detect strains as small as 0.2% but has a low sensing range (<1%) due to the limited stretchability of the paper. Another flexible and printable paper-based strain sensor using patterned graphite film [12] has an improved resolution of 0.038%, but its sensing range is limited to less than 1%. Similarly, a strain sensor using a graphite pencil to draw on a Xerox paper forming a resistive stripe was fabricated with high sensitivity but has highly limited range [13]. Strain sensors based on highly stretchable piezoresistive graphene-nanocellulose nanopaper [14] were also developed. They can be stretched to 100% but cannot provide adequate resolution and sensitivity with a gauge factor of only 2 at 5%. Besides, piezoresistive strain sensors typically suffer from drifting [15], [16].

In this letter, we fabricate strain sensors based on a supercapacitive sensing mechanism using functionalized paper. The new sensor provides ultrahigh sensitivity, and at the same time, large sensing range. Supercapacitors have previously been mostly explored to be used as energy storage devices [17] and have only recently been used as force sensors [18], [19], [25]. They have never before been utilized for strain sensing in the literature.

II. PAPER-BASED SOLID ELECTROLYTE STRENGTHENED WITH SILICATE NANOPARTICLES

The new physical sensing principle used for the measurement of strain is as follows: A solid-state paper-based electrolyte gets stretched in response to strain and changes its contact area with metallic electrodes, as shown in Fig. 1(a). Embodiments of the strain sensor are shown in Fig. 1(b) and (d) and an explanation of the sensor is provided immediately after the figure.

The proposed sensing mechanism requires a highly flexible and stretchable electrolyte. Ionic-gel electrolytes that incorporate ionic liquid into a cross-linkable polymer matrix have been shown previously to provide both mechanical stability and high electrical conductivity [20]–[22]. However, a traditional ionic gel has very limited flexibility and stretchability. Some researchers have shown that by incorporating cellulosic materials into the ionic gel, the crystallinity of the polymer is weakened, resulting in an improvement in the softness and extensibility properties of the film [23]–[25]. Inspired by this idea of incorporating cellulose into ionic gel to improve flexibility, this letter uses paper (containing cellulose) as a substrate and coats ionic gel on top of the paper substrate. This results in a transparent and flexible thin film of electrolyte [see Fig. 2(b)]. Further, we strengthen the electrolyte by embedding silicate nanoparticles into the paper-based ionic gel matrix. Under stress, the presence of nanoparticles promotes the debonding of the polymer from the nanoparticles, creating local voids that dissipate energy and stop crack propagation.

Corresponding author: Rajesh Rajamani (e-mail: rajamani@umn.edu).
Associate Editor: Y. Suzuki.
Digital Object Identifier 10.1109/LSENS.2019.2893522

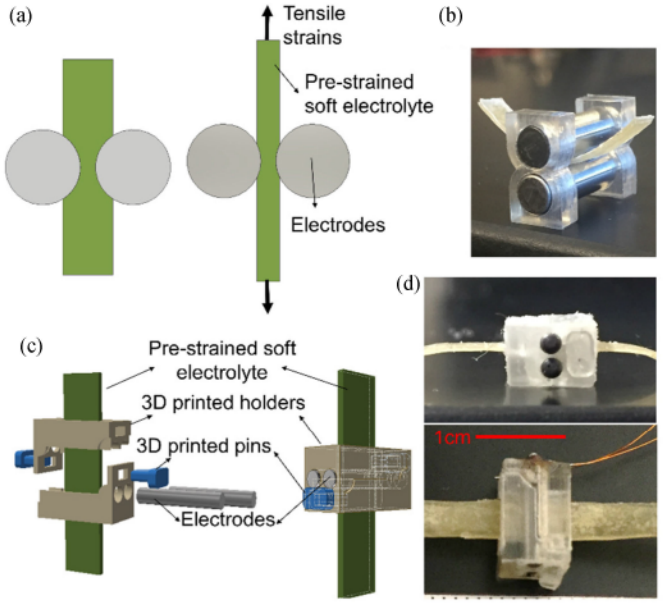

Fig. 1. (a) Mechanism of the paper-based strain sensor. (b) Prototype of the strain sensor. (c) Schematic of a smaller strain sensor. (d) Photograph of the strain sensor.

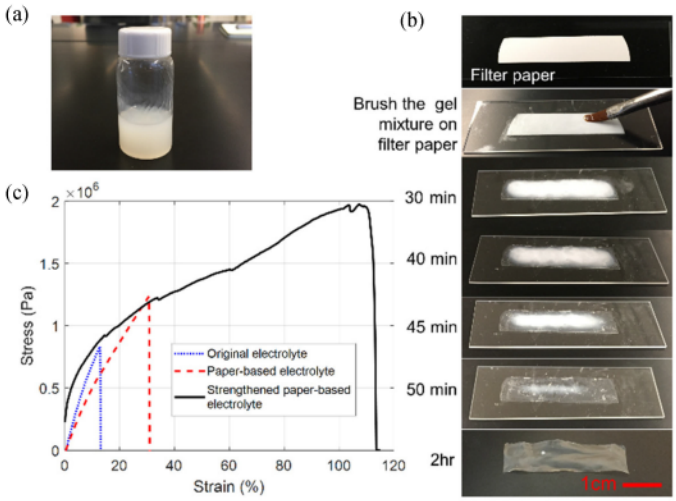

Fig. 2. (a) Photograph of ionic gel mixture with silicate nanoparticles. (b) Photographs showing the dissolving of filter paper in the ionic gel mixture. (c) Mechanical properties of the strengthened film.

The ionic gel was mixed with silicate nanoparticles before being brushed on to the filter paper. The detailed fabrication process is as follows: 0.2 g silicate nanoparticles (Laponite RDS, pellets size ~20–25 nm) were mixed in 6.5 g deionized (DI) water using vortex and sonication (2 h). A clear solution was obtained. Then, 1 g ionic liquid (1-ethyl-3-methylimidazolium tricyanomethanide, IOLITEC Inc.), 0.8 g PEG diacrylate (Mw = 575 g mol^{-1}) monomers (Sigma–Aldrich), and 0.2 g photo initiator (2-hydroxy-2-methylpropiophenone, Sigma–Aldrich) were added to the solution. The mixture was put into a mixer for mixing and defoaming for 20 min and stirred overnight. A free-flowing gel with light white color was obtained [see Fig. 2(a)]. The gel was brushed onto the filter paper (Millipore, 0.45 μm HATF04700) and exposed under UV light for 1 min. As shown in Fig. 2(b), right after brushing the gel onto the filter paper and UV exposure, it started turning transparent slowly as the filter paper gradually dissolved in the ionic gel, as shown in Fig. 2(b). After 2 h at room temperature, the water evaporated, the filter paper was fully dissolved in the ionic gel, and the electrolyte turned into a clear film. A real photo of the nanoparticle-strengthened electrolyte film is shown in the inset of Fig. 2(b) and can be seen to be a transparent thin film.

The deformation response of the nanoparticle-strengthened electrolyte film was tested on a dynamic mechanical analyzer (DMA) machine (RSA-G2, TA Instruments) by measuring stress and strain while stretching the film until failure occurs. A comparison between the stretchability of the original ionic gel electrolyte (without cellulose) and of the modified paper-based electrolyte are shown in Fig. 2(c). As seen from the results in Fig. 2(c), the paper-based electrolyte film can achieve an ultimate tensile strength (maximum stress before failure) that is 50% larger, a toughness that is 3.55 times higher and a maximum elongation strain that is 2.5 times larger in comparison with the unmodified standard ionic gel electrolyte without cellulose [25]. Further, after adding silicate nanoparticles, the stretchability and toughness of the strengthened paper-based electrolyte are additionally improved, as shown in Fig. 2(c). The strengthened electrolyte can be stretched to more than 100% strain before failure occurs. Thus, the strengthened electrolyte film is highly suitable for the strain sensor proposed in this article.

III. STRAIN SENSORS BASED ON THE STRENGTHENED ELECTROLYTE FILM

The nanoparticle-strengthened electrolyte film was used to fabricate a supercapacitive strain sensor. Several electrolyte films were stacked together to increase the thickness and create a thick electrolyte. Then the electrolyte was prestrained and assembled between two cylindrical electrodes, as shown in Fig. 1(a). A simple prototype to demonstrate feasibility was first made as shown in the photograph in Fig. 1(b). The sensor consists of a thick electrolyte slab made of multiple stacked strengthened electrolyte films, compressed between two electrodes made of stainless steel pins, which are fixed by two holders at both ends of the pins. The gap between the two electrode pins is smaller than the thickness of the electrolyte film. Due to the prestrain in the electrolyte, a tensile strain will stretch the electrolyte and reduce the contract area between the electrolyte and the electrodes, which gives a measurable signal proportional to strain.

To prevent the electrolyte from bending while stretching in real-world applications, two identical three-dimensional (3-D) printed holders (Stratasys, Veroclear) were custom designed. First, the strain sensor was scaled down using shorter pins and the 3-D printed holders were used both to assemble the pins and electrolyte together and to keep the electrolyte straight without bending near the region of contact with electrodes, as shown in Fig. 1(c) and (d). Five layers of paper were brushed with the gel mixture embedded with silicate nanoparticles and then stacked together. When tensile loads are applied at both ends of the electrolyte, the thinning of the film leads to a decrease in the contact area between the electrodes and the electrolytes, consequently a decrease in capacitance. The electrodes (dowel pin, steel, 1.5 × 10 mm) used here were 1.5 mm in diameter bought from a local hardware store. The thickness of the stacked electrolyte is about 0.45 mm, while the gap between the two electrodes is about 0.3 mm. The entire sensor was made using just paper and a few dollars of purchases from a local hardware store. The convenience, easy fabrication, and low cost of the sensor are its advantages. The same sensor could be microfabricated in a clean room and could then be made very small. But then it would no longer have the advantages of easy fabrication without cleanrooms.

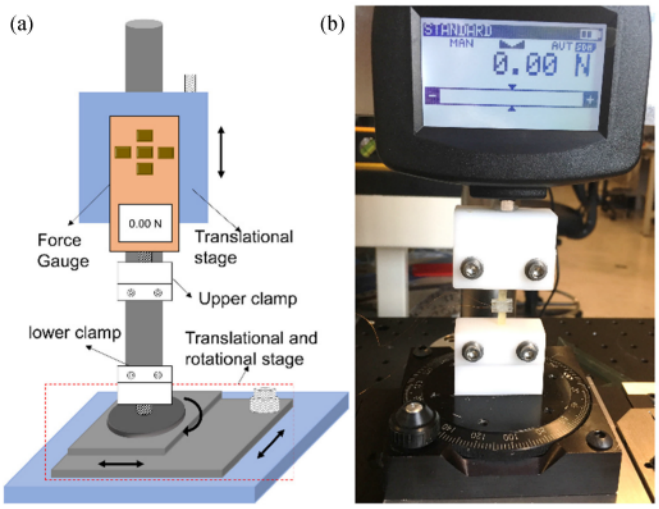

Fig. 3. (a) Schematic and (b) photo of the calibration setup.

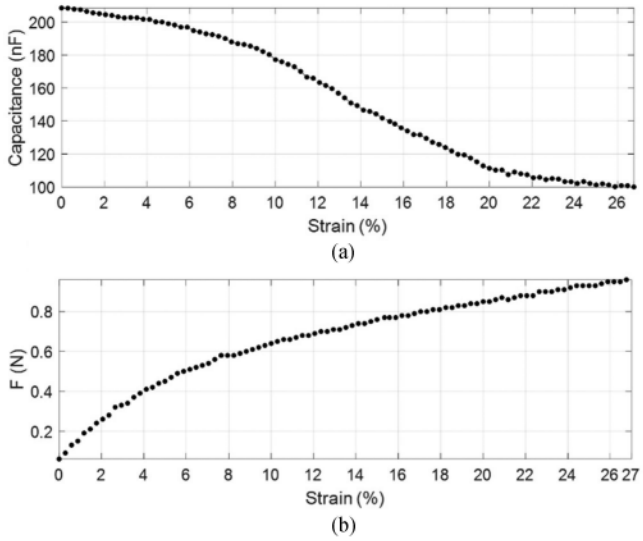

Fig. 4. (a) and (b) Force response curves of the strain sensor.

IV. LABORATORY TESTING AND SENSOR PERFORMANCE

The sensor was first tested as shown in Fig. 3 using a custom laboratory setup. A force gauge (Torbal, FC50, 50NX0.01N) was installed on a translational stage, which can move along *Z*-axis. An upper clamp was installed on the shaft of the force gauge, while a lower clamp was installed on a translational and rotational stage. The strain sensor was held in these two clamps as shown in Fig. 3(b). While gradually moving the force gauge up by turning the knob on the translational stage in steps of 5 μm, the force readings from the force gauge were recorded and at the same time the capacitance changes were recorded using a multimeter (Rigol, DM3068). The distance changes were read from the vernier (Newport SM-13) on the translational stage.

The results are shown in Fig. 4(a) and (b). As the applied forces increase, the capacitance decreases due to the thinning of the electrolyte film, which leads to smaller contact area between the electrode pins and the electrolyte. Above a strain of ~25%, the capacitance saturates, where the thickness of the film has decreased to become close to the value of the gap between the two electrode pins. While the capacitance

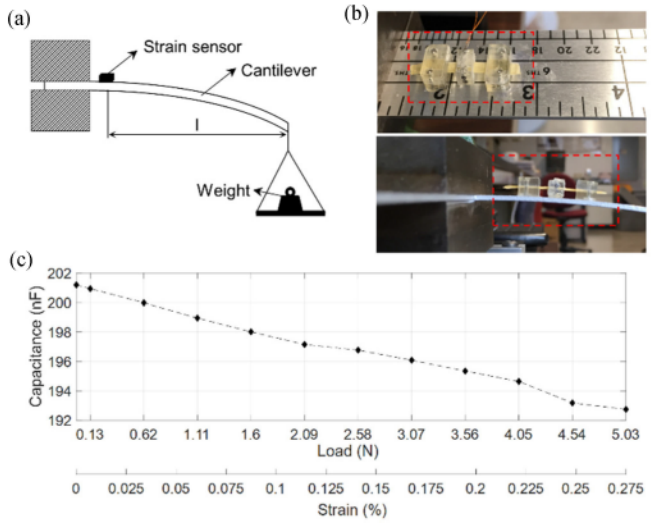

Fig. 5. (a) Cantilever with end load. (b) Strain sensor installed on a ruler cantilever. (c) Strain sensor response on the gradually loaded ruler cantilever.

to strain response is a nonlinear relationship, it is easy to fit a nonlinear polynomial calibration curve to the capacitance readings so that the output of the polynomial has a linear relationship with strain. It should be noted that theoretically the range of the sensor can be further extended by decreasing the gap further between the two electrode pins since the maximum strain the electrolyte film can handle is more than 100% as shown in Fig. 2(c).

To further investigate the sensitivity of the sensor and its capability to measure very small strains, another laboratory setup was designed by installing the strain sensor on an aluminum ruler used as a cantilever [see Fig. 5(a) and (b)]. The sensor was clipped at both ends of the electrolyte film using two 3-D printed clamps, which were glued to the ruler using a UV curable glue (RapidFix, liquid plastic adhesive), as shown in Fig. 5(b). Weights ranging from 0 to 513 g were added in steps of 50 g at the free end of the cantilever. The capacitance from the strain sensor was recorded. The strain of the surface where the sensor is installed is estimated using

$$\varepsilon = \frac{\sigma}{E} \tag{1}$$

where E is the Young's modulus of the cantilever, and the stress σ on the ruler surface at the location where the sensor is installed can be expressed as

$$\sigma = \frac{mglh}{2I} \tag{2}$$

where h is the thickness of the ruler (h). The moment in the ruler at the fixed end is $M = mgl$, where m is the mass of the weight, l is the distance from the sensor to the point where load is applied, and I is the moment of inertia.

For the cantilever with a rectangular cross section of height h and width b, the moment of inertia I is

$$I = \frac{bh^3}{12}. \tag{3}$$

By combining all the above equations, the strain on the surface where the sensor is installed is expressed as

$$\varepsilon = \frac{6mgl}{Ebh^2}. \tag{4}$$

The sensor response to the strain obtained from (4) is shown in Fig. 5(c). The change in capacitance with the load is also shown in the same figure. As the load increases, the capacitance from the supercapacitive strain sensor decreases. The sensor is very sensitive and can differentiate a strain less than 0.025% (since a capacitance change of 50 pF can be measured very accurately using commercial inexpensive capacitance measurement chips). The sensitivity of the sensor is between 14.3 and 55 nF per 1% strain.

V. CONCLUSION

A new method for fabricating flexible and stretchable solid-state electrolytes based on the use of a paper substrate coated with a nanoparticle embedded ionic gel is presented. Strain sensors using this highly stretchable electrolyte, which provide both high sensitivity and high sensing range, are developed. The strain sensor can measure strain as large as 25% and has distinctive detectability of microstrain (0.025%). The sensor is fabricated without the use of clean room facilities using paper, ionic gel, and metal pins as electrodes. The strain sensing principle presented in this letter is a new and advantageous method of measuring strain.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant EFRI 1830958.

REFERENCES

[1] H. J. Xian *et al.*, "Flexible strain sensors with high performance based on metallic glass thin film," *Appl. Phys. Lett.*, vol. 111, no. 12, pp. 1–6, 2017.

[2] E. Puyoo *et al.*, "Metallic nanoparticle-based strain sensors elaborated by atomic layer deposition," *Appl. Phys. Lett.*, vol. 110, no. 12, 2017, Art. no. 123103.

[3] R. Sun *et al.*, "Kirigami stretchable strain sensors with enhanced piezoelectricity induced by topological electrodes," *Appl. Phys. Lett.*, vol. 112, no. 25, pp. 1–6, 2018.

[4] Q. Li, K. Wang, Y. Gao, J. P. Tan, R. Y. Wu, and F. Z. Xuan, "Highly sensitive wearable strain sensor based on ultra-violet/ozone cracked carbon nanotube/elastomer," *Appl. Phys. Lett.*, vol. 112, no. 26, pp. 1–4, 2018.

[5] A. W. Martinez, S. T. Phillips, and G. M. Whitesides, "Three-dimensional microfluidic devices fabricated in layered paper and tape," in *Proc. Nat. Acad. Sci.*, vol. 105, no. 50, pp. 19606–19611, 2008.

[6] X. Li, J. Tian, G. Garnier, and W. Shen, "Fabrication of paper-based microfluidic sensors by printing," *Colloids Surfaces B: Biointerfaces*, vol. 76, no. 2, pp. 564–570, 2010.

[7] Y. Xia, J. Si, and Z. Li, "Fabrication techniques for microfluidic paper-based analytical devices and their applications for biological testing: A review," *Biosens. Bioelectron.*, vol. 77, pp. 774–789, 2016.

[8] A. Apilux, W. Dungchai, W. Siangproh, N. Praphairaksit, C. S. Henry, and O. Chailapakul, "Lab-on-paper with dual electrochemical/colorimetric detection for simultaneous determination of gold and iron," *Anal. Chem.*, vol. 82, no. 5, pp. 1727–1732, 2010.

[9] G. Grau, R. Kitsomboonloha, S. L. Swisher, H. Kang, and V. Subramanian, "Printed transistors on paper: Towards smart consumer product packaging," *Adv. Funct. Mater.*, vol. 24, no. 32, pp. 5067–5074, 2014.

[10] S. Ahmed, M. P. N. Bui, and A. Abbas, "Paper-based chemical and biological sensors: Engineering aspects," *Biosens. Bioelectron.*, vol. 77, pp. 249–263, 2016.

[11] H. Liu, H. Jiang, F. Du, D. Zhang, Z. Li, and H. Zhou, "Flexible and degradable paper-based strain sensor with low cost," *ACS Sustain. Chem. Eng.*, vol. 5, no. 11, pp. 10538–10543, 2017.

[12] X. Liao *et al.*, "Flexible and printable paper-based strain sensors for wearable and large-area green electronics," *Nanoscale*, vol. 8, no. 26, pp. 13025–13032, 2016.

[13] X. Liao *et al.*, "Flexible and highly sensitive strain sensors fabricated by pencil drawn for wearable monitor," *Adv. Funct. Mater.*, vol. 25, no. 16, pp. 2395–2401, 2015.

[14] C. Yan *et al.*, "Highly stretchable piezoresistive graphene-nanocellulose nanopaper for strain sensors," *Adv. Mater.*, vol. 26, no. 13, pp. 2022–2027, 2014.

[15] S. Zhang, R. Rajamani, L. Alexander, and A. Serdar Sezen, "Note: Development of leg size sensors for fluid accumulation monitoring," *Rev. Sci. Instrum.*, vol. 87, no. 5, pp. 1–4, 2016.

[16] Y. Liu, H. Wang, W. Zhao, H. Qin, and X. Fang, "Thermal-performance instability in piezoresistive sensors: Inducement and improvement," *Sens. (Switzerland)*, vol. 16, no. 12, pp. 1–23, 2016.

[17] B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, New York, NY, USA: Springer, 1999.

[18] B. Nie, R. Li, J. Cao, J. D. Brandt, and T. Pan, "Flexible transparent iontronic film for interfacial capacitive pressure sensing," *Adv. Mater.*, vol. 27, no. 39, pp. 6055–6062, 2015.

[19] A. B. A. Manaf, K. Nakamura, and Y. Matsumoto, "Characterization of miniaturized one-side-electrode-type fluid-based inclinometer," *Sens. Actuators A, Phys.*, vol. 144, no. 1, pp. 74–82, 2008.

[20] M. A. B. H. Susan, T. Kaneko, A. Noda, and M. Watanabe, "Ion gels prepared by in situ radical polymerization of vinyl monomers in an ionic liquid and their characterization as polymer electrolytes," *J. Amer. Chem. Soc.*, vol. 127, no. 13, pp. 4976–4983, 2005.

[21] Q. Sun *et al.*, "Transparent, low-power pressure sensor matrix based on coplanar-gate graphene transistors," *Adv. Mater.*, vol. 26, no. 27, pp. 4735–4740, 2014.

[22] J.-H. Choi *et al.*, "Random network transistor arrays of embedded ZnO nanorods in ion-gel gate dielectric," *J. Mater. Chem.*, vol. 20, no. 35, pp. 7393–7397, 2010.

[23] Q. Chen, H. Chen, L. Zhu, and J. Zheng, "Fundamentals of double network hydrogels," *J. Mater. Chem. B*, vol. 3, no. 18, pp. 3654–3676, 2015.

[24] S. Liang, J. Wu, H. Tian, L. Zhang, and J. Xu, "High-strength cellulose/poly(ethylene glycol) gels," *Chem. Sus. Chem.*, vol. 1, no. 6, pp. 558–563, 2008.

[25] Y. Zhang, A. S. Sezen, M. Ahmadi, X. Cheng, and R. Rajamani, "Paper-based supercapacitive mechanical sensors," *Sci. Rep.*, vol. 8, Dec. 2018, Art. no. 16284.