Paper as a substrate and smart material for electronics, packaging, and robotics

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***Abstract*—As a material, cellulose/paper has attracted significant attention for its fibrous and bendable properties. Paper is a renewable resource with the most common forms coming from trees. This brief article describes efforts to create electronics "on" and "in" paper. Examples of electronics on paper include touch sensors and cold plasma-based sanitizers. The skin-like touch sensors use capacitance and patterned resistive networks for passive, scalable sensing with a reduced number of interconnects. When touched or wetted with water, the interdigitated electrodes in the resistive networks detect significant changes in electrical impedance. The plasma generators with layered and patterned sheets of paper use a simple and flexible format for dielectric barrier discharge to create atmospheric plasma without an applied vacuum. Examples of electronics in paper include sheets with tunable electrical conductivity and piezoresistive force sensors, along with functionalized paper-based electrodes capable of detecting small proteins and clinically relevant biomarkers. These papertronic devices have the potential to supply multi-functionality to new forms of smart bandages, skin-like sensing, food packaging, and robotic sensing and actuation.**

Keywords—paper; cellulose; robotics; electronics; skin-like sensing; packaging; cold plasma; electrochemical sensing

I. Introduction

The cellulose in thin, fibrous paper comes primarily from wood [1], [2]. For more than a decade, efforts to create electro-chemo-opto-mechanical devices made of paper have resulted in demonstrations of transistors, circuits, wearable devices, and electronic skins [3]–[6]. Papertronic devices aim to manipulate the flow of fluids, heat, light, charges, magnetic fields, and forces/stresses [6]. These efforts to tune the properties of paper have also resulted in cellulosic materials that are transparent, manipulate light, or have high strength [7]–[9].

As a material, cellulose/paper has attracted significant attention for its fibrous, renewable, and bendable properties. Consisting primarily of polymeric cellulose, paper is a multi-scale material with millimeter-scale structures built on interlocking micro and nano fibers/fibrils [10]. This fibrous network permits wicking/handling of liquids for electro-chemo-mechanical sensors and devices [11]. Paper also has tunable stress-strain relationships, which can be soft with similar mechanical impedance to biological tissue or hard with a theoretical elastic modulus for cellulose nanocrystals greater than steel and similar to Kevlar [12]. Cellulosic fibers are also compatible with metallization, conductive coatings, nanotubes, and graphene for patterned electrical properties [13]–[15]. This brief article will describe efforts to create electronics "on" and "in" paper.

II. Electronics on Paper

A. Papertronic Skin-like Sensors

1) Touch pads

The inspiration for creating touch pads came from envisioning a new class of microelectromechanical systems (MEMS) made of thin sheets of paper [16]. One approach to building paper-based MEMS was to use a cellulose-based material paired with a conductive layer. Metallized paper with a 10-nm layer of evaporated aluminum is a readily available commodity that we began to pattern with a laser engraver to create distinct conductive traces capable of integration with conventional electronics. Once we began patterning metallized paper, we created interdigitated electrodes with high sensitivity to human touch [17].

Initially, the designs focused on multi-layer architectures using force to close the gap between conductive sheets to increase capacitance. Nonetheless, using the conductivity of human flesh to bridge interdigitated electrodes resulted in significant changes in effective capacitance even through thin gloves. We were also able to perform capacitive sensing with Arduino hardware using an open library to facilitate simple programming. We also demonstrated a simple method for creating touch pads on metallized paper, which we even integrated with an alarmed cardboard box that required keying in a password to avoid setting off an alarm.

We have leveraged this platform for educational purposes. At Rutgers, we have taught first-year undergraduate students how to incorporate paper-based capacitive touch pads into their projects for 1-credit Byrne Seminars [18]. In small teams of 4-5 students, students have used metallized paper in creating a pinball game, origami figures and a map with embedded lighting, a touch-sensitive dog that wagged its tail, a Super Mario display, a New York skyline, a candy dispenser, a

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carousel, a launcher of paper planes, and other papertronic projects.

2) Scalable resistive touch pads

One of the drawbacks of our initial approach to creating paper-based capacitive touch pads was the need for a conductive lead to go to each button [17]. We were able to share the electrical ground on arrays of buttons, but we were using an individual channel or multiplexing a conductive lead to each button. While multiplexing is not trivial at the micro and nano scales, semiconductor- and integrated circuit-based manufacturing approaches have resolved issues with interconnects and wiring between components. Flexible electronic devices at the millimeter scale still suffer from difficulties and interconnects are a technical challenge.

To overcome the need for an individual channel/lead for each capacitive button, we employed patterned resistive networks for passive, scalable sensing with a reduced number of interconnects [19]. We designed a ladder with a series of taps for each button. When touched or wetted with water, the sensors in the resistive networks detected significant changes in electrical impedance. Even though human touch had quite a bit of variability, we were able to detect touch from multiple buttons using only two lead running into an impedance analyzer. When replacing the human figure with conductive pads, we were able to detect presses on a 31-button keypad with only two leads. This approach has the potential to reduce the number of interconnects required for skin-like sensing but comes at the cost of requiring the use of more complex circuitry to characterize electrical impedance with high resolution.

B. Paper-based Devices Using Cold Plasma

1) Sanitization and inactivation of bacteria

During the tragic outbreak of Ebola in Sierra Leone, we began to think about techniques for using flexible electronics to create wearable personal protective equipment (PPE) that would be capable of active antimicrobial protection. In an effort toward achieving this goal, we began using our techniques for laser engraving metallized paper to create conductive traces suitable for generating cold or atmospheric plasma. The plasma generators with layered and patterned sheets of paper provide a simple and flexible format for dielectric barrier discharge (DBD) to create atmospheric plasma without an applied vacuum [20]. When electrically driven with oscillating peak-to-peak potentials of ±1 to ±10 kV, the paper-based devices produced plasmas capable of killing greater than 99% of Saccharomyces cerevisiae (yeast) and greater than 99% of Escherichia coli cells with 30 s of noncontact treatment. While these initial results are promising, there is still a technological gap to scale the size and safety of DBD devices to be suitable for wearable PPE.

2) Food packaging

Building on the effectiveness of paper-based plasma sanitizers, we have expanded our efforts to inactivate bacteria on fresh produce. Inactivation of foodborne bacteria through volume or surface DBD are showing promise [21], but both have yet to receive approval for food processing. For our work, the hypothesis is that using foldable devices that conform to the three-dimensional geometry of objects, such as food, will facilitate efficient and uniform inactivation of bacteria that is responsible for foodborne disease. Our current efforts focus on cutting planar and foldable DBD devices out of metallized paper, which can inactivate bacteria on spinach and tomatoes. The initial results are promising in showing 3-log or greater inactivation of foodborne bacteria. Surface properties, including texture/roughness, affect the degree of inactivation. Tunable exposure to plasma also influences food quality.

3) Smart bandages for wound healing

Another application of cold plasma involves wound healing. The reactive oxygen species in cold plasma are capable of interacting with physiological pathways, and plasma jets have shown the ability to enhance wound healing [22], [23]. Nonetheless, these plasma jets are bulky and require the use of specialized equipment administered by a clinical professional. Our efforts focus on building DBD patches that we can integrate in smart bandages that would be capable of providing intermittent treatments. While we have yet to demonstrate that paper-based devices enhance wound healing, we have work with fabric-based devices that have shown inactivation of wound-relevant bacteria and that application in a patch-based format did not harm a mouse.

III. Electronics in Paper

A. Tuning Volumetric Electromechanical Properties

To fabricate highly porous and uniform conductive paper, we have modified a water-efficient, foam-laying process for papermaking [24]. The surfactant in the foam-laying process helps lower the surface tension of the aqueous suspension containing cellulosic fibers. Then, the suspension foams when mixed with air. The bubbles in the foam separate and redistribute fibers in an enlarged volume, which also prevents flocculation. Vacuum filtration densifies and drains out the bubbles, which helps to form a porous mat of cellulose fibers after drying.

By embossing such paper, its porosity decreases while its conductivity increases. Tuning the porosity of composite paper alters the magnitude and trend of conductivity over a spectrum of concentrations of conductive particles. The largest increase in conductivity from 8.38×10-6 S/m to 2.5×10-3 S/m by a factor of ~300 occurred at a percolation threshold of 3.8 wt% (or 0.36 vol%) with the composite paper plastically compressed by 410 MPa, which causes a decrease of porosity from 88% to 42% on average.

This piezoresistive composite paper has functioned as a tunable platform for creating capacitive and resistive sensors through embossed patterns, showing promise in applications for skin-like sensing for touch and pressure, intelligent packaging protection, and fabrication of other flexible electronics. The increasing resistance of the material during the damaging process has the potential to detect and assess the impact on applied surfaces, monitor structural health of buildings and vehicles, and alert people of danger. Overall, this work presents a potentially scalable process for manufacturing sheets of uniform porous composite paper with tunable electrical conductivity and piezoresistivity, adaptable for new applications on flexible substrates.

B. Electrochemical Sensing

Another way in which we are modifying the volumetric properties of paper is through functionalization for immunoassays. The hypothesis is that manipulation of the morphology or surface-to-volume ratio of micro porous paper would affect sensitivity in electrochemical measurements of small protein-based binding. We have created customized papertronic devices that are capable of having varied electrochemical activity and affinity for small proteins, such as cortisol. Tuning the volumetric properties of papertronic devices instead of pursuing more conventional approaches that leverage the surface roughness or nanoporosity for immunoassays still poses an open question concerning high sensitivity and specificity.

IV. Paper-based Robotic Actuators

Leveraging advances in pneumatic soft robotics [25], [26], we have demonstrated techniques for stacking and designing paper-based robotic actuators. These pneumatic actuators based on Yoshimura patterns [27] have a power-to-mass ratio greater than 80 W/kg and are capable of gripping and manipulating objects. They can also perform modest locomotion. We have yet to embed electronic sensing within these robotic actuators, but the actuators hold promise as disposable end effectors.

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References

[1] R. J. Moon, A. Martini, J. Nairn, J. Simonsen, and J. Youngblood, "Cellulose Nanomaterials Review: Structure, Properties and Nanocomposites," *Chem. Soc. Rev.*, vol. 40, no. 7, pp. 3941–3994, Jun. 2011, doi: 10.1039/C0CS00108B.

[2] H. Zhu *et al.*, "Wood-Derived Materials for Green Electronics, Biological Devices, and Energy Applications," *Chem. Rev.*, vol. 116, no. 16, pp. 9305–9374, Aug. 2016, doi: 10.1021/acs.chemrev.6b00225.

[3] D. Tobjörk and R. Österbacka, "Paper Electronics," *Adv. Mater.*, vol. 23, no. 17, pp. 1935–1961, May 2011, doi: 10.1002/adma.201004692.

[4] A. J. Steckl, "Circuits on cellulose," *IEEE Spectr.*, vol. 50, no. 2, pp. 48–61, Feb. 2013, doi: 10.1109/MSPEC.2013.6420146.

[5] J. M. Nassar *et al.*, "Paper Skin Multisensory Platform for Simultaneous Environmental Monitoring," *Adv. Mater. Technol.*, vol. 1, no. 1, p. 1600004, Apr. 2016, doi: 10.1002/admt.201600004.

[6] T. Liang, R. K. Pal, X. Zou, A. Root, and A. D. Mazzeo, "Flexible and Stretchable Paper-Based Structures for Electronic Applications," in *Handbook of Flexible and Stretchable Electronics*, M. M. Hussain and N. El-Atab, Eds. CRC Press, 2019.

[7] H. Zhu, Z. Fang, C. Preston, Y. Li, and L. Hu, "Transparent paper: fabrications, properties, and device applications," *Energy Environ. Sci.*, vol. 7, no. 1, pp. 269–287, Dec. 2013, doi: 10.1039/C3EE43024C.

[8] P. Grey *et al.*, "Combining Soft with Hard Condensed Matter for Circular Polarized Light Sensing and Logic Operations," *Adv. Opt. Mater.*, vol. 9, no. 6, p. 2001731, Mar. 2021, doi: 10.1002/adom.202001731.

[9] H. Zhu *et al.*, "Anomalous scaling law of strength and toughness of cellulose nanopaper," *Proc. Natl. Acad. Sci.*, vol. 112, no. 29, pp. 8971–8976, Jul. 2015, doi: 10.1073/pnas.1502870112.

[10] J. Rojas, M. Bedoya, and Y. Ciro, "Current Trends in the Production of Cellulose Nanoparticles and Nanocomposites for Biomedical Applications," in *Cellulose: Fundamental Aspects and Current Trend*, M. Poletto, Ed. IntechOpen, 2015, pp. 193–228.

[11] E. J. Maxwell, A. D. Mazzeo, and G. M. Whitesides, "Paper-based electroanalytical devices for accessible diagnostic testing," *MRS Bull.*, vol. 38, no. 04, pp. 309–314, 2013, doi: 10.1557/mrs.2013.56.

[12] Y. Habibi, L. A. Lucia, and O. J. Rojas, "Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications," *Chem. Rev.*, vol. 110, no. 6, pp. 3479–3500, Jun. 2010, doi: 10.1021/cr900339w.

[13] D. Y. Kim and A. J. Steckl, "Electrowetting on Paper for Electronic Paper Display," *ACS Appl. Mater. Interfaces*, vol. 2, no. 11, pp. 3318–3323, Nov. 2010, doi: 10.1021/am100757g.

[14] V. L. Pushparaj *et al.*, "Flexible Energy Storage Devices based on Nanocomposite Paper," *Proc. Natl. Acad. Sci.*, vol. 104, no. 34, pp. 13574–13577, Aug. 2007, doi: 10.1073/pnas.0706508104.

[15] Q. Huang, M. Xu, R. Sun, and X. Wang, "Large scale preparation of graphene oxide/cellulose paper with improved mechanical performance and gas barrier properties by conventional papermaking method," *Ind. Crops Prod.*, vol. 85, pp. 198–203, Jul. 2016, doi: 10.1016/j.indcrop.2016.03.006.

[16] X. Liu, M. Mwangi, X. Li, M. O'Brien, and G. M. Whitesides, "Paper-based piezoresistive MEMS sensors," *Lab. Chip*, vol. 11, no. 13, p. 2189, 2011, doi: 10.1039/c1lc20161a.

[17] A. D. Mazzeo *et al.*, "Paper-Based, Capacitive Touch Pads," *Adv. Mater.*, vol. 24, no. 21, pp. 2850–2856, 2012, doi: 10.1002/adma.201200137.

[18] C. Bowman, *The Art of Electronics*. Rutgers University: YouTube Rutgers Today, 2016.

[19] X. Zou *et al.*, "Paper-Based Resistive Networks for Scalable Skin-Like Sensing," *Adv. Electron. Mater.*, vol. 4, no. 8, p. 1800131, Aug. 2018, doi: 10.1002/aelm.201800131.

[20] J. Xie, Q. Chen, P. Suresh, S. Roy, J. F. White, and A. D. Mazzeo, "Paper-based plasma sanitizers," *Proc. Natl. Acad. Sci.*, vol. 114, no. 20, pp. 5119–5124, May 2017, doi: 10.1073/pnas.1621203114.

[21] N. N. Misra, X. Yepez, L. Xu, and K. Keener, "In-package cold plasma technologies," *J. Food Eng.*, vol. 244, pp. 21–31, Mar. 2019, doi: 10.1016/j.jfoodeng.2018.09.019.

[22] A. Schmidt, S. Bekeschus, K. Wende, B. Vollmar, and T. von Woedtke, "A cold plasma jet accelerates wound healing in a murine model of full-thickness skin wounds," *Exp. Dermatol.*, vol. 26, no. 2, pp. 156–162, 2017, doi: 10.1111/exd.13156.

[23] T. V. Woedtke, A. Schmidt, S. Bekeschus, K. Wende, and K.-D. Weltmann, "Plasma Medicine: A Field of Applied Redox Biology," *In Vivo*, vol. 33, no. 4, pp. 1011–1026, Jul. 2019, doi: 10.21873/invivo.11570.

[24] T. Liang *et al.*, "Tunable Electrical Properties of Embossed, Cellulose-Based Paper for Skin-like Sensing," *ACS Appl. Mater. Interfaces*, vol. 12, no. 46, pp. 51960–51968, Nov. 2020, doi: 10.1021/acsami.0c15073.

[25] F. Ilievski, A. D. Mazzeo, R. F. Shepherd, X. Chen, and G. M. Whitesides, "Soft robotics for chemists," *Angew. Chem.*, vol. 123, no. 8, pp. 1930–1935, 2011.

[26] R. V. Martinez, C. R. Fish, X. Chen, and G. M. Whitesides, "Elastomeric Origami: Programmable Paper-Elastomer Composites as Pneumatic Actuators," *Adv. Funct. Mater.*, vol. 22, no. 7, pp. 1376–1384, 2012, doi: 10.1002/adfm.201102978.

[27] Yoshimaru Yoshimura, "On the mechanism of buckling of a circular cylindrical shell under axial compression.," 1955.