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Review

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Paper as a Platform for Sensing Applications and Other Devices: A Review

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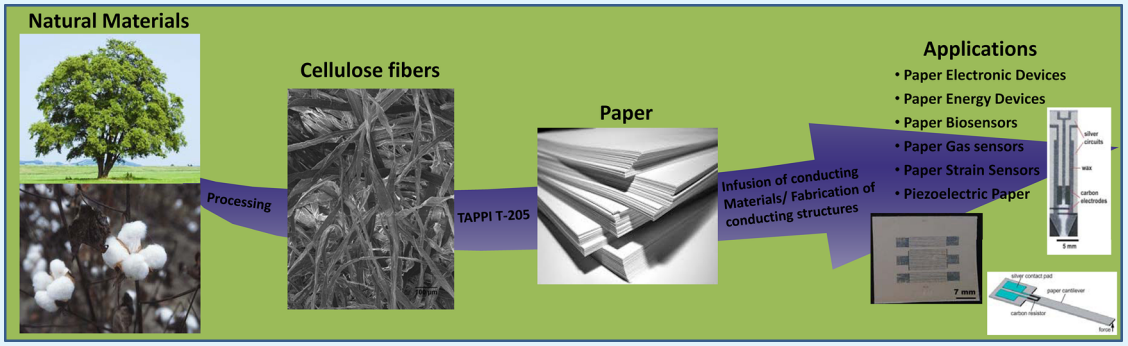
Supporting Information



ABSTRACT: Paper is a ubiquitous material that has various applications in day to day life. A sheet of paper is produced by pressing moist wood cellulose fibers together. Paper offers unique properties: paper allows passive liquid transport, it is compatible with many chemical and biochemical moieties, it exhibits piezoelectricity, and it is biodegradable. Hence, paper is an attractive low-cost functional material for sensing devices. In recent years, researchers in the field of science and engineering have witnessed an exponential growth in the number of research contributions that focus on the development of cost-effective and scalable fabrication methods and new applications of paper-based devices. In this review article, we highlight recent advances in the development of paper-based sensing devices in the areas of electronics, energy storage, strain sensing, microfluidic devices, and biosensing, including piezoelectric paper. Additionally, this review includes current limitations of paper-based sensing devices and points out issues that have limited the commercialization of some of the paper-based sensing devices.

KEYWORDS: *wood cellulose fiber, paper devices, paper sensors, and piezoelectric paper*

1. INTRODUCTION

Paper is produced by pressing moist fibers together; these are typically cellulose fibers. Cellulose fibers are primarily extracted from wood pulp, found in plants as microfibrils, and are separated from the source (wood chip, stem, or other plant parts) either by chemical or mechanical pulping processes. While in chemical pulping processes, cellulose fibers are extracted by degrading lignin and hemicellulose into small particles that are suspended in water without depolymerizing, mechanical pulping processes physically tear the cellulose fibers one from another.[1,2] Anselme Payen was the first to discover cellulose in 1838; he isolated it from plant matter and also determined its chemical formula. The molecular formula of cellulose, $(C_6H_{10}O_5)_n$, classifies it as a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1 \rightarrow 4)$ linked D-glucose units.[3] About 33% of all plant matter is cellulose; cotton possesses the largest amount of cellulose at 90%, and that of wood is 40−50%.[4] A sheet of paper is typically composed of microfibrils with diameters of several nanometers to one micron and lengths up to 40 mm (Figure 1a, b), having cellulose I crystal structure as suggested by X-ray diffraction analysis, that show diffraction peaks at 15.6° and 23° corresponding to the (1 1 0), and (2 0 0) planes, respectively[5,6] as shown in Figure 1c.

Since its discovery, cellulose and its derivatives have been used in a variety of products; in general, cellulose is regenerated by dissolving it in organic solvents to produce a fiber called rayon, which is a vital fiber used in the textile industry. Cellulose nitrate is used in smokeless gun powder, and it has been used as the base material for celluloid for photographic and movie films until the mid-1930s. Many water-soluble adhesives and binders (for example methyl cellulose and carboxymethyl cellulose) are made from cellulose. Cellulose also finds its application in the pharmaceutical industry as inactive filler in tablets and in the food processing industry as thickener and stabilizer. Cellulose is used in the laboratory as the stationary phase for thin layer chromatography and to create a filter bed of inert material.

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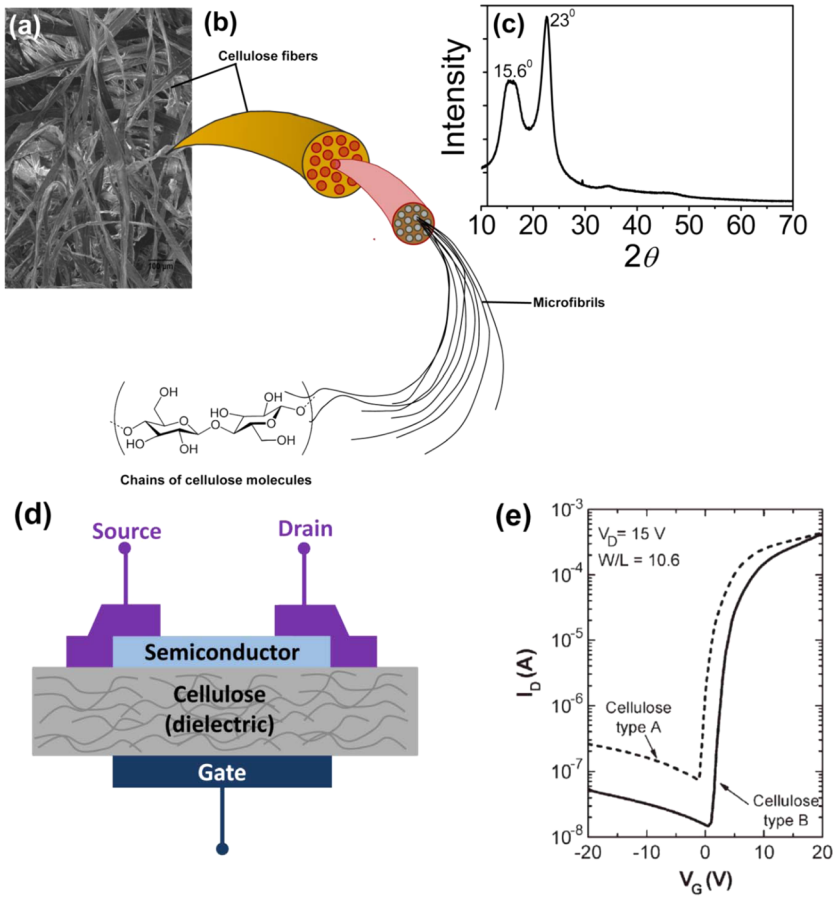

Figure 1. (a) Microphotograph of wood cellulose fibers on the surface of a paper hand sheet, (b) structural configuration of a cellulose fiber, and (c) X-ray diffraction pattern of a paper hand sheet. (d) Configuration of a paper-based field effect transistor and (e) *I*−*V* characteristics of a paper-based field effect transistor developed by Fortunato et al. A sheet of paper is used as a dielectric layer, and zinc oxide-based material is deposited on both sides of the paper by RF sputtering to act as a semiconductor and gate electrode, respectively. Reproduced with permission from ref 16: Copyright 2008 IEEE.

Table 1. Glance at the Various Sensors and Devices Developed Using Paper[a]

Type of Sensor/Device		Year	Role of Paper	Remarks	ref
Electronic devices	Field effect transistor (FET)	2008	Substrate and device dielectric layer	---	14
	Diode	2010	Substrate to support semiconducting material	---	15
	Touch pad	2012	Structural support	---	16
Energy devices	Supercapacitors and battery	2012	Support of electrode and electrolyte	---	17
	Fuel cell	2012	Reservoir	---	18
Microfluidics-based biosensors	Microfluidic device	1949	Substrate	---	19
	Microfluidic device	2007	Substrate	---	20
	μPAD	2010	Substrate	Compatible with commercial glucometer	21
	Instrument-free μPAD	2012	Substrate	Incapable to provide quantitative results	22
Sensors	Strain sensor	2010	Substrate	---	23
	Gas sensor	2010	Substrate to support electrode and gas sensing layer	Photographic paper	24
Piezoelectric paper	Cellulose EAPap	2000	---	Requires multistep processing	25

[a]μPAD: microfluidic paper analytical device, EAPap: electroactive paper.

Cellulose insulation is popular as an environmentally preferable material for building insulation.[7,8]

Paper, or cellulose in general, is attractive for sensing applications for several reasons: (i) paper is biodegradable, abundant, easily available, lightweight, and easy to process, and thus is an inexpensive material; (ii) wood cellulose fibers can be functionalized, in other words the properties of wood cellulose fibers, such as hydrophilicity, permeability, reactivity, etc., can be tailored according to specific requirements;[9] (iii) paper has the ability to let liquid substances pass through its hydrophilic matrix without the aid of external forces;[10] and (iv) wood cellulose is also known to have piezoelectric properties.[11−13]

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In recent years, researchers have demonstrated a wide range of paper-based sensors and devices, including microfluidic, energy storage, and strain gauges, to mention just a few. Table 1 provides an overview of the various sensors and devices developed using paper. Most of the works published so far have focused on developing low-cost and simple fabrication methods to build paper sensors and on exploring new applications of paper-based sensors. It is the aim of this review to provide an overview of the research reported to date on the development of paper-based devices and sensors such as microfluidic devices, electronic devices, energy storage devices, and strain and gas sensors, including piezoelectric paper. Finally we summarize this report with concluding remarks including the limitations of the paper-based devices/sensors and current trends.

2. PAPER-BASED DEVICES

2.1. Paper-Based Electronic Devices. Wood, the most encountered naturally available raw material, is a dielectric up to 3 GHz with a relative electrical permittivity of $\varepsilon_r \cong 3.3$;[26] it could therefore be used as a substrate to build flexible electronic devices, simply by means of depositing and patterning electrically conducting structures onto it. The performance of paper-based electronic devices (resistors, antennas, or radio frequency (RF) devices, etc.) depends on the conductive properties of the structures fabricated on paper, which strongly depend on the density and the connectivity of the conducting material.[27] Approaches employed to construct conductive structures on paper substrates include inkjet printing,[28,29] pen-on-paper, and pencil-on-paper techniques,[30] as well as sputter, spray coating, and photolithography.[31,32] Researchers have developed many paper-based electronic devices and evaluated their performance. This section provides an overview of the research focused on the development of paper-based electronic devices, such as transistors, diodes, and touch pads.

Transistors and diodes are the key building blocks of electronic circuits. While transistors have been used for applications such as voltage and current amplifier circuits, switching, and impedance matching, diodes have been employed to protect circuits by limiting the voltage, rectifying AC into DC, etc. Transistors and diodes have been traditionally produced on either glass or crystalline silicon substrates; nowadays, significant research efforts are focused on the use of paper for electronic applications.[33]

Paper-based field effect transistors (FET) were first developed by Fortunato et al.[14] In their approach, a hybrid FET was realized on paper without any surface treatment at room temperature. In this example, paper functions simultaneously as a substrate and as the device dielectric layer. An active layer was deposited on both sides of the paper via RF sputtering, where gallium indium zinc oxide (GIZO) and indium zinc oxide (IZO) were patterned as a semiconducting layer and gate electrode, respectively, as shown in Figure 1d. The electrical resistivity of the IZO coated paper (1×10^{-3} to 1.3×10^{-3} Ω cm) was slightly higher than IZO coated glass (4×10^{-4} Ω cm) but comparable to the results found on polymeric substrates.[34] A mobility of 30 $cm^2/(V\ s)$ and on/off ratio of about 10^4 were achieved (Figure 1e), yet the magnitude of the off current I_{OFF} is larger than that of GIZO transistors fabricated employing SiO_2 as a dielectric layer, and this was ascribed to the porous nature of the paper substrate. A concurrent study by Yun et al.[33] reported a mobility of 5.8×10^{-3} to 7.8×10^{-3} $cm^2/(V\ s)$ for solution processed carbon nanotube−cellulose composite paper. Multiwalled carbon nanotubes (MWNT) were introduced into paper as a conducting channel by covalent bonding between the cellulose chains and the MWNTs. A transistor was directly fabricated on this composite paper without the need of any semiconducting or insulating layer. The gate, source, and drain gold electrodes were deposited onto it and patterned using photolithography. Not surprisingly, the on/off ratio was found to strongly depend on the concentration of the MWNTs in the composite paper.[33] A subsequent study[35] reported a significant improvement in mobility and on/off ratio by using single walled carbon nanotubes (SWNTs). The alignment of the SWNTs was found to have a significant influence on the electrical performance of the device; the I_{OFF} and on/off ratio was improved to 10^{-1} μA and 12.4, respectively, due to SWNTs alignment achieved via mechanical stretching of the SWNT−cellulose composite during the fabrication process.

Optically transparent and foldable transistors were developed by J. Huang and co-workers,[36] wherein they employed mechanically strong (ultimate strength σ_u = 200−400 MPa and Young's Modulus E = 7.4−14 GPa) cellulose nanopaper as substrate. Cellulose nanopaper is made by a chemical process that is similar to traditional paper making, except fibers with much smaller diameter are used to reduce optical scattering. Transistors were built on cellulose nanopaper by depositing a semiconducting layer (NTCDI-F15, a naphthalenetetracarboxylic diimide derivative), a dielectric layer (poly methyl methacrylate; PMMA), a gate electrode (single walled carbon nanotubes), and silver source and drain electrodes. The optical transmittance of the device was measured to be 84%, while it exhibited a carrier mobility around 4.3×10^{-3} $cm^2/(V\ s)$ and an on/off ratio of only 200. Interestingly, the mobility of the devices was reduced by only 10% when it was bent and folded several times. High mobilities (59 $cm^2/(V\ s)$) have also been reported for transistors made by the pencil-on-paper approach.[37] The transistor is created on normal printing paper with a pencil marking and an ionic liquid gel as active element and dielectric layer, respectively. A paper substrate with pencil trace markings formed using a commercial HB pencil along with silver contacts, and a top gate dielectric was baked at 150 °C for 10−15 min. The electrical resistivity of the pencil traces was measured to be 0.24−0.17 mΩ-m. However, paper fraying may reduce the electrical conductivity of the electrode significantly, and as a result, it is necessary to be careful while drawing. The electrical properties of various paper transistors reported in the literature are provided in Table S1 (Supporting Information).

Diodes allow current flow in a particular direction. This is achieved by the migration of electrons and holes across a p−n junction; the associated nonlinear current−voltage behavior finds application in signal transmission, radio demodulation, and various basic electronic components. p−n junctions are made mainly using silicon-based semiconducting materials, yet in the past two decades intense research focused on organic p−n junction fabrication.[38,39] To date many organic p−n junctions have been reported.[40,41] Though organic p−n junctions do not match or surpass the switching speed of silicon-based devices, they offer benefits of flexibility and light weight and environmental-friendly options.[42] Direct growth of semiconducting zinc oxide (ZnO) on a paper substrate and its p−n diode functionality was demonstrated by Manekkathodi et al.[15] In their approach, 1D nanostructures of ZnO were synthesized hydrothermally on a paper substrate at low temperature (85−90 °C). The device showed a maximum current of 30 μA (forward bias) at 4 V; interestingly, the device showed no degradation in its electrical performance when subjected to bending at different positions

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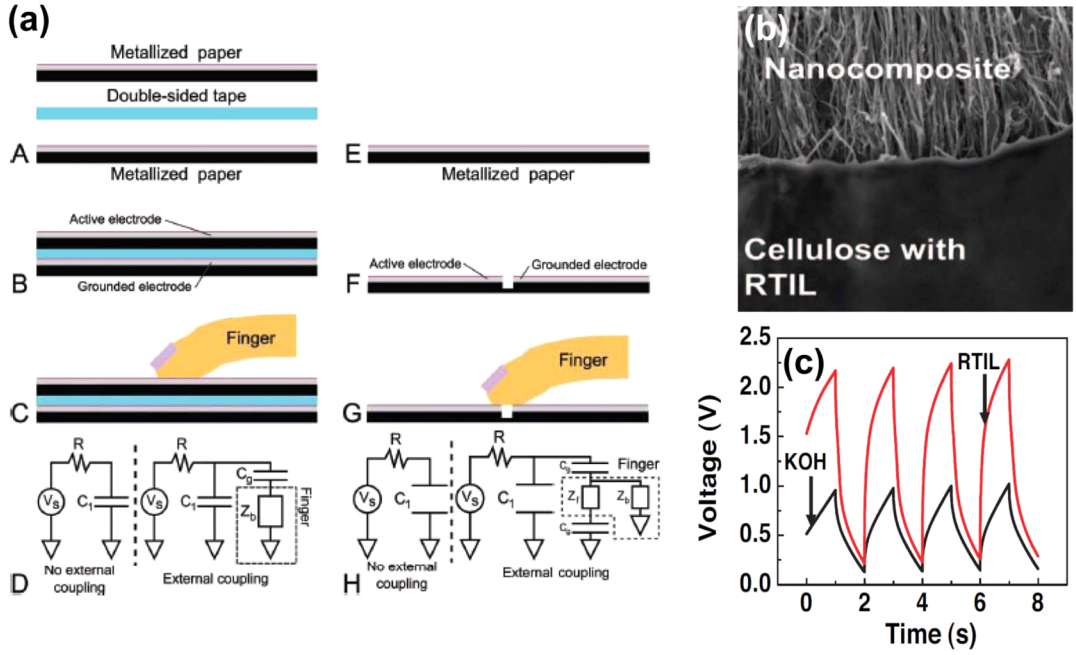

Figure 2. (a) Layout of two types of paper-based capacitive key made with two metallized papers (A, B, C) and a single metallized paper (E, F, G) with equivalent electric circuits (D, H). Reproduced with permission from ref 55: Copyright 2012 Wiley-VCH Verlag GMBH & Co. KGaA, Weinheim. Typical characteristics of paper-based energy storage devices; (b) SEM image and (c) charge−discharge behavior of cellulose nanocomposite paper. Adapted with permission from ref 56. Copyright 2007 National Academy of Sciences, USA.

across the junction. However, nanostructures fabricated on paper via the hydrothermal route were nonuniformly distributed, and the fabrication process required several hours.

Zhang et al.[43] reported a paper-based p−n junction diode made out of two oppositely charged cellulose layers. Anionic and cationic cellulose layers were prepared by chemical modification of microfibrillated cellulose (MFC), in which the n-type cationic MFC possesses $[N(CH_3)_3]^+$ ions on its backbone with Cl^- or OH^- as counterions. The p-type cellulose layer consisted of anionic MFC with SO_3^- ions on its backbone and Na^+ or H^+ counterions. Together these two layers formed a p−n junction. The negatively charged MFC contained Na^+ and H^+ ions, while positively charged MFC contained Cl^- or OH^- ions, and this kind of charge distribution inside the paper resulted in selective transport of cations and anions under positive and negative bias. The device showed a maximum current of 0.985 mA under forward bias and 0.0079 mA under reverse backward bias with a rectification ratio of 12.4 at 6 V of applied voltage. However, in order to conduct the current, the device had to be kept moist, as cellulose itself is not conductive. Also, the performance of the paper diode was significantly affected by moisture content and paper thickness.

Using commercially available metallized paper, Mazzeo and co-workers[16] reported a capacitive touch pad for applications in smart packaging. Their metallized paper was mainly cellulose coated with polymer and evaporated aluminum, in which the cellulose acts as the structural support, the evaporated aluminum acts as the conductive layer, and the polymer coating ensures adhesion of the metal layer to the cellulose and also protects the metallized layer from environmental damage or any damage that may be caused during handling. They demonstrated two capacitor configurations; one required two sheets of metallized paper pasted together with double-sided tape, wherein the bottom sheet acted as a ground electrode, the top sheet acted as active electrode, and the other configuration used only a single sheet of metallized paper in which both active and ground electrodes were patterned next to each other (shown in Figure 2a) with a vertical gap between the metal surfaces. A laser cutter was employed to selectively ablate the conductive layer to create distinct regions of conductivity on the metallised paper, and hence, it was possible to create any number of individual capacitors within the surface, and each one corresponded to a specific key on the pad. The keys were then linked to an external power source and to an electronic circuitry to detect when a given key was touched. These touch pads are low cost and disposable, and they can be made at a price of \$0.25/m^2. Paper touch pads can be integrated into any form of packages, food packaging, and medical devices, for example.

In summary, significant research effort has recently focused on utilizing paper as a substrate to build various electronic devices. However, paper-based electronic devices have yet to find commercial applications, and this technology is still in the development stage. Furthermore, the performance of these devices does not match commercial silicon-based devices; for example, the mobility of commercial silicon-based FETs is 1400 cm^2/V s, while the maximum mobility achieved with paper-based FETs to date is 59 cm^2/V s, and hence, it is necessary to improve their performance through appropriate material chemistry and device fabrication processes. A summary of the key features of various paper electronic devices reported in the literature so far is given in Table S2 (Supporting Information).

2.2. Paper-Based Energy Devices. The energy/weight of lithium batteries has become one of the limiting factors in the development of ultrathin, lightweight, and flexible personal digital devices. The recent development of paper-based energy storage devices by a team of researchers from the Rensselaer Polytechnic Institute aimed at addressing these issues. They made a paper energy storage device by combining sheets of wood cellulose with conducting materials such as carbon nanotubes (Figure 2b), and ionic liquid.[17] The capacity and energy density

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of the developed device were reported to be 110−430 mAh/g and 13 Wh/kg, respectively, and it stores electricity in the same way as conventional lithium-ion batteries; in addition, these paper devices have the ability to integrate all components into a bendable sheet of paper. Using such a sheet of paper, they developed a hybrid energy device by combining a supercapacitor and a battery for providing both long-term and steady power and bursts of energy. In addition, paper-based energy storage devices are flexible, ultrathin, nontoxic, and environmentally friendly.

In general, there are three simple and cost-effective techniques that have been reported in the literature for fabricating paper-based energy storage devices, including printing,[14] solvent casting/processing,[45−47] and solvent free drawing.[48] The main step involved in any of these fabrication techniques is the infusion of conducting materials into a sheet of wood cellulose paper. Wood cellulose is highly porous by nature and allows rapid diffusion of ionic species.[17] A variety of nanostructured materials, such as carbon nanotubes, graphite/graphene, ionic liquid or conjugated polymers,[17,44−49] etc., were used as the conducting material. The transport properties of the most important conducting materials employed in paper energy storage devices are provided in Table S3[51−54] (Supporting Information).

Most of the paper energy storage devices reported so far have been fabricated by employing solvent casting or solution processing in conjunction with other processes to deposit the conducting material. In this method, either a conducting material is deposited directly onto a pristine paper substrate or wood cellulose is dissolved in a suitable solvent to infuse the conducting material.[45−47] In the approach reported in ref 17, first vertically aligned multiwalled carbon nanotubes (MWNT) are grown by thermal-chemical vapor deposition and the MWNTs are infused with cellulose-ionic liquid, resulting in nanocomposite paper that is used for building the device. Here MWNTs act as the working electrode, and the residual ionic liquid in the nanocomposite as the self-sustaining electrolyte.

An electrochemical measurement on cellulose-carbon nanotube (CNT) nanocomposite paper[17] showed good capacitive behavior, tested by using aqueous KOH and nonaqueous room temperature ionic liquid (RTIL) electrolytes as shown in Figure 2c. The device yielded a capacitance of 22 F/g and 36 F/g in RTIL and KOH electrolyte, respectively. The lower specific capacitance of the device in RTIL was attributed to its lower dielectric constant and ionic mobility, but it operated at much higher voltage (∼2.3 V). In addition to aqueous KOH and RTIL, the nanocomposite device was also operated using human bodily fluids as electrolytes, showing good capacitive behavior of the device (specific capacitance of 12 F/g and 18 F/g for sweat and blood, respectively), suggesting usefulness of the device as a dry-body implantable energy device wherein a drop of sweat placed on the surface of the device diffused into the cellulose. The nanocomposite supercapacitor operated over a wide temperature range (195−423 K) in RTIL electrolyte and showed an increase in power density with temperature due to improved ionic conductivity at higher temperature. A flexible Li-ion battery was also made using cellulose-CNT nanocomposite paper, consisting of a thin evaporated Li-metal layer coated nanocomposite without ionic liquid sandwiched between two pieces of aluminum foil. In this device, the lithium layer acts as an anode, the nanocomposite as a cathode, and the aluminum foil as electrode (current collector). An aqueous solution of lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate and dimethyl carbonate was used as electrolyte. The nanocomposite battery reported a large irreversible-capacity (∼430 mAh/g) during initial charge- discharge cycles. The authors in ref 17 have also demonstrated the integration of a battery and a supercapacitor into a device that acts as a dual energy device. This was achieved by connecting both battery and supercapacitor units in parallel. In such a configuration, the supercapacitor is charged by the adjacent battery unit.

In ref 49 graphene was made by an oxidation and reduction process, and it was then dispersed in a solvent before being deposited on a filter paper (graphene cellulose paper; GCP) by vacuum filtration from either side. A similar approach was adopted by Hu et al.[50] to prepare paper energy storage devices, in which they coated conductive carbon nanotube−silver nanowire ink on ordinary printing paper using a Mayer rod coating approach. Mayer rod coating uses a stainless steel rod with a stainless steel wire of varying diameter wound around it. The rod is used to control the coating thickness and remove the excess coating solution. A capacitance of up to 120 F/g in sulfuric acid (H_2SO_4)−poly(vinyl alcohol) gel electrolyte was demonstrated for GCP with good cycling stability, i.e. 1% loss in capacitance over 5000 cycles.[49] Cyclic voltammetry curves of GCP were found to be rectangular and symmetric and retained the capacitive behavior at a high scan rate (200 mV s^{-1}). The high capacitance per geometric area of 81 mF/cm^2, recorded for GCP, was comparable to other flexible devices reported in the literature.[55,56] Besides the GCP electrodes being free from binders and their fabrication method being simple and scalable, the capacitance per geometric area could be improved further by means of various graphene functionalization processes. Analogous to the previous approach, Zheng and co-workers[48] have made a paper supercapacitor by directly drawing graphite on cellulose paper, referred to as "solvent-free drawing". Here the supercapacitor electrodes were directly drawn on copy paper using a graphitic rod or a pencil with the help of a ruler; drawing was repeated several times along the paper machine direction along the fiber alignment and perpendicular to it to achieve a uniform coating. They reported the graphitic electrodes thus fabricated were stable even after bending the paper several times down to a 2 cm radius. Solvent-free drawing is simple and does not require any expensive equipment or chemicals, compared to printing and solvent casting/processing. However, one has to take utmost care while drawing to preclude paper fraying, which would reduce the electrical conductivity of the electrodes significantly. A capacitance of up to 2.3 mF/cm^2 at a current density of 10 mA/g was reported for such supercapacitors. When increasing the current density from 10 to 100 mA/g, the capacitance decreased from 2.3 to 0.85 mF/cm^2, and the device showed a 100% capacity retention up to 3000 cycles and the capacitance loss after 15,000 cycles was about 10% for 500 mA/g. This loss in capacitance was attributed to graphitic surface oxidation by sulfuric acid.

CNT ink applied on paper by the Meyer rod coating technique, with specific capacitance of 200 F/g, specific energy of 30−47 Wh/kg, and a specific power of 200,000 W/kg with respect to CNT mass, has also been described.[50] It was found that only 3% and 0.6% capacitance loss was observed in sulfuric and organic electrolytes, respectively, when a CNT paper supercapacitor was operated for 40,000 cycles. Here the CNT paper itself functioned as a current collector and hence eliminated the use of heavy metallic current collectors, thereby reducing the weight of the device by 20% and also enhancing the cycle life of the supercapacitor. Moreover, the CNT paper is mechanically strong and no noticeable disintegration of the bonding between the paper and the CNTs was observed after the CNT paper was

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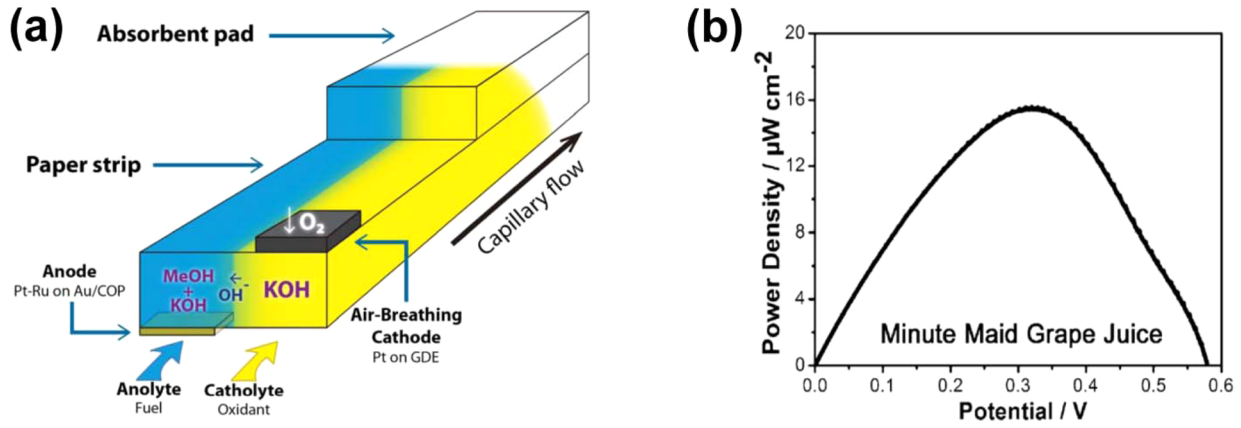

Figure 3. (a) Configuration of paper-based fuel cell proposed by Esguivel and team. Adapted with permission from ref 62. Copyright 2014 Royal Society of Chemistry. (b) Power density of paper-based fuel cell as a function of voltage, when Minute Maid grape juice was used as biofuel. Adapted with permission from ref 18. Copyright 2012 Elsevier BV.

soaked in aqueous and organic electrolytes for 2 months, demonstrating its excellent chemical stability.

Another way of introducing conducting material into paper is the "soak and polymerization" method developed by Yuan et al.,[46] in which ordinary printing paper is first soaked in a monomer for a specific time and then transferred to a solution containing dopant and oxidizing agent to activate the polymerization process. Conductive paper made of cladophora cellulose, and polypyrrole (PPy) reinforced with carbon strands was fabricated using this method and was used as an energy storage device. A charge capacitance of 200 C/g was achieved at a scan rate of 500 mV/s, while cell capacitances of 60−70 F/g were reported with respect to PPy and the device showed no loss in cell capacitance during charging/discharging at 7.7 A/g over 1500 cycles.[45] Recently, a capacitance of 0.42 F cm^{-2} was reported for a PPy-cellulose paper, obtained through coating PPy on normal printing paper,[46] and showed a specific capacitance of 370 F/g at a 1 mA cm^{-2} discharge current. The device capacitance increased during the first 1000 cycles due to self-activation, and it then progressively decreased; at the end of 10,000 cycles the capacitance retention was about 75.6%, whereas the columbic efficiency was 100% during the entire 10,000 cycles. Hu et al.[44] were the first to adopt a printing method for paper energy storage device fabrication using inkjet printing to create an array of supercapacitors on paper. Inkjet printing is one of the most commonly used methods and is an inexpensive method for creating conducting structures on paper; it involves dispensing conductive ink by drop-on-demand onto the paper substrate. Inkjet printing offers many advantages, including the precise control over the amount of conducting material dispensed on the paper substrate as well as the high precision of droplet placement and accurate size and shape of the deposition pattern. This method is simple, scalable, and suitable for applications requiring miniaturized power devices. However, this method is slightly more expensive compared to solvent casting/processing but the higher cost is justifiable as one can precisely control the deposited amount of SWNT or of other conducting material. Similarly, many researchers have employed an inkjet printing method to deposit conductive structures on paper substrates using silver ink,[57,58] carbon nanotube ink,[28] etc. In the inkjet printing approach employed by Hu et al.[44] for paper energy storage device fabrication, the paper substrate was first treated with polyvinylidene fluoride (PVDF), which avoids short circuits of the device due to the penetration of carbon nanotubes through the pores. Supercapacitor arrays were inkjet printed on PVDF-treated paper using conductive ink composed of SWNT and surfactant. A thin layer of ionic liquid electrolyte coating on top of the CNT/paper has been noted to exhibit an extremely large specific capacitance 135 F/g at 2 A/g,[47] and the specific capacitance tends to decrease with increasing current density; 82% of the specific capacitance was retained at 30 A/g. The power and energy densities were found to be 164 kW/kg and 41 Wh/kg, respectively, and the device showed no obvious degradation in capacity retention up to 4000 charge/discharge cycles at 15 A/g.

Multiple research groups have recently started to integrated detectors (luminescence, electrochemical, etc.) into paper-based diagnostic devices to increase their functionality and sensitivity.[59] This requires a low-cost on-board power source that can supply a low amount of power (typically in the range of $\mu W/cm^2$ to mW/cm^2) for a short duration to obtain output from these devices. To address this, researchers have recently developed paper-based fuel/biofuel cells that can be integrated into μPADs as a source of energy to power on-board detectors. The configuration of a paper-based fuel cell is shown in Figure 3a. As discussed earlier the wicking property of paper enables the passive transport of fluids without the aid of an external pump with a flow rate of 2−3 μL/min; this ensures power generation through the constant flow of fluids over a long time at low volume consumption.

Most of the paper-based fuel cells reported so far have been fabricated by adopting photolithography in conjunction with other processes to deposit conducting material. In ref 18 a paper-based fuel cell was made by combining photolithography and a solution process; first, the paper was patterned with photoresist to create hydrophobic and hydrophilic barriers, followed by printing conductive carbon ink using screen printing. Further, a bioanode (glucose dehydrogenase/carbon nanotube/ionic liquid mixture) and a biocathode (bilirubin oxidase/carbon nanotube/ionic liquid mixture) were constructed and dried at 4 °C overnight to obtain a paper fuel cell. A maximum power density of 13.5 $\mu W\ cm^{-2}$ was achieved when it was filled with 30 μL of biofuel (mixture phosphate buffer solution and glucose), which was sufficient to operate the fuel cell for 45 min. The authors also studied commercial beverages as biofuel, and their fuel cell showed a significant increase in its power density with Nescafe instant coffee and Minute maid grape juice (Figure 3b). A paper-based microbial fuel cell that generates a maximum power density of 5.5 $\mu W\ cm^{-2}$ was demonstrated by Fraiwan et al.,[60,61]

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wherein they employed sulfonated sodium polystyrenesulfonate infiltrated paper as a proton exchange membrane and patterned paper as reservoirs of anolyte and catholyte. The device generated a current density of 74 μA/cm^2 immediately after introducing the sample (*Shewanella oneidensis*), and it kept providing power for more than 15 min. Esquivel and team[62] have achieved a maximum power density of 3.2 mW/cm^2 at a current density of 15.5 mA/cm^2 with 4.0 M methanol in water and reported a further improvement in its performance by increasing the electrolyte conductivity. Their device was able to provide a power density of 2.0 mW/cm^2 continuously for 4.2 min when fed with 150 μL of reactant.

A novel and simple paper-based fuel cell was recently reported by Arun and co-workers;[63] they utilized a Whatman filter to create a Y-shaped fuel cell using a laser engraving system and deposited graphite electrodes on it through pencil strokes. This paper fuel cell produces a power density of 32 mW cm^{-2} over a prolonged duration of around 1000 min when formic acid and sulfuric acid were supplied as fuel and oxidant, respectively, to the fuel cell through the Y-shaped channel.

In summary, paper is highly porous by nature and researchers have taken advantage of this unique property to develop energy devices. These paper-based energy storage devices are made by combining an active material (conducting material) with a paper substrate. As revealed in this section, the largest capacitances, and energy densities of 200 F/g, and 47 Wh/kg, respectively, have been obtained when carbon nanotubes and silver nanowires are integrated into paper as a conduction material, and they also exhibited excellent capacity retention up to 40,000 cycles. The energy density of paper-based energy storage devices is still considerably lower than that of metal-based devices (for example the energy density of modern lithium-ion batteries varies from 100 to 265 Wh/kg). However, paper-based devices offer excellent flexibility and cost advantages compared to their counterparts. Table S4 (Supporting Information) shows the performance of paper-based energy storage devices reported in the literature.

2.3. Paper-Based Microfluidic Devices for Biosensing Applications. Paper has the ability to transport liquid without the assistance of, and in opposition to, external forces such as gravity due to capillary action. Capitalizing on this unique property of paper, researchers have developed a wide variety of microfluidic-based paper devices for point-of-care diagnostic applications. Although the invention of the modern day paper microfluidic device is credited to Yager and Whitesides, it actually dates back to 1949, when Müller and his group[19] demonstrated the preferential elution of pigments from a mixture inside a channel created in paper. They patterned filter paper by impregnating a paraffin barrier on the paper substrate, and studied the sample diffusion process and separation of various components of the sample mixture within the confined channel. Since then a wide variety of paper microfluidic devices for application in the field of diagnostics and biosensing have been developed; recently, a few articles have reviewed the latest developments in paper microfluidics and biosensing technology, covering aspects of fabrication, and analysis methods and their applications.[64−70]

Fabrication of paper microfluidic devices involves creating micron-scale channels within the paper substrate in order to constrain the fluid flow. Such microchannels in the paper can be fabricated simply by patterning hydrophilic channels on paper that are separated by water repellent barriers. The following fabrication techniques for creating the microchannels have been reported in the literature to date: (i) *Photolithography* involves hydrophobization of the entire paper substrate using the photoresist SU-8 as a patterning agent followed by the creation of hydrophilic channels through selective dehydrophobization,[71] meaning selective removal of SU-8 with developer after photopatterning. However, microfluidic channels created by photolithography may be damaged during paper folding or bending, which can lead to breakage of the brittle SU-8 barrier. (ii) *Analogue plotting* involves printing of elastomeric polymer: polydimethylsiloxane (PDMS) as a patterning agent using a plotter to fabricate microchannels on paper via selective hydrophobization.[72] PDMS is a flexible silicone rubber and therefore allows bending or folding of the paper device without damaging the microchannels. (iii) *Inkjet printing/etching* uses an inkjet printer to fabricate microfluidic channels. A paper substrate is first treated with a highly hydrophobic polymer (polystyrene), which is followed by toluene printing. Toluene dissolves polystyrene locally and thereby creates hydrophilic flow channels.[73] (iv) *Plasma treatment*: In this process, microfluidic channels are fabricated by hydrophobization of the entire paper substrate followed by selective dehydrophobization. Paper is first treated with a hydrophobic agent such as alkyl ketene dimer (AKD) to make it completely hydrophobic. Hydrophilic microfluidic channels are then formed via plasma treatment for the case of the treated paper substrate being sandwiched between metal jigs with the desired channel patterns.[74] (v) *Paper cutting*: this is one of the simplest ways to fabricate microfluidic devices in which the paper substrate is cut to a required shape and size using a computerized X-Y knife plotter. Then the paper is sandwiched between polymer films (vinyl and polyester) to prevent sample evaporation and contamination during the assay process.[75] (vi) *Wax printing* uses solid wax as a patterning agent. Here wax patterns are first printed on paper by hand drawing either with a wax pen or with a wax printer, followed by heating, which results in melting of the wax, and its penetration into the paper leads to the confinement of microfluidic channels.[76] In conjunction with wax printing, Noiphung et al.[77] have proposed a *wax dipping technique* for electrochemical detection of glucose in whole blood. In this approach, Whatman paper and Whatman blood separation membranes were first cut into the required shape and size; then these paper and membrane pieces were aligned and placed onto a glass slide. A previously prepared metal jig was then placed onto the paper, and it was temporarily held together using a magnet. Finally the whole assembly was dipped into a wax bath maintained at 105−130 °C. During this process wax penetrates into the paper substrates, resulting in the bonding of the two different papers and in the creation of microfluidic channels of shape and size similar to that of the metal jig. The devices consist of a detection zone located in between two separation zones; the plasma was separated from the whole blood, once it was introduced into the separation zone, and then transported to the detection zone through the channel connecting the separation and detection zones. Thus, glucose in the isolated plasma was detected by measuring the electrochemical signals obtained due to hydrogen peroxide generated from the reaction between glucose and the enzyme (glucose oxidase); detection occurred through a Prussian blue modified screen printed electrode underneath the detection zone. (vii) *Flexography printing* involves the physical deposition of a hydrophobic patterning agent on the paper substrate using rollers. A flexography printing unit typically consists of three rollers (impression roll, plate roll, and anilox roll) and a doctor blade. The ink (polystyrene in toluene) is first transferred from a reservoir onto the anilox roll;

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the doctor blade then removes the excess ink from the anilox roll. At the beginning of the printing process, the anilox roll accelerates and undergoes four rotations to distribute the ink; then the plate roll and the impression roll perform one revolution and thereby transfer the ink onto the paper substrate affixed to the impression roll.[78] (viii) *Screen printing* uses solid wax as a hydrophobic patterning agent that is printed onto the paper substrate using a screen. This process is similar to wax printing but employs a screen instead of a printer. Here, the solid wax is rubbed through a screen onto paper, and it is then melted using a hot plate to form barriers.[79] (ix) *Laser treatment* employs hydrophobic paper (parchment paper, wax paper or palette paper) as the substrate. This process creates hydrophilic channels on the paper through a selective dehydrophobization process using laser treatment. The laser treatment results in melting and resolidification of the hydrophobic paper coating and causes the formation of a porous structure that provides space for liquid transport in microfluidic applications.[80] (x) *One-step plotting* was proposed by Nie and his team.[81] In this approach, a paper microfluidic device is fabricated within a few minutes, using commerically available permanent markers and a template (any required pattern). The ink used in permanent markers is typically a mixture of colorant, solvent, and hydrophobic resin; the ink penetrates into the paper according to the plotting pattern, and upon solvent evaporation, the resin remains on the paper, resulting in the formation of a hydrophobic barrier and thereby creating hydrophilic channels. The analytical capability of devices produced in this manner was demonstrated for detection of a protein target (namely the prostate-specific antigen; PSA) with high sensitivity and selectivity. Compared to other existing methods, "one-step plotting" is very simple and inexpensive, and it does not require any specialized equipment or skills, but it requires a laser cutter to fabricate a metal template with the specific pattern in a metal sheet. This wide range of fabrication processes provides a number of choices for fabricating paper microfluidic devices. Selection criteria may include the type of material, the modification required, and the device cost. (xi) *3D device fabrication*: Many applications involve multiple steps for the analysis of a specific target. Under such circumstances, 3D devices are advantageous, as they let the fluid move in all three dimensions (*x*-, *y*-, and *z*-directions) through multiple layers of paper; 3D devices can accommodate more assay compared to their counterparts (2D devices). Hence this architecture eliminates the loss of sample due to evaporation and improves sample transport, as the fluids can pass rapidly in all three directions through multiple layers of paper and can be distributed and combined with different reagents. Fabrication of 3D paper-based microfluidic devices and their applications has been discussed by many researchers in the past.[82,83] 3D paper microfluidic devices are in general created by one of two methods: (i) placing patterned paper and double-sided adhesive (DSA) tape with through holes together alternatively in an ordered fashion, or (ii) using a simple Origami technique,[84] wherein a patterned single sheet of paper is folded into a 3D stack. An extensive review of additional 3D microfluidic paper device fabrication techniques can be found in refs 64−66. Recently, Han et al.[85] developed an efficient method called "benchtop fabrication" to create reconfigurable, 3D microfluidic devices. The process involves fabricating microchannels on a DSA taped paper substrate, that is followed by attaching another paper onto the bottom adhesive surface. The whole assembly is then immersed into a bath containing PDMS for 30 min, and the excess PDMS on the surface of the channel is removed manually. Finally, after baking at 80 °C, another paper with inlet and outlet holes is fixed on top of the assembly to form a channel. This approach is very simple and capable of producing microchannels with a width of as little as 100 μm, and any geometry can be fabricated in 2 h on a laboratory bench without the need of special equipment.

Quantitative analysis with paper-based microfluidic devices can be carried out by employing suitable transduction methods which may require additional reagents and instrumentation. Following are the four most important types of detection approaches that have been successfully implemented on paper-based microfluidic devices, and based on the desired output type (qualitative, semiquantitative, or quantitative), one can choose the appropriate detection method. *(i) Colorimetric detection* is the most ubiquitous, economical, and simplest technique, in which color change due to an enzymatic or chemical interaction is detected by eye. This approach is suitable when a "yes/no" answer or a semiquantitative result is sufficient. Martinez[71] was the first to implement the colorimetric approach for bioassaying of glucose and protein on paper-based microfluidic devices. His work was based on the color change in the reaction zone due to the introduction of a sample. The detection range of their device was 0.38−7.5 mM for bovine serum albumin and 2.5−50 mM for glucose. Following his work, to date many researchers have successfully implemented a colorimetric approach to detect lactate and uric acid,[86] and ketones,[87] etc. *(ii) Chemiluminescence* is a highly sensitive and inexpensive technique, in which the intensity of light produced due to a chemical reaction is measured. Here, a quantitative analysis can be achieved through the correlation of analyte concentration and peak intensity of the emitted light. This method has been exploited by Ge et al.[88] to detect blood cancer markers in a whole blood sample (20 μL). The results obtained by chemiluminescence showed acceptable accuracy comparable with that of commerical techniques. There are also studies that quantify glucose and uric acid[89] in real biological samples, while this method was also employed to detect adenosine triphosphate (ATP) in a clinical human serum sample using a microfluidic paper analytical device (μPAD) that is integrated with a paper supercapacitor and an internal light source.[59] *(iii) Electrochemiluminescence* is a combination of optical and electrochemical detection methods, and based on the luminescence generated by an electrochemical reaction, the combination of these two methods enables a larger detection range with a greater selectivity. Many studies involving paper-based microfluidic devices have implemented electrochemiluminescence for the detection of anaytes[90] and ions,[91] and the measurement of biomarkers and point-of-care testing.[92] *(iv) Electrochemical detection* is one of the key analysis methods that have been effectively implemented on paper-based microfluidic devices. Compared to the colorimetric detection method, it offers highly accurate results, as it is insensitive to light, dust, and insoluble compounds. But it requires additional fabrication steps to deposit electrodes (often electrochemical detection techniques require three electrodes: working, reference, and counter electrode), usually low-cost conducting material-based inks have been employed for this purpose; for example, carbon ink is used for both the working and counter electrodes, while silver/silver chloride ink for fabricating the reference electrode. In paper-based microfluidic devices all three electrodes are placed at the reaction zone. This method has been successfully explored by different research groups for detection of glucose,[21] cholesterol,[21] drugs,[93] and other studies published on environmental monitoring of heavy metals[94] in model solutions and biological

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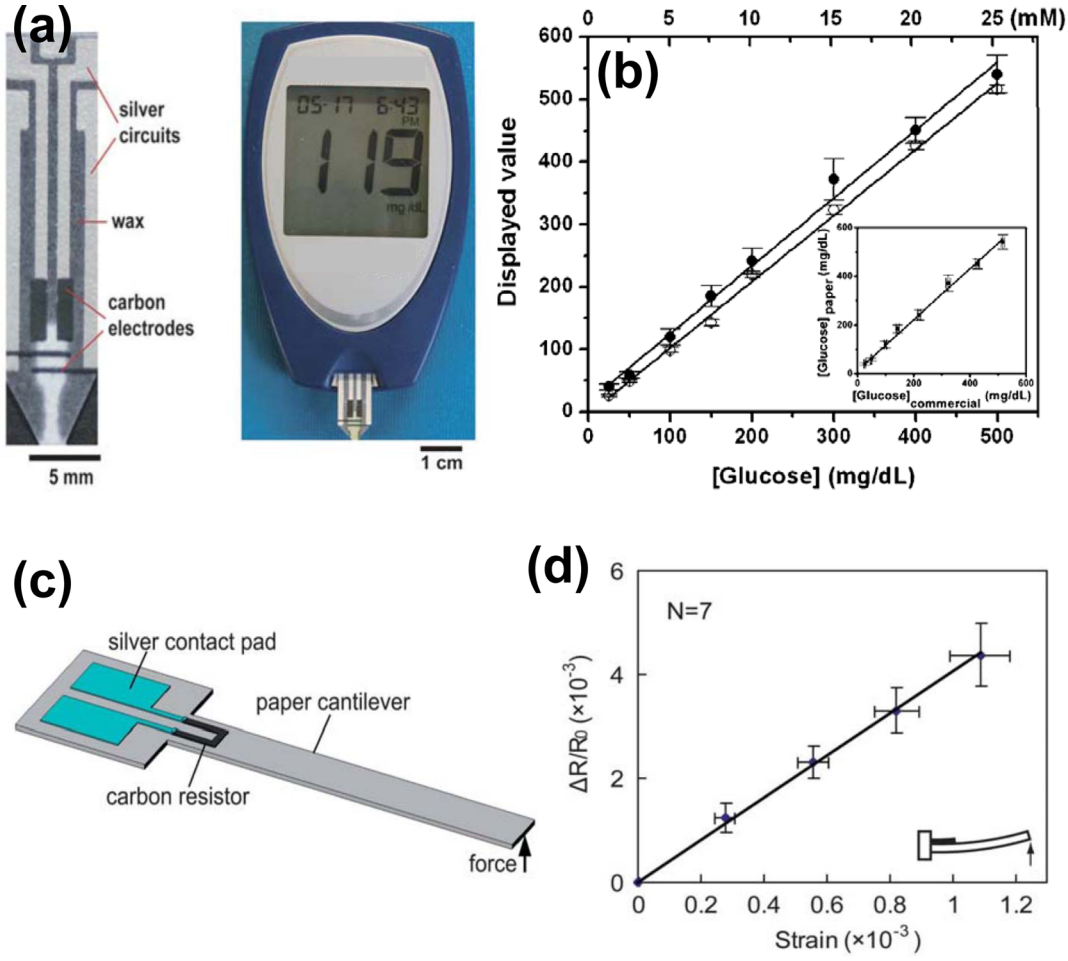

Figure 4. (a) A microfluidic paper device can be used with a commercial electrochemical reader and (b) comparison of results obtained with commercial test strips and paper devices: *open symbol*, commercial test strips; *closed symbol*, microfluidic paper device. The wax printing approach was adopted to fabricate microfluidic channels on a chromatography paper substrate. Adapted with permission from ref 21. Copyright 2010 Royal Society of Chemistry. (c) Schematic of paper-based piezoresistive MEMS sensor demonstrated by Liu et al. and (d) its response to strain. Adapted with permission from ref 115. Copyright 2011 Royal Society of Chemistry.

samples. Whitesides and his group[21] have successfully designed a micropaper-based analytical device (μPAD) that can be used with commercial glucometers, allowing quick analysis of blood or urine. The μPAD was designed such that it can fit into a commercial glucometer port, and it was fabricated using Whatman paper by wax printing (Figure 4a). Wires, contact pads, and electrodes were printed on the patterned paper using silver ink and graphite ink, respectively, and circuits designed on the μPAD were similar to those of test strips sold for glucometers. The compatibility between the glucometer and the μPAD was corroborated by comparing the results of blood glucose concentration measured by commercial plastic test strips and μPADs (Figure 4b). In both the cases, a linear calibration curve was obtained with a slope of 1.05 and 1.09 units per mg dL^{-1}, respectively, for the range of 0−500 mg dL^{-1}. Compared to their commercial counterparts, μPADs showed a small difference in sensitivity due to errors associated with manual fabrication procedures. The same group also demonstrated the capability of μPADs and a glucometer to measure the concentration of other biological compounds such as cholesterol, L-lactate in human plasma, and ethanol in aqueous solution.

The paper-based microfluidic devices provide an inexpensive and portable analytical platform for environmental monitoring and diagnosis. Nevertheless, sealing the microchannels in μPADs was particularly important, as the open channels are vulnerable to contamination and loss of sample due to evaporation. Recently, Martinez and his group[22] successfully overcame this obstacle using printing toner to fabricate fully enclosed μPADs. The fabrication involves four simple steps; (i) paper patterning by wax printing, (ii) toner coating on top of the device, (iii) introduction of reagents into the reagent zone, and (iv) final toner coating on the back of the device. It was required to coat at least four layers of toner to make the surface completely impermeable. The practicability of the device for colorimetric detection of glucose and alkaline phosphate (ALP) was demonstrated and was based on a change in color when a sample filled the reaction zone. Compared to conventional open channel μPADs, the fully enclosed μPADs are simple, as they do not require individual packaging and also can be applied to low-cost point-of-care diagnostic applications. At present, fully enclosed μPADs do not have the capability to provide quantitative results and are suitable to use when a "yes or no" answer is sufficient for analysis. Multifunctional μPADs capable of detecting various chemical and biological analytes with a sub-attomolar detection limit ($<10^{-18}$ M) were developed by Abbas et al.[95] by employing a lithography-free process using a simple cut and drop method. They designed the μPADs with star-like shape that allows rapid flow of liquids and gold nanorods into the

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cellulose microfibers through the fingers, thus providing a preconcentrated and optically active detection spot without the need of microchannels. Recently, a new paper-based sensor was developed by Gerbers and his team[96] for point-of-care diagnostics that is capable of performing complex multistep immunodetection using an enzyme-linked immunosorbent assay (ELISA). They used paper layers and tape[9] to create their device, and they embedded multiple directional valves to autonomously direct different fluids in a different direction sequentially over the detection area. They also demonstrated that their device was capable of performing an immunoassay with rabbit IgG as the model analyte and showed a detection limit of about 4.8 fM.

A summary of the key features of microfluidics-based paper devices developed for biosensing applications is provided in Table S5 (Supporting Information). So far, numerous simple and cost-effective fabrication processes have been developed to fabricate hydrophobic walls to constrain fluid flow within micron-scale channels in the paper substrate. Recent advances in analysis techniques, the integration of the μPAD with a commercial glucometer for example, an instrumentation free detection approach such as fully enclosed μPADs, and multidetection capability (3D paper devices), show the potential for commercialization of paper-based diagnostic devices.

3. PAPER-BASED SENSORS

3.1. Paper-Based Strain Sensors. Strain sensors have a wide range of applications and are also employed to directly measure strain in structural health monitoring of critical infrastructure, to prevent catastrophic failure, and to identify any initiation of damage in real time. Based on their working principle, strain gauges or transducers are classified into optical sensors, resistance-based sensors, and piezoelectric sensors. Among these, the resistance-based sensors are the least expensive and most versatile sensors commercially available, and they are capable of detecting slowly changing strain, displacement of structures subjected to severe loading, or unexpected impact due to extreme events. Conventional resistance-based strain gauges consist of metallic wires or thin films, operated in a voltage bridge configuration. Recent research efforts have focused on developing flexible and highly sensitive strain sensors that have the potential to be easily fabricated at low cost. This led to the development of various nanomaterial-based strain sensors, including carbon nanotubes,[97] ZnO nanowires,[98] graphene,[99] buckypaper,[100] etc., but material and process costs are still high, and also, nanomaterial-based sensing technology is still in the early stages of development. In this context, researchers have made an effort to exploit the advantages of paper to develop paper-based strain sensors.

The strain sensitivity of paper-based materials is mainly due to the piezoresistive properties of conductive material deposited on the paper substrate. The alteration of the conductive material network due to mechanical deformation causes a change in its resistance, and this difference in resistance is directly related to the amount of strain experienced by the paper substrate. Gullapalli et al.[23] reported the use of paper and ZnO nanostructure composite for sensing strain under both static and dynamic loading. They produced a continuous coating of ZnO nanostructures on a paper substrate using an aqueous synthesis route. Here, the nanostructured ZnO crystallized on the substrate by immersing a seed layer coated paper substrate in the aqueous solution of a precursor and a solvent maintained at low temperature, typically less than 100 °C. To assess the strain sensing capabilities of ZnO paper, a piece of ZnO paper was attached to a brass beam, and its response to a change in strain was measured by monitoring the output current. The ZnO paper strain sensor showed a shift in current output at different strain levels. The sensor showed excellent performance, and when used as a resistive device, the gauge factor (21.12) was on par with generally recorded values for commercial strain gauges. Liu et al.[101] constructed force sensors using paper as a structural material as shown in Figure 4c. The working principle of their sensors is based on the piezoresistive effect of the screen printed conductive material (high-resistivity graphite ink) on paper. The paper force sensor showed a reasonable performance with a resolution of 120 mN and a sensitivity of 0.84 mV mN^{-1} as shown in Figure 4d. They further implemented their strain sensors in a paper balance with a measurement range of 15 g and a resolution of 0.39 g. However, it showed poor performance when compared to commercial sensors and could only be used for detecting low-frequency signals or static forces, as paper strain sensors have a very low natural resonant frequeny (~25 Hz) compared to that of silicon-based commercial sensors (~12 kHz). On the other hand, paper force sensors have several advantages in terms of cost ($0.04 per device) and fabrication techniques, as there is no need for a cleanroom and the fabrication requires less time (<1 h). Ren et al.[102] have attempted to reduce the cost of paper force sensors further by replacing many of the fabrication tools. While the former group used filter paper (Whatman), laser equipment, graphite, and silver ink as a substrate, patterning tool, and sensing and electrode material, respectively, the latter replaced it by commercial printing paper, scissors, a graphite pencil, and copper foil. They also drew the carbon resistors directly on the paper instead of using a screen printing process, thereby significantly reducing the device cost (50%) and fabrication time (75%) with a larger force range (50 mN), and improved force resolution (500 μN) and sensitivity (0.9 mV/mN) compared to the device developed by Liu et al.[101]

Khajeh et al.[103] demonstrated percolation-based resistive strain gauges in a paper substrate. Conductive lines of carbon black (CB) were printed onto Northern Bleached Softwood Kraft (NBSK) paper using inkjet printing. NBSK paper is composed of large fibers, resulting in large pore sizes that help with the transport of the deposited CB particle suspensions into the paper. The device response to cyclic loading was recorded; they studied the various parameters such as concentration of CB and binders, and found the highest sensitivity with a gauge factor (GF) of up to 70 but limited reproducibility with 3 wt % CB and 0.1 wt % binder; a higher reproducibility was achieved for a smaller GF. A commercial office printer (EPSON Workforce 30) was utilized by Meiss et al.[104] to develop percolation-based resistive microelectromechanical system (MEMS) sensors for inertial sensing. CB was printed on a photographic paper as a resistor and was connected with conductors by printing commercial silver ink lines with a resistivity of 1 Ω/sq. The paper substrate was then cut and folded to form a 3-dimensional structure that was used as a tactile sensor and as an inertial sensor. The device showed a sensitivity of 8 mV/(V g), but it also showed some drift. However, the proposed design and fabrication method are simple and fast, hence allow rapid prototyping of resistive MEMS devices. Lin et al.[105] have demonstrated a resistive strain gauges in a paper substrate using a pencil-on-paper approach. Pencil-on-paper[106] is an extremely simple and versatile approach established to build conductive structures on paper. In this approach, conductive tracks on paper are obtained simply by drawing on paper leading to graphitic

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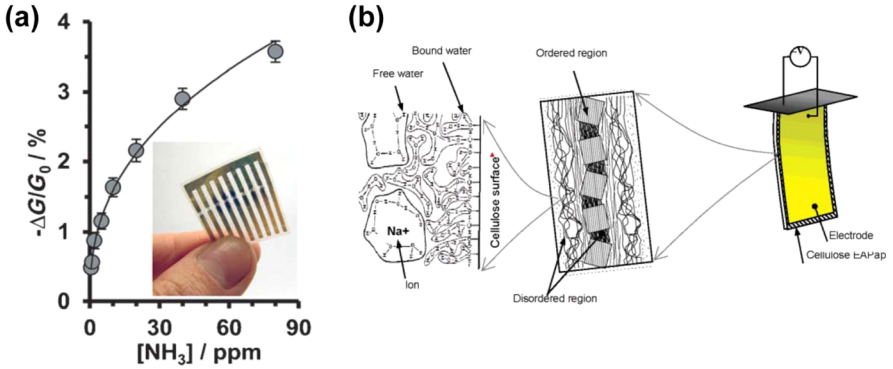

Figure 5. (a) Response of paper-based gas sensor toward NH_3 gas; the inset shows the photograph of the sensor. Adapted with permission from ref 110. Copyright 2012 Wiley-VCH Verlag GMBH & Co. KGaA, Weinheim. (b) Concept of electroactive paper (EAPap). Adapted with permission from ref 25. Copyright 2006 American Chemical Society.

deposits that adhere to the paper matrix. The sheet resistance of a graphitic resistor formed this way was around 223 Ω/sq[106] and it can be controlled through the thickness of the pencil-trace. To construct paper strain gauges, Lin et al.[105] have drawn U-shaped solid rectangles that act as active sensing elements, on a piece of office paper using commercially available pencils. The paper was cut into a beam structure containing the resistors, and outward/inward deflection or bending of the structure caused a change in its resistance due to compression/stretching of the graphite particle network in the parallel segments of the U-shaped trace. They employed four different commercial pencils, namely 9B, 6B, 2B, and HB for drawing the sensing elements on the paper substrate. Among these, the element drawn with the HB pencil exhibited the highest sensitivity, due to the presence of a large amount of conductive carbon particles, and the sensor showed excellent repeatability and reusability.

In summary, researchers in the field of science and engineering have recognized paper as a useful low-cost substrate for building piezoresistive strain sensors. Typically, paper strain sensors are fabricated by depositing conductive material onto the paper, sometimes by infusing the paper with a conductive material. The change in its resistance due to mechanical deformation is related to the amount of strain experienced by the paper substrate. A gauge factor of 70 was achieved with inkjet printing of conductive carbon black onto NBSK paper, while that of commercial strain gauges (single crystal silicon) can reach up to −125 or +200. Inkjet printing offers precise control over the amount of active material per area on or in the paper. Alternatively, researchers have proposed the simple and inexpensive methods of screen printing and pencil-on-paper, but these suffer from low gauge factors. Table S6 (Supporting Information) provides a summary of the key features of various paper-based strain sensors reported in the literature so far.

3.2. Paper-Based Gas Sensors. Volatile organic compounds (VOCs) are common ingredients in many industrial processes, household products, and food and beverages. Above certain concentrations, VOCs can pose a serious threat to health and safety; hence, it is necessary to detect and identify VOCs. To date, gas chromatography mass spectroscopy (GC-MS) is the most reliable technique for detecting and analyzing various gases and VOCs. However, the instrumentation is expensive, is bulky, and requires skilled technicians to carry out data analysis. On the other hand, various alternative VOC detection technologies were developed, these techniques rely on changes in electrical, optical, or gravimetric signals,[107,108] and these systems yet suffer from reproducibility, limited shelf life, etc. Significant research efforts have been recently devoted to developing chemiresistive sensors using paper as a substrate. The sensing of VOCs with paper materials relies on the change in electrical resistance of a VOC-sensitive material deposited on the paper due to the absorption of VOC gas molecules. Arena et al.[24] were the first to demonstrate the feasibility of glassy cellulose paper as a substrate for flexible sensors capable of detecting ethanol at room temperature. They made sensors by depositing a sensing layer made up of a mixture of ITO nanopowder and poly diallyldimethylammonium chloride (PDDA), on top of an electrode (mixture of carbon nanotube and PDDA) previously deposited onto the glassy cellulose paper substrate. Here, PDDA acts as a binder and promotes the adhesion of carbon nanotubes and indium tin oxide (ITO) particles to the paper substrate and promotes easy dispensing of the mixture through a deposition tool. They employed a custom-made microcontroller-based deposition system to deposit sensing and electrode material onto the paper substrate. The sensor showed a shift in the current signal at different ethanol concentration levels. This change in electrical response of the sensor arises due to the charging−discharging of the double layer at the interface of the electrode and the sensing material. The sensor showed excellent performance in the range of 80−320 ppm ethanol. Yang et al. grew graphene on a poly(methyl methacrylate) supported copper foil via a CVD technique.[109] The graphene was transferred onto commercial cleanroom paper; this graphene-based flexible nitrogen dioxide (NO_2) sensor on paper showed immediate response once it was exposed to NO_2 gas at a concentration level of 200 ppm under 0.5% strain with a response time of less than 100 s. The sensor showed a relative change in electrical resistance of about 35% upon exposure to NO_2, while the signal-to-noise ratio of the sensor was reported to be 2.2. However, it showed poor recovery due to slow desorption of NO_2 molecules from graphene.

Mechanical drawing of gas sensors on a paper substrate was demonstrated by Mirica et al.,[110] wherein they used paper, CNTs, and gold, as a substrate and sensing and electrode material, respectively. The gas sensor was fabricated in just two steps by manual mechanical abrasion of a pellet made of CNTs on a paper substrate (Figure 5a). Initially, the pellet was formed by compressing CNTs in a die by applying suitable pressure using a hydraulic press. The CNTs were then transferred to the gap between the gold electrodes that had previously been deposited onto the paper substrate by rubbing the pellet. This led to the transfer of a randomly oriented network of CNTs onto the paper; the resistance of the device prepared in this manner was 10−30 kΩ. They fabricated several sensors using different types

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of paper (weighting paper, cardboard, and filter paper) and examined their ammonia (NH_3) sensitivity. Their sensors showed a broad dynamic range (0.5−5000 ppm), and all the sensors examined showed a linear response to NH_3 at low concentration levels 0.5−10 ppm and a nonlinear response above 10 ppm. Among them, the sensors prepared with weighting paper exhibited coefficients of variance of 5 ± 1% with a detection limit of 0.36 ppm. This performance is comparable with many other CNT-based devices fabricated by solution-phase methods, yet the devices in ref 110 suffer from partial reversibility. By adopting a mechanical drawing approach, a subsequent study by the same group[111] reported a significant improvement in reversibility, reproducibility, and selectivity of their sensors, which is achieved by blending nanostructured carbonaceous material (SWNT, MWNT, and Graphite) with selectors—small molecules capable of interacting chemically with specific gas/VOCs. In addition, the proposed fabrication approach is simple, solvent-free, and cost-effective and offers rapid prototyping of chemiresistive gas sensors on paper.

A simple and low-cost method called "pen-on-paper (POP)" has been developed and used by Analisa Russo et al.[30] to pattern conductive structures on paper. POP is a unique approach that uses a commercially available roller ball pen for dispensing conductive inks. The ball pen is filled with a colloidal suspension of silver ink for writing conductive structures. Silver ink consists of silver nanoparticles prepared via a chemical process by reducing silver nitrate in the presence of poly(acrylic acid) and diethanolamine. Conductive structures written using the POP method show excellent electrical performance with a demonstrated constant electrical resistance, even after 10,000 bend cycles. Interestingly, the POP approach was employed to construct any kind of complex features on paper, as well as high frequency devices. Jia et al.[112] have adopted a similar approach for writing polypyrrole (PPy) arrays on paper for gas sensing. A PPy written paper sensor was fabricated in just two simple steps, wherein, first, ferric chloride ($FeCl_3$) lines were drawn manually on office printing paper, and then, it was exposed to pyrrole vapors, resulting in quick interfacial polymerization of pyrrole due to oxidation between pyrrole and $FeCl_3$. This paper chip with PPy strips was exposed to NH_3 to quantify its sensing ability, and the device showed a change in its electrical conductivity (3.08%) after exposing it to 100 ppm of NH_3, yet the output current was too weak to record at low concentration of NH_3. This was addressed by introducing poly(sodium-*p*-styrenesulfonate) as a PPy dopant, leading to significant improvement in its sensitivity. Their sensor showed a broad detection range (5−3000 ppm) to NH_3, with a high sensitivity up to 900 ppm and lower sensitivity above 900 ppm. The detection limit of the sensor was calculated to be 1.2 ppm, and the sensitivity of the device to other VOCs was also reported.

Analogous to a previous approach, Lin and co-workers[105] made paper chemiresistors by directly drawing pencil traces on paper, referred to as "pencil-on-paper". Herein active sensing elements and electrodes were directly drawn manually on printing paper using a flexible toy pencil and an HB pencil, respectively, and these active layers were found to be stable. Upon exposure to VOCs, these sensors showed an immediate change in their electrical resistance. A flexible toy pencil lead is made of graphite particles embedded in polyvinyl chloride; upon exposure, the VOC vapor swells the polymer matrix in the active sensing layer of the device and pushes the graphite particles apart, which results in a change in its electrical resistance. Their sensor showed a different response for each of the VOCs tested, namely, acetone, methanol, ethyl acetate, THF, toluene, and hexane, and their sensor also showed good reversibility and selectivity, but its detection range and detection limit are unknown. More recently, Liu and his team[113] have successfully integrated PbS quantum dots (QDs) into a paper substrate and demonstrated their sensing capability toward VOCs. The device is fabricated in two simple steps; first a gold electrode was patterned on the paper substrate by RF sputtering, which was followed by the integration of QDs into the substrate through a layer-by-layer approach in combination with $NaNO_2$ treatment. This QD-based paper chip is exposed to five different target gases to assess its sensing ability. The device showed a large change in its electrical conductivity after exposing it to NO_2, and a negligible response to SO_2, NO, H_2S, and NH_3. Interestingly, the device showed a small reduction in its performance (7.1% of initial value) even after subjecting it to 5000 fatigue (bending-unbending) cycles and, also, independent of strain applied. The authors have also studied and evaluated the VOC sensing performance of devices made with a variety of substrates (ceramic, Al_2O_3, polymer, PET, and paper), among these, the paper-based device showed the best response (12 s) and recovery (37 s) time with a high sensitivity toward NO_2.

In summary, paper was employed as a low-cost substrate for building VOC sensors by depositing VOC sensing material either between paper and electrode material or directly onto an electrode on the paper. Various simple and inexpensive approaches, such as pencil-on-paper, pen-on-paper, mechanical drawing, etc., have been demonstrated to infuse active sensing material into paper. Table S7 (Supporting Information) highlights the key features of paper-based VOC sensors reported so far. As shown in this review, paper-based VOC sensors showed excellent reproducibility and selectivity with a detection limit of 0.36 ppm when carbonaceous material was mixed with a selector—small molecules designed to react chemically with specific gaseous analytes, whereas a highly sensitive gas sensor (detection limit = 84 ppb) was made by using QDs as an active material that showed a high response toward NO_2 (12 s response and 37 s recovery time) and negligible response to SO_2, NO, H_2S, and NH_3.

4. PIEZOELECTRIC PAPER

Piezoelectricity, discovered by Jacques and Pierre Curie in 1880, is the ability of certain materials (such as crystals, certain ceramics, and biological matter, such as bone, DNA, and various proteins, certain polymers, and wood) to generate an electric charge in response to applied mechanical stress. The piezoelectric effect is a reversible process in that materials exhibit the direct (electrical charge generation due to an applied mechanical force) and the reverse (mechanical strain generation due to an applied electrical field) piezoelectric effect, and it is used in many applications such as the production and detection of sound, generation of high voltages, electronic frequency generation, microbalances, driving an ultrasonic nozzle, and ultrafine focusing of optical assemblies. It is also the basis of a number of scientific instrumental techniques with atomic resolution such as scanning probe microscopes.

Since the pioneering work by Bazhenov[11] in 1950, piezoelectricity in wood has been known to scientists, and it was experimentally confirmed by Fukada,[12] who verified that wood exhibits both the direct and the converse piezoelectric effect. He demonstrated that the cellulose crystallites were mainly responsible for the observed shear piezoelectricity. Ever since, many researchers have studied the various parameters (for

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example wood defects, grain, pitch, water content, knots, types of wood, etc.) that impact the piezoelectricity of wood.[114,115] Despite this early work on wood piezoelectricity, there have been no efforts to use cellulose as an active material for sensing.

In the year 2000, Kim and his team[25] demonstrated the application of cellulose as a biomimetic actuator (Figure 5b). They fabricated actuators from cellulose paper by coating it with a very thin metal electrode on both sides, and they produced a mechanical deformation when stimulated by an external electric field and they named the structure electroactive paper (EAPap). After a series of experiments they concluded that the actuation mechanism of EAPap is based on the combination of ion migration and the piezoelectric effect associated with dipole orientation.[25,116] Typically, EAPap is made by dissolving wood fibers in organic solvents such as *N,N*-dimethylacetamide (DMAc) and lithium chloride (LiCl) at high temperature under mechanical agitation. A translucent solution is obtained by this process, and it is then centrifuged to remove undissolved fibers and remnant salt. This solution is spin-cast on a glass substrate or silicon wafer and cured by washing with a mixture of isopropanol alcohol and deionized water, and prior to drying it under ambient conditions, this regenerated cellulose film is subjected to piezoelectricity enhancing processes such as stretching, heating, and poling. Finally, cellulose EAPap is obtained after depositing thin metal electrodes on both its sides.[117] Many piezoelectric improvement processes, such as heat treatment,[118] corona poling,[119] or mechanical deformation,[120] were applied to wet film in order to enhance its piezoelectric properties. Among them, mechanical stretching of cellulose was reported to effectively enhance its piezoelectric coefficient, as the stretching process induces the cellulose chains in the disordered regions to align along the stretching direction, and this increases the piezoelectric coefficients.[120] The reported piezoelectric constant of cellulose EAPap was on par with that of poly(vinyledene fluoride), another popular piezoelectric polymer. However, EAPap preparation requires chemical processing of wood cellulose fibers, and regrettably, it suffers from discrepancy in the piezoelectric properties from batch to batch. In addition, the regeneration process involves the use of toxic chemicals. Apart from biodegradability and being lightweight, EAPap also has several advantages over conventional electroactive polymers (EAP): (a) unlike EAPs, EAPap does not require an electrolyte solution and can be activated in air, and (b) it consumes little electrical power (<10 mW/m^2) and can be activated at low voltage (requires as low as 0.25 V to produce a displacement of one micron; 0.25 V/μm).[121] The same group[122] also developed prototype flexible speakers using this piezoelectric cellulose film. The paper speakers produced a sound pressure level (SPL) of 40 dB in the frequency range of 10−20 kHz at a short distance of 10 cm, while they did not show any notable difference at larger distances at 20 and 30 cm. They found that the acoustic performance of circular shaped speakers is better than that of rectangular ones. The vibration sensing capability of cellulose EAPap was also examined by the group.[123] The sensor was fabricated by depositing metal electrodes on both sides of the piezoelectric cellulose and finally packaging it with thin laminating polymer films. Its vibration sensing behavior was assessed by attaching it on the surface of an aluminum cantilever beam, and the response of cellulose EAPap to vibrations of the beam was measured. A cellulose EAPap with interdigitated electrodes as an acoustic wave sensor has been reported for detecting isopropyl alcohol (IPA); here piezoelectric cellulose acted as both substrate and sensing layer. The velocity of the acoustic wave of the sensor was reported to be 2400 m/s at a resonant frequency response of 58.2 MHz, comparable to other piezoelectric materials.[124] Although the authors have reported a shift in resonant frequency due to exposure of the device to IPA, no data were available about its performance, sensitivity, and concentration of target VOC.

Significant research effort has been recently focused on developing piezoelectric paper, and most of the work reported to date essentially involves synthesis of nanostructured zinc oxide (ZnO) on a paper substrate in the low-temperature regime. Gullapalli et al. have reported the strain sensing and energy harvesting capability of the ZnO-paper, wherein they successfully grew piezoelectric ZnO nanostructures on printing paper by adopting a wet-chemistry route.[23,125] Kim et al. have grown vertically aligned ZnO nanorods on metal-coated paper substrate and demonstrated their capability as a flexible piezoelectric nanogenerator; interestingly, their nanogenerator exhibited stable current output even at 200 °C.[126] Soomro et al. have directly grown the ZnO nanorods on a cleanroom paper through a wet-chemistry approach and demonstrated their energy harvesting capability.[127] Although the hydrothermal synthesis approach is a simple and cost-effective method to fabricate piezoelectric paper, this technique poses several challenges to mass production of such paper. For instance, (i) it requires mechanically strong paper substrates, as paper can soften in the heated growth solution during synthesis of ZnO nanostructures on it. (ii) In-homogeneous growth of nanostructures on the paper substrate occurs due to random orientation of fibers, and (iii) it is time-consuming, as hydrothermal synthesis requires several hours to grow the nanostructures. To address these issues recently, Mahadeva et al.[128] proposed a method to produce low-cost and environmentally friendly hybrid functional paper that can be used as piezoelectric substrate for sensing applications. The fabrication method is very simple and it does not employ any sophisticated equipment. This approach involves attaching nanostructured barium titanate ($BaTiO_3$) to the wood cellulose fibers through fiber functionalization. This is achieved through a layer-by-layer approach, that leads to the creation of a positively charged surface on the wood fibers. Immersion of the treated wood fibers into a $BaTiO_3$ suspension leads to the electrostatic binding of the negatively charged $BaTiO_3$ to the wood cellulose fibers. The piezoelectric properties of the paper were estimated as a function of $BaTiO_3$ content, and they were found to increase with $BaTiO_3$ loading. Piezoelectric paper with 48 wt % $BaTiO_3$ exhibited a large piezoelectric coefficient ($d_{33} = 4.8 \pm 0.4$ pC/N) and also showed the highest sensitivity and a linear response to a change in compression force and impact loading.[129] Compared to d_{33} (75−190 pC/N)[132] of bulk $BaTiO_3$, hybrid piezoelectric paper showed lower piezoelectric coefficients. This is most likely due to the absorption of a large proportion of the applied stress by the wood fiber network that reduces the effective strain in the nanoparticles due to the reduced adhesion between the functionalized wood fibers.[128] To address this, more recently they modified the piezoelectric paper fabrication process that involves activation of functionalized wood fiber with paper-strength-enhancing additives (carboxymethyl cellulose) prior to paper making. This process resulted in a piezoelectric paper that is as strong as printing paper and at the same time possess a large piezoelectric coefficient d_{33} = 37−45.7 ± 4.2 pC/N. The large piezoelectric coefficient of CMC added piezoelectric paper is most likely due to a reduced absorption of the applied stress by the wood fiber network and a more effective transfer of strain to

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the nanoparticles in the piezoelectric paper as a result of the improved fiber−fiber bonding.[133]

As discussed in this section, dissolution and regeneration of wood cellulose fiber in a DMAc/LiCl solvent system results in a large piezoelectric coefficient (d_{31} = 27.3 pC/N) but suffers from discrepancy in the piezoelectric properties from batch to batch. Alternatively, piezoelectric paper can be made by incorporating nanostructured piezoelectric material into wood cellulose fiber prior to the paper-making process. This manufacturing method is cost-effective, as it does not employ any sophisticated equipment and it can also be easily integrated into the existing paper-making process; paper produced through this route showed a large piezoelectric coefficient (d_{33} = 37−45.7 ± 4.2 pC/N). This is the largest d_{33} value reported for paper to date, and it is comparable to the piezoelectric coefficient of commercially available piezoelectric polymers such as polyvinylidene fluoride (PVDF; d_{33}= 20- 35 pC/N). Table S8[130,131] (Supporting Information) compares the piezoelectric constants of different types of piezoelectric paper with that of piezoelectric polymers.

5. CONCLUDING REMARKS AND OUTLOOK

The use of paper as a low-cost functional material for a variety of sensing devices is becoming common, as paper is advantageous over conventional polymer substrates in terms of (i) cost (i.e. paper is made by using naturally available renewable resources and hence is cheaper than conventional polymer or silicon substrates; for example, softwood craft pulp costs US$ 850−900 per ton while PDMS costs US$ 60 per kg and a six inch silicon wafer costs US$ 10−30 depending on thickness, doping, and type) and (ii) disposability and environmental benefits (i.e. paper is flammable in nature and hence paper-based devices could be easily and safely disposed though incineration).

At present, the performance of paper-based electronic devices does not match the silicon-based devices. As revealed in this review, the maximum on/off ratio of 5.9×10^4 was achieved with a carrier mobility of 6.7 cm^2/V s for a paper transistor made by employing a highly porous cellulose substrate. In order to improve the performance of paper-based electronic devices, issues associated with paper electronic device fabrication need to be addressed such as roughness, porosity, and impurities. The effect of chemical impurities in the paper and of environmental conditions such as temperature and humidity can cause significant dimensional changes in the paper and can also lead to fluctuations in the conductivity of printed conductive structures on paper.

The porous nature of paper is particularly useful for applications to energy storage. Paper-based energy devices developed using carbon nanotubes and silver nanowires as a conduction material show the highest performance with a capacitance of 200 F/g, storage capacity of 150 mAh/g, energy density of 47 Wh/kg, and power density of 200 kW/kg. The energy density of paper-based energy storage devices is still considerably lower than that of commercially available devices. However, paper-based devices are particularly suitable where flexibility and environmental friendliness matters. There is an opportunity for more fundamental research to improve the performance of paper-based devices.

Paper has an enormous potential for disposable point-of-care (POC) devices, yet improvements in the design and in the fabrication process are still required to match the performance of conventional analytical techniques. The change of analyte concentration in the paper microchannel due to evaporation is the most often encountered problem in paper microfluidic devices; one way to address this problem is to coat printing toner on the top and bottom of the channel region.[106] Recent advances in analysis techniques, such as the design of μPAD devices that are compatible with a commercial glucometer, or an instrumentation free detection approach, such as fully enclosed μPADs, or the multidetection capability of 3D paper devices are stepping stones toward commercialization of paper-based diagnostic devices.

Moreover, paper has been recognized as a low-cost substrate for piezoresistive strain sensors in recent research. Liu et al.[101] have developed paper-based MEMS force sensors and a MEMS balance, with a resolution of 120 μN and 24 mg, respectively. Further, Ren et al.[102] have reduced the cost of paper-based MEMS force sensors further from $0.04 per device to $0.01 per device by adapting fabrication methods proposed by Liu et al.[101] However, when using paper substrates for strain sensing, it is important to consider the properties of the paper itself; these properties are significantly influenced by type of fibers, grammage, etc.

Piezoelectric paper is another class of functional materials. Electroactive paper has been prepared by chemical processing of wood pulp. Although the piezoelectric coefficients of EAPap (d_{31} = 27.3 pC/N) match that of commercial piezoelectric polymers such as PVDF (d_{33} = 20−35 pC/N), piezoelectric EAPap requires additional processing and thereby increases the cost significantly. Also, EAPap processing involves the use of toxic chemicals, and their biodegradability is questionable. To overcome these issues, researchers have directed their effort to incorporate piezoelectric nanomaterials through fiber functionalization. This process is cheap and can be integrated into the existing paper-making process without any difficulty. So far, a variety of sensing devices has been demonstrated using piezoelectric paper.

Many of the paper-based sensing devices reported so far work very well in laboratory scale proof of principle experiments, yet when it comes to the repeatability and reproducibility, they do not match the performance of commercial devices. Fine tuning of the design and production aspects of these paper devices is therefore necessary to enhance their performance. Studies on the impact of different physical properties of paper, such as surface energy, deterioration, temperature, and humidity on device performance are necessary to bring the paper-based sensing devices closer to market. It might require a concrete effort of researchers in the paper industry, materials, bioscience, and electrical engineering to transform the prototypes into commercial products.

To date, numerous fabrication techniques have been developed to construct conducting structures or to incorporate hydrophobic barriers into paper substrates, for paper-based sensing devices fabrication. Many of these techniques do not require any expensive equipment, and they can be executed in ordinary laboratory conditions without the need of cleanroom facilities. The efficiency of these fabrication methods is excellent at laboratory scale, but they fail to meet the industry standard when it comes to scaling up to large-scale manufacturing.

The pulp and paper industry uses a wide variety of fibers from different sources to produce paper with different grammage or quality. Yet, most of the paper-based sensing devices discussed in this review or reported in the literature were fabricated from Whatman filter paper or commercial printing papers. The influence of paper type on device performance has not been determined yet, even though this is especially very important for mechanical sensors such as strain, inertial, force sensing, etc.

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Hence, it is necessary to investigate the influence of paper type on sensor performance, because the properties of paper, such as porosity, mechanical damping, etc., are significantly influenced by the grammage, type of fibers, and their orientation, etc. Also, most of the reports published to date are dedicated to developing scalable fabrication techniques and demonstrating newer applications of the paper-based devices. However, comprehensive mathematical modeling of the paper-based devices has not been undertaken yet, while the modeling of the electrical, ionic, and fluidic characteristics of paper could provide solutions to many of the problems associated with paper-based devices.

■ ASSOCIATED CONTENT

Supporting Information

Tables that compare the performance characteristics of different devices of a given category as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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