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Research Article

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Handwriting Iontronic Pressure Sensing Origami

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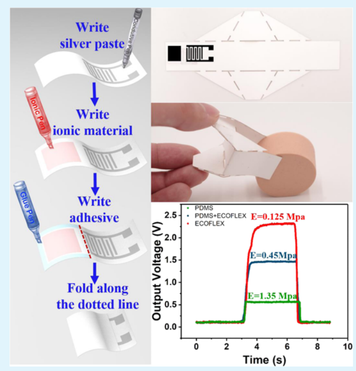
Supporting Information

ABSTRACT: Origami, the ancient paper folding art, has been investigated from paper electronics to medical equipment and even spaceflight for its amazingly rich scientific foundation of building a complex three-dimensional (3D) structure, saving space, transmitting force, and establishing a load-bearing structure. Introducing origami into flexible pressure sensing will bring a new function to the planar electrical component. In this paper, a flexible iontronic sensing mechanism, handwriting process, and origami were combined into a pressure sensing platform, providing a handwriting iontronic pressure sensing origami with high performance, customized design, and 3D sensing ability. The handwriting process provides a simple, low-cost, efficient, no equipment limitation, and customized manufacturing method in preparing the pressure sensing origami using one commercial paper, while an ionic−electrode interface can be easily constructed by folding. Moreover, the device integrates the advantages of origami of forming a 3D structure, force transmission, and structural support with the pressure sensing function. Notably, the handwriting iontronic pressure sensing origami offers a high device sensitivity of 1.0 nF/(kPa cm^2), a detection limitation of 5.12 Pa, a rapid mechanical response time of 6 ms and a reset time of 4 ms, and an ultrahigh repeatability under periodic pressure. Benefiting from the unique properties of origami and the remarkable performances, the proposed handwriting iontronic pressure sensing origami can be highly advantageous for the emerging applications such as STEM education, customized electronic design, human−machine interfaces, etc., where high performance, rapid prototype, and 3D sensing are required.



KEYWORDS: *pressure sensor, handwriting, origami, iontronic, ionic liquid gel*

INTRODUCTION

Origami, the ancient paper folding art, originally used to make toys and trinkets, has existed in different forms for centuries in many countries.[1] Over the past few decades, scientists and engineers have begun to investigate the amazingly scientific foundations of origami, which includes the characteristics of building a complex three-dimensional (3D) structure, saving space, transmitting force, and establishing a load-bearing structure, thus widening the applications of origami from paper electronics to medical equipment and even spaceflight as a hotspot in scientific and engineering research areas.[1−3] Due to the specialty of generating a complex 3D structure, the origami method is considered to be an effective technique for establishing 3D structural electronics.[4−6] Highly folded, stereo, and space-saving 3D structures can be built directly via origami and have been used in practical applications, such as electrochemical detectors, analysis devices, triboelectric nanogenerators, photodetectors, antennas, and lithium-ion batteries.[7−11] Flexible pressure sensing is a novel technology that utilizes a two-dimensional (2D) planar sensing component to detect the force, force direction, and its distribution and has been widely researched for robotic tactile sensing, wearable health monitoring, interaction between a human and an object, etc.[12] However, limited by its 2D structure, the role of flexible pressure sensing in stereo force detection and new feature measurement are also limited.[13] Therefore, introducing the concept of origami into flexible pressure sensing and taking advantages of its characteristics of stereo structure, force transmission, and structural support are potential methods to solve these problems.

Traditionally, origamis are made from paper, a common material in everyday life consisting of natural or artificial cellulose fibers. Unlike the substrates such as silicon, glass, and plastic, paper contains the integrated advantages of low cost, light weight, mechanical flexibility, environmentally friendly, natural porous structures, printable, writable, and origami-able.[13,14] The paper-based pressure sensors previously reported are mainly based on two simple structures, i.e., the functional paper sandwiched between two conductive paper electrodes or the functional paper contacted with a patterned conductive

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paper electrode.[13] According to the difference of the sensing mechanisms, the functional paper can be categorized as a resistive paper, a dielectric paper, a triboelectric paper, and an iontronic paper.[8,13,15,16] Generally, they are modified from common papers via printing, spraying, and dip-coating functional additives such as metal nanowires, conductive polymers, graphene, carbon nanotubes, poly(dimethylsiloxane) (PDMS), poly(vinylidene difluoride) (PVDF), ionic gel, etc.[13,15,17−19] The resistive paper-based pressure sensors detect the variations of the resistance induced by deformation upon the applied pressure. However, they face the problems of nonlinearity and reduced sensitivity as the pressure increases.[15] The capacitive paper-based pressure sensors typically utilizes the distance variation of the parallel conductive paper electrodes under pressure.[16] However, such sensing capacitors are typically measured on the order of tens to hundreds of pF, which is susceptible to the environmental conditions, particularly the parasitic capacitance noises caused by humans, resulting in reduced device accuracy and stability. The triboelectric paper-based pressure sensors measure the induced triboelectric voltage generated at dynamic pressure. Due to its physical limitations, the sensors are insensitive to static forces.[8] Recently, a novel pressure sensing mechanism, called flexible iontronic sensing (FITS), has been introduced that utilizes pressure-induced capacitance changes at the electrode/ionic material interface.[20] Notably, once the ions come in contact with the electrodes, an electric double layer (EDL) is formed at the interface of the electrodes to constitute an EDL capacitor. Since the distance between two charge layers is very small (typically less than 0.5 nm), this capacitor has a particularly high unit area capacitance (UAC) up to several $\mu F/cm^2$ in a sub-MHz spectrum.[21,22] Based on the EDL theory, the measured capacitance of the EDL pressure sensor is proportional to the UAC of the iontronic interface and the contact area between the electrode and the ionic surface, which can be increased by the enhanced pressure applied to the sensor. As a result, the iontronic pressure sensor has shown extremely high sensitivity and resolution, while the parasitic noises can be largely negligible, given its ultrahigh signal-to-noise ratio (SNR).[21−23] Several types of iontronic pressure sensors based on different iontronic materials have been developed, including the droplet pressure sensors based on ionic liquids, transparent film-type pressure sensors based on solid ionic liquid gel, fabric sensors based on electrospinning iontronic fabric, epidermal sensors using skin itself as the iontronic sensing material, etc.[21,23−25] Moreover, based on FITS, we have reported an all-in-one iontronic sensing paper that utilizes the natural microporous structure of the paper and ionic liquid gel to form a novel sensing modality with the unique printable, cuttable, and foldable features of the paper.[13]

The functional modification of common paper is the key to achieve a pressure sensing paper device. Various processing technologies have been developed to integrate a resistive, dielectric, triboelectric, or ionic precursor with a cellulose assembly to form a functional composite. Common semiconductor fabrication methods such as sputtering or evaporation of a functional precursor on common paper provide high uniformity, but their high cost and process complexity limit their applications to inexpensive, fast preparation, and customized designed devices.[26,27] Printing techniques such as inkjet printing, screen printing, and wax printing are becoming increasingly popular in manufacturing functional paper due to their superior characteristics such as low cost and rapid prototyping.[28−31] However, such printing processes require customized instruments and trained personnel.[14] In addition, adding the functional precursor, such as a soluble ionic gel into the paper pulp during the papermaking procedure, leads to a functional paper with uniform and isotropy electrical properties, but this process is complex and time-consuming.[13] Therefore, cost-effective, easy to operate, and low device dependency fabrication methods to prepare functional paper for fast and customized prototyping are needed. For such significant needs, the handwriting process for manufacturing electronic devices has emerged.[14,32−36] The handwriting process is a simple and rapid manufacturing method that is inexpensive, no instruments requirement, and is highly compatible with paper substrates.[32] These features endow untrained personnel with the capability to manufacture paper-based electronic devices on demand for specific on-site applications.[34] Therefore, in designing and preparing a low-cost and customized functional paper used in pressure sensing, the handwriting processes will provide an efficient fabrication strategy.

In this work, a handwriting iontronic pressure sensing origami based on an iontronic mechanism was developed. The handwriting process provides a low-cost and efficient manufacturing method in preparing functional paper, while an ionic−electrode interface can be easily constructed by folding. Notably, by well-designing the structure, a complicated 3D pressure sensing origami with specific mechanical characteristics and new functions can be made. The handwriting iontronic pressure sensing origami showed a high device sensitivity of 1.0 $nF/(kPa\ cm^2)$, a single Pascale resolution of 5.12 Pa, a rapid mechanical response time of 6 ms and a reset time of 4 ms, and an ultrahigh repeatability under periodic pressure. In addition, a variety of demonstrations have been performed based on the 3D structural pressure sensing origami, such as a paper crane with force sensing ability to detect the load for different words' output, a paper microforce gauge for weighting, and a pressure sensitive origami gripper to identify the hardness of objects while grapping, indicating the potential applications by integrating the natural characteristics of origami with the pressure sensing function. The key innovation is to have all of the functional materials built on a single-layer planar paper substrate, from which the specific folding procedures would enable the appropriate device architecture to be constructed into a 3D format. In such implementation, we can build the entire functional devices solely relying on handwriting and origami, which is facile and inexpensive, while still maintaining high device sensitivity.

RESULTS AND DISCUSSION

The single-point handwriting iontronic pressure sensing origami unit follows a simple double-layer sensing architecture, that is, handwritten interdigital electrodes faced the ionic gel layer with an adhesive bonding frame, as shown in Figure 1a, of which the base substrate is a commercial copy paper. Figure 1b demonstrates the simple handwriting preparation process flow of the handwriting iontronic pressure sensing origami. Conductive silver paste filled in a ballpoint pen was first written on a commercial copy paper to form an interdigital electrode. Afterward, ionic ink, which contains an ionic liquid, a polymer, and a solvent, was written by an ionic pen, followed by writing with an acrylate emulsion adhesive to form an adhesive bonding frame. After evaporating the solvent at atmosphere or in an oven, the multicomponent structure can

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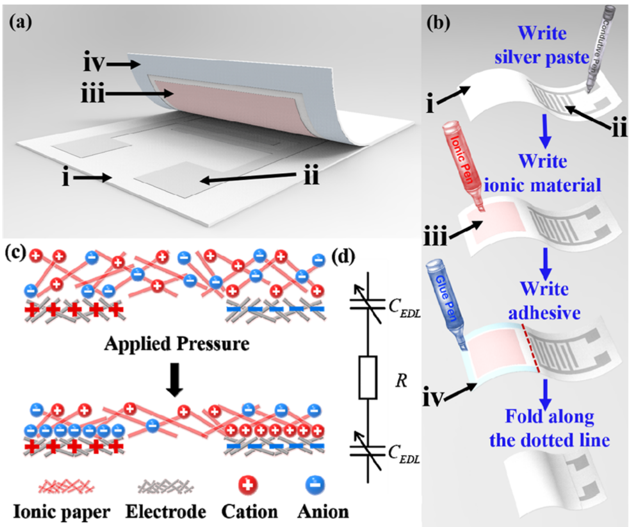

Figure 1. (a) Schematic illustration of the handwriting iontronic pressure sensing origami ((i) paper, (ii) interdigital electrodes, (iii) ionic gel, and (iv) adhesive). (b) Handwriting iontronic pressure sensing origami processing flow chart. (c) Working principle of the handwriting iontronic pressure sensing origami. Physical contacts between the ionic paper fiber and conductive layer vary under external mechanical stimuli. (d) Equivalent electrical circuit of the handwriting iontronic pressure sensing origami.

be folded into a sensing device with a face-to-face contact between the interdigital electrodes and the ionic region. It is worth noting that such a process can be applied on different kinds of paper substrates such as commercial copy paper, heavy-duty cardboard paper, tissue paper, etc., as long as they are compatible with the handwriting process. Moreover, with folding to form the iontronic sensing interface and handwriting to deposit and pattern the functional materials, the process is especially suitable for rapid customized design or education where a simple process, rapid prototyping, and low device dependency are needed.

The pressure sensing of the handwriting iontronic pressure sensing origami depends on the direct contact between the conductive and ionic cellulose fibers. Commercial copy paper can be treated as the natural cellulose fiber assembly with a porous microstructure (Figure 2b). Through the writing process, the ionic ink was evenly coated on the surface of the cellulose fiber and formed an ionic gel coating on the surface, modifying it into the ionic cellulose fiber with a high ionic mobility. Meanwhile, some cellulose fiber was also modified into the conductive fiber by direct writing the conductive paste. Through folding, the iontronic interface can be formed by the face-to-face contact between the ionic fiber area and the conductive fiber area. The equivalent circuit of the handwriting iontronic pressure sensing origami (a pair of interdigital electrodes) can be regarded as the series connection of two EDL capacitors, which refer to the interfaces between the electrodes and the ionic gel region, and one resistor, which refers to the resistance of the ionic gel region between the electrodes, as shown in Figure 1d. When no pressure is applied to the handwriting iontronic pressure sensing origami, the contact area between the electrodes and the ionic gel region is relatively low due to the porous fibrous structure of the paper. Under external pressure, the ionic fiber and the conductive fiber at the interface will bend correspondingly, increasing the contact point between the

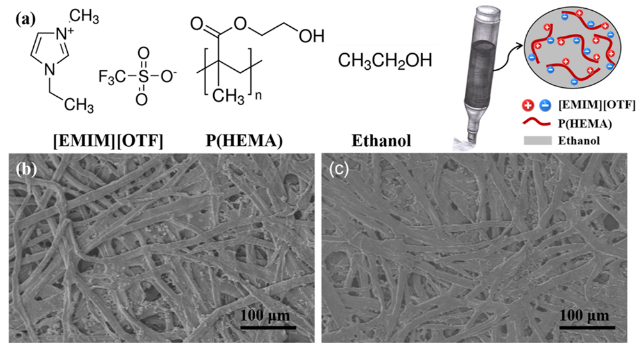

Figure 2. (a) Illustration of the molecular structures of the ionic liquid, the matrix, and the solvent: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][OTF]), poly(hydroxyethyl methacrylate) (P(HEMA)), and ethanol. (b) Scanning electron microscopy (SEM) photo of the copy paper surface structure. (c) SEM photo of the copy paper structures written with the ionic material of P(HEMA)−[EMIM][OTF] at a weight ratio of 1:2.

ionic−conductive fibers, advancing the contact area between the electrodes and the ionic gel region, and resulting in the rise in the overall EDL capacitance of the device.

To further detect the theoretic relationship between the EDL capacitance (C) of the device and the pressure (P) applied, the pressure−capacitance sensing model of the paper sensor has been derived from classical compression behavior of fibrous assemblies in our previous work.[13,37] The detailed derivation process can be found in the Supporting Information of our previous paper.[13] The change in the contact area between the ionic region and the electrodes caused by compression produces a corresponding capacitance change at the EDL interface. According to the fibrous assembly compression model, the main reason for changing the contact area between the ionic region and the electrodes under compression is the bending deformation of the single fiber.[38] When the paper fibrous assemblies are compressed, the air is extruded, increasing the volume fraction of the fibrous assemblies, which corresponds to an increase in the contact area between the ionic region and the electrodes. For the device with a unit sensing area (A), the device pressure−capacitance relationship can be expressed as

$$C = c_0 \frac{A}{2\pi}\left[\left(\frac{P}{KE} + V_{f_0}^3\right)^{1/3} - V_{f_0}\right] \quad (1)$$

where K represents the spatial distribution and characteristics of the cellulose fiber, which is a constant for a given paper, E is the elastic modulus of cellulose fiber, V_{f_0} is the initial volume fraction of the fiber assembly when $P = 0$, and c_0 represents the unit area capacitance (UAC) of the ionic−conductive interface. The UAC, which is directly proportional to the EDL capacitance of the device, can be defined as the measured capacitance of the unit area (1 cm^2) ionic−conductive interface with full contact and is directly measured by apply extremely high pressures (50 MPa) on the interface. UAC is the intrinsic property of the materials and can be treated as a constant for given ionic−conductive interface at a specified temperature, humidity, and alternating electric field frequency and voltage. It can be seen from the above formula that the EDL capacitance of the device has a positive relationship with the UAC (c_0), sensing area (A), and pressure (P), while the elastic modulus of the fiber (E) and the initial fiber volume

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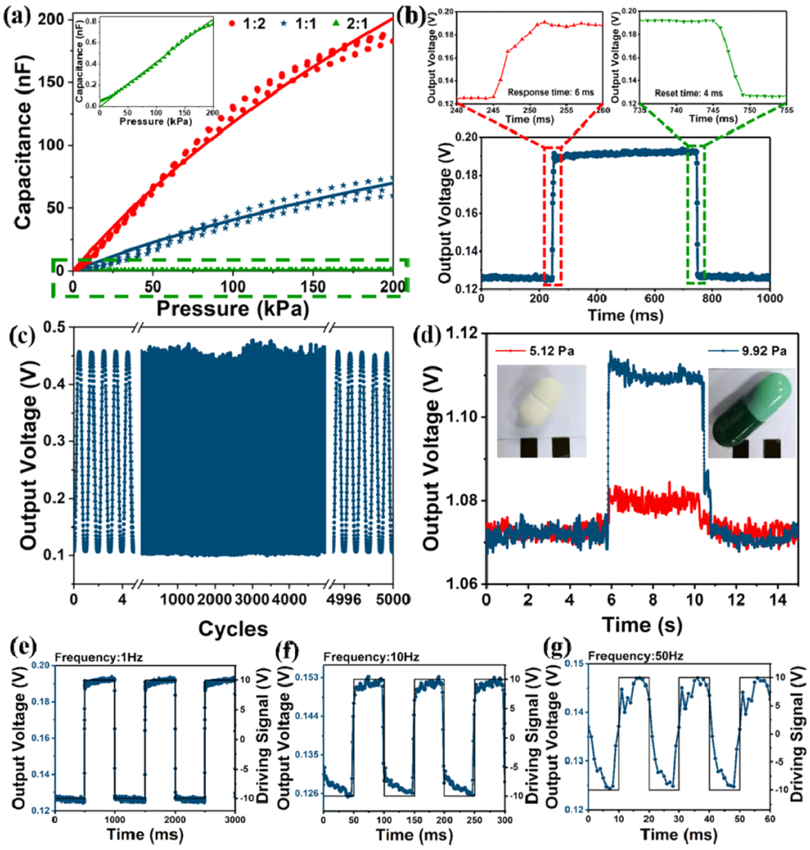

Figure 3. (a) Plots of the experimental and theoretical handwriting iontronic pressure sensing origami sensitivities. The measurement results are plotted as dots, and the sensitivity predicted by the theoretical model is shown with solid lines. (b) Response time and reset time of the handwriting iontronic pressure sensing origami. (c) Measurement stability of the handwriting iontronic pressure sensing origami under cyclic mechanical loads of 10 Hz for 5000 cycles. (d) Measured output voltage curve of the handwriting iontronic pressure sensing origami device under an ultralow pressure applied by a pill. Mechanical response of the handwriting iontronic pressure sensing origami with the ionic material of P(HEMA)–[EMIM] [OTF] 1:1 wt % under varying periodic stimuli of (e) 1 Hz, (f) 10 Hz, and (g) 50 Hz.

fraction (V_{f_0}) have inverse influence on the capacitance of the device. For a given paper substrate, K, E, and V_{f_0} have been decided, so c_0 becomes the most important factor in controlling the performance of the pressure−capacitance relationship as it can be easily changed by modifying the ionic ink formula.

The ionic ink is the key factor for the UAC of the ionic region, thus affecting the pressure response of the device. The ionic material used in this study was an ionic liquid gel composed of 3-methylimidazolium trifluoromethanesulfonate ([Emim][OTF]) with poly(hydroxyethyl methacrylate) (P-(HEMA)). [EMIM][OTF], as a nontoxic, hydrophilic, room-temperature ionic liquid, offers sufficient mobile ions in the gel to generate EDL capacitance.[13] P(HEMA) is a widely used acrylate polymer in the adhesive industry and can be dissolved in various solvents including water, alcohol, acetone, etc. [EMIM][OTF] tends to disperse in the P(HEMA) matrix to form an ionic liquid gel for their similar solubility parameter (25.4 MPa for [EMIM][OTF] and 26.9 MPa for P(HEMA)) and polarity.[39,40] For the handwriting purpose, the ionic liquid gel was predissolved in the solvent to form a writable low-viscosity ink. Considering the requirements of handwriting like fast curing and nontoxic, alcohol with a low boiling point of 78 °C was thus chosen. The prepared ionic ink was injected into the mark pen and directly written on the paper. After the removal of the solvent via evaporation, [EMIM][OTF] molecules are expected to be uniformly dispersed into the polymer chain matrix to form an ionic liquid gel coated on the cellulose fibrous network. Figure 2b,c demonstrates the SEM images of the micromorphology of the copy paper with a fibrous structure before and after writing of the ionic ink with a weight ratio among [EMIM][OTF], P(HEMA), and alcohol of 2:1:1. Obviously, the ionic liquid gel can be evenly coated on the surface of the cellulose fiber, with the fibrous morphology of the paper remained.

To further evaluate and optimize the electrical properties of the handwriting iontronic pressure sensing origami, we configured the devices by handwriting the ionic ink with different formulas and detected their mechanical−capacitive characteristics. Several key device parameters can be deduced from the pressure−capacitance curve of the device, of which sensitivity (S) is one of the most important one. For a pressure sensor, the sensitivity is defined as the ratio of the electric output to the pressure input,[41] while in the iontronic sensor case, it is the ratio of the measured capacitance change to the pressure change, i.e., $S = \mathrm{d}C/\mathrm{d}P$, which can be regarded as the slop rate of the pressure−capacitance curve. As a result, derived from eq 1, the device sensitivity can be expressed as

$$S = \frac{\mathrm{d}C}{\mathrm{d}P} = \frac{Ac_0}{6\pi KE}\left(\frac{P}{KE} + V_{f_0}^3\right)^{-2/3} \quad (2)$$

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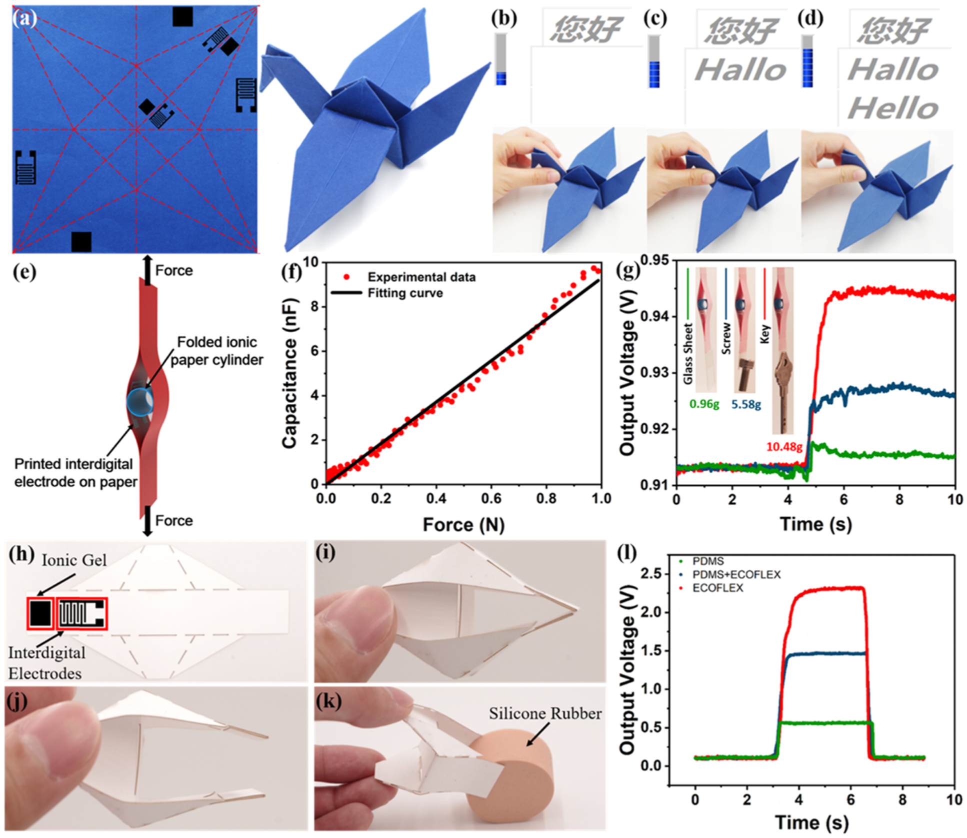

Figure 4. (a) Preparation of the paper crane with four pressure sensing units using handwriting and folding. (b−d) Apply different pressures on the neck of paper crane. (e) Structure of the microforce gauge. (f) Tension−capacitance curve of the microforce gauge. (g) Detected output voltage (proportional to the capacitance of the sensor) curves of the microforce gauge under different weights applied. (h) Preparation of the origami gripper with one pressure sensing unit. (i) Origami gripper in its closed state. (j) Origami gripper in its open state. (k) Photograph of the origami gripper clamping rubber. (l) Detected output voltage of the origami gripper clamping objects of different hardnesses.

Therefore in this study, by establishing a unit area device, we can compare the influence of the ionic ink formula on the sensitivity of the device. As shown in Figure 3a, the experimental measurements of the capacitance as a function of pressure loads were represented by dots, while the theoretical predictions were represented by lines. The curve in the low pressure range (1−25 kPa) is shown in Figure S5 in the Supporting Information. Various ionic inks with the weight ratios between [Emim][OTF] and P(HEMA) ranging from 1:2 and 1:1 to 2:1 were written to form the ionic gel with different ionic liquid concentrations, while the weight ratio between P(HEMA) and alcohol remains 1:1. Specifically, the handwriting iontronic pressure sensing origami with 2:1 weight ratio of P(HEMA)/[Emim][OTF] had a mean pressure sensitivity of 0.0041 nF/(kPa cm^2) below 200 kPa, whereas the handwriting iontronic pressure sensing origami with a composition of 1:1 weight ratio had a sensitivity value of 0.35 nF/(kPa cm^2) in the same pressure range. Moreover, the handwriting iontronic pressure sensing origami with a higher ionic liquid content (1:2 weight ratio) showed a higher sensitivity of 1.0 nF/(kPa cm^2) below 200 kPa. It can be seen that the sensitivity of the handwriting iontronic pressure sensing origami is positively correlated with the concentration of the ionic liquid. With higher ionic liquid concentrations in the ionic liquid gel, more cations and anions can be transferred to the ionic−conductive interface and contribute to the increase of the UAC.[42] Correspondingly, the UACs of the ionic region on a copy paper written using the ionic ink with the weight ratios between [EMIM][OTF] and P(HEMA) of 1:2, 1:1, and 2:1 are 115.39, 1180.98, and 3224.88 nF/cm^2, respectively, as shown in Figure S1, fitting well with the theoretic prediction that the sensitivity is directly proportional to the UAC value. Therefore, writing the ionic ink with higher ionic liquid concentrations during the handwriting iontronic pressure sensing origami preparation is an effective method to increase the sensitivity of the device.

Short mechanical response time and reset time are the key factors in the device's ability to effectively handle rapid external stimuli. We used a piezoelectric actuator driven by square wave signals to apply periodic mechanical load to the sensor. The output of the handwriting iontronic pressure sensing origami was sampled at 1 kHz and recorded using a data acquisition card in the voltage from an amplifying circuit shown in Figure S2 in the Supporting Information. When periodic loads were applied at frequencies of 1, 10, and 50 Hz, the handwriting iontronic pressure sensing origami output voltage generally followed the same shapes as the drive signal, exhibiting small delays and hysteresis, as shown in Figure 3e−g. The output voltage had shown some fluctuation at 50 Hz frequency in Figure 3g. It was mainly caused by the fluctuation of the piezoelectric actuator at high frequencies.[43] The response times and the reset times of the handwriting iontronic pressure sensing origami calculated from the curve at 1 Hz and the curve at 50 Hz were almost the same. The response time of 6 ms and reset time of 4 ms can be extracted from a single pressure cycle (with a frequency of 1 Hz), as illustrated in

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Figure 3b. A fast response time and an extremely fast reset time ensure accurate sensing under rapidly changing pressures, which indicates the device's potentially superior performance in monitoring high-frequency mechanical signals. The repeatability and stability of the handwriting iontronic pressure sensing origami were tested using an electromagnetic actuator driven by a square wave signal (10 Hz) to periodically apply load on the sensor. As shown in Figure 3c, the initial sensor output voltage without pressure and the peak sensor output voltage under pressure have almost no change in 5000 pressure cycles, which indicates that the handwriting iontronic pressure sensing origami has high stability and repeatability. Finally, taking advantages of the high noise immunity of the iontronic sensing mechanism, the handwriting iontronic pressure sensing origami exhibited ultralow detection limitation, as shown in Figure 3d. Single pascal (approximately 5.12 Pa) level detection of ultralight objects has been successfully demonstrated (e.g., a pill of 0.32 g placed on a handwriting iontronic pressure sensing origami with 2.5 × 2.5 cm^2 sensing area).

To demonstrate the advantageous features of the handwriting iontronic pressure sensing origami, such as high sensitivity, ease of processing, and 3D structuring, it has been incorporated into several application scenarios, such as a pressure-sensitive origami crane for education, a paper microforce gauge serving as a simple measuring instrument, and a pressure-sensitive origami gripper for identifying the hardness of objects. The pressure-sensitive crane was prepared by direct writing electrode materials and ionic materials in corresponding positions on the square paper, followed by folding to form a stereo pressure sensing origami. Four pressure sensing units were distributed in the neck, body, wings, and tail of the paper crane, as shown in Figure 4a. The paper crane was connected to a data acquisition circuit and displayed by LabView software. When pressures were applied to various parts of the paper crane, the software would display the corresponding greetings (Hello, Welcome, Thanks, and Goodbye). As the pressure increased, the greetings would be displayed in Chinese, German, and English, respectively. As shown in Figure 4b–d, when we gently pressed the paper crane's body, the screen would display "Hello" in Chinese. As the pressure increased to 50 kPa, the screen displayed Hello in both Chinese and German. When the pressure increased further to 150 kPa, Hello was displayed on the screen in Chinese, German, and English (for a detailed demonstration process, please refer to Movie 1 in the Supporting Information). The handwriting method to configure the 3D functional origami is simple and rapid; it allows untrained people to personally create the stereo sensor for education purposes. In summary, this curriculum incorporates handcrafted, physical principles and language teaching, which help improve students' comprehensive ability for better education.

In addition to the STEM education application illustrated above, the handwriting iontronic pressure sensing origami was configured as a paper microforce gauge for force measuring, as shown in Figure 4e. It has an ionic paper cylinder written with ionic ink placed between two strips of paper with written interdigital electrodes. Without tension, the contact area between the ionic cylinder and the written interdigital electrodes is relatively low. As the tension increases, the similar parallelogram mechanism of the sensor transforms the tension into the pressure of the paper cylinder, resulting in the flattening of the paper cylinder and increasing the contact area with the electrodes; thus, the measured capacitance shows an increase. Figure S3 shows the simulation of the stress of the paper microforce gauge under difference loads (0.96, 5.58, and 10.48 g). Figure 4f summarizes the tension–capacitive characteristics of the paper microforce gauge, where experimental measurements of the capacitance as a function of tension were represented by dots, while the linear fitting were represented by lines. The measured capacitance shows an increase as the tension rises with an average sensitivity of about 10 nF/N. Shown in Figure 4g, the paper microforce gauge can easily distinguish the weights of different items, wherein the key weight is 10.48 g, the bolt weight is 5.58 g, and the glass piece weight is 0.96 g. From the above demonstration, the force transmission characteristic of origami transforms the tension into the pressure at the iontronic interface, introducing a new function to the pressure sensing device via a simple structure.

To further explore the potential applications of the handwriting iontronic pressure sensing origami on simple instrument manufacturing, we integrated our sensor into an origami gripper, which was adapted from Spencer Magleby's works.[44] The gripper origami's design is based on the spherical kinematic configuration of several action origami models and can be made by simply cutting and folding a flat paper. Similar to the foregoing paper crane, electrode materials and ionic materials were written on the head of the gripper and the gripper origami was formed by laser cutting and folding, as shown in Figure 4h. The gripper has a sensing unit with an 10 × 10 mm^2 effective sensing area, and the closed and open states of the origami gripper are shown in Figure 4i, j, respectively. Before the experiment, to obtain samples of different hardnesses, we prepared three cylinders with a diameter of 50 mm and a height of 10 mm using pure PDMS (sylgard 184), PDMS/Ecoflex(00-10) silica gel mixture of 1:1 in weight, and pure Ecoflex, and their Young's moduli are 1.35, 0.45, and 0.125 MPa, respectively.[45,46] During the experiment, we respectively clamped these samples using the gripper origami for about 4 s and then released them. Figure 4l summarizes the results, and it is found that the increase of the hardness leads to the decrease of the output of the device, of which the absolute output value can be used to estimate the hardness of the object. In theory, hardness is associated with the compliance of an object.[47] When an object is clamped by the gripper origami, the same load from the bending of the paper is applied to the object through the gripper head as the specific structure of the gripper,[44] the object will deform, and the deformation rate is related to the Young's modulus of the object. When the force (F) applied to the sensor is a constant, the theoretic output of the device can be expressed as

$$C = c_0 \frac{F}{2P\pi}\left[\left(\frac{P}{KE} + {V_{f_0}}^3\right)^{1/3} - V_{f_0}\right] \quad (3)$$

Obviously, the capacitance decreases with the increase of the pressure, which means the contact area between the sensor and the object clamped increases. The mathematical proof process can be found in the Supporting Information. Figure S4 shows the simulation of the deformation of the three different hardness rubbers under the same load. The load direction is inclined to the rubber plane, as the origami gripper is also tilted when clamping the rubber. Since the Ecoflex is the softest, its deformation is relatively large and the contact with the origami gripper head under the same force is also the largest, so the pressure applied on the contact region is the lowest, thus

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increasing the value of the output voltage. By handwriting the iontronic pressure sensing unit on the gripper origami, a new function is introduced to the mechanical functional unit, making it available to detect multiple properties of the object clamped.

■ CONCLUSIONS

In summary, a high-performance and stereo handwriting iontronic pressure sensing origami was fabricated. As an alternative to conventional paper pressure sensors, the novel device provides a high sensitivity of 1.0 nF/(kPa cm^2), a single Pascale resolution of 5.12 Pa, a rapid mechanical response time of 6 ms and reset time of 4 ms, and an ultrahigh repeatability under periodic pressure. Importantly, the handwriting process provides a simple, low-cost, efficient, no equipment limitation, and customized manufacturing method in preparing the pressure sensing origami using one commercial paper, while an ionic−electrode interface can be easily constructed by folding. Moreover, the device integrates the advantages of origami of forming a 3D structure, force transmission, and structural support with the pressure sensing function. In view of these characteristics, the handwriting iontronic pressure sensing origami shows high potential to be applied in daily life, such as STEM education, customized electronic design, human−machine interfaces, etc., where high performance, rapid prototype, and 3D sensing are required.

■ EXPERIMENTAL SECTION

Preparation of the Ionic Material. Anhydrous ethanol and hydroxyethyl methacrylate were mixed in a weight ratio of 1:1, and a small amount of 2-hydroxy-2-methylpropiophenone (photoinitiator) was added. After the three liquids were uniformly mixed, the mixture was exposed to a 2000 W UV lamp for 1 min to produce poly(hydroxyethyl methacrylate). By adding different weights of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate to poly(hydroxyethyl methacrylate), ionic materials having different ratios of ionic liquids can be obtained.

Preparation of Ionic Pens, Conductive Pens, and Glue Pens. Empty mark pens, acrylate emulsion adhesives, and ballpoint pens filled with a conductive silver paste are commercially available. The previously prepared ionic material and acrylate emulsion adhesive were injected in the empty mark pens, and the pens were kept flat for 1 h before using.

Preparation of a Single-Point EDL Pressure Sensor. Commercial printer paper (manufactured by Double A Public Co., Ltd.) with a thickness of 100 μm was selected as the substrate due to its low cost, high flexibility, and light weight. The outlines of interdigitated electrodes and the ionic region were designed by AutoCAD and printed out on paper substrates by a commercial printer. Then, the blank spaces of the printed outlines were filled with a conductive pen and an ionic pen, each area being written only once. A glue pen was used to apply the acrylate emulsion adhesive on the edges of the sample and encapsulated it so that the sensor could be made.

Measurement Setup. The capacitance−pressure characteristics of the handwriting iontronic pressure sensing origami were characterized by measuring the capacitance of the device under an external pressure. The device with a sensing area of 1 × 1 cm^2 was fixed on the motorized translation stage (MTS50-Z8, Thorlabs) and pushed to a dynamometer (M5-2, Mark-10) by the stage. The external pressure values were obtained by the dynamometer. A 2 × 2 cm^2 silicone rubber (PDMS) was placed between the handwriting iontronic pressure sensing origami and the dynamometer probe to make the stress uniformly distributed. The capacitance of the device was obtained by an LCR meter (Tonghui 2838A) under the sinusoidal input of 1000 Hz and peak voltage of 500 mV; thus, the capacitance−pressure curves of the device were obtained. Mechanical response characterization of the handwriting iontronic pressure sensing origami was conducted by driving a piezoelectric actuator with a 20 V peak-to-peak square wave to apply a periodic contact pressure to the device, while the electromagnetic actuator driven by a 10 V peak-to-peak square wave signal (10 Hz) was used in the repeatability and stability test. The real-time capacitance curve of the device was recorded by a data acquisition card (DAQ, NI USB-6361, National Instruments Corporation). The test system for the handwriting pressure sensing origami is shown in Figure S2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b16780.

> Measurement of the unit area capacitance (UAC) over interrogation frequencies of the ionic region of the handwriting pressure sensing origami; test system for the handwriting pressure sensing origami; simulation of the stress of the paper microforce gauge under difference loads; simulation of the deformation of the three different hardness rubbers under the same load; mathematical derivations for the contact area-to-Capacitance behavior under same force; and experimental and theoretical capacitance−pressure curves (PDF)
>
> Paper crane (MP4)

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Notes

The authors declare the following competing financial interest(s): Y. Chang and T. Pan are involved startup companies that are developing wearable sensing technologies. No potential conflicts of interest exist for the other authors.

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■ REFERENCES

(1) Lang, R. J. The Science of Origami. *Phys. World* **2007**, *20*, 30.

(2) Maanasa, V.; Reddy, S. R. L. J. I. J. C. E. T. Origami-Innovative Structural Forms & Applications in Disaster Management. *Int. J. Curr. Eng. Technol.* **2014**, *4*, 3431−3436.

(3) Callens, S. J.; Zadpoor, A. A. From Flat Sheets to Curved Geometries: Origami and Kirigami Approaches. *Mater. Today* **2018**, *21*, 241−264.

(4) Fang, H.; Li, J.; Ding, J.; Sun, Y.; Li, Q.; Sun, J.-L.; Wang, L.; Yan, Q. An Origami Perovskite Photodetector with Spatial Recognition Ability. *ACS Appl. Mater. Interfaces* **2017**, *9*, 10921−10928.

(5) Rogers, J.; Huang, Y.; Schmidt, O. G.; Gracias, D. H. Origami Mems and Nems. *MRS Bull.* **2016**, *41*, 123−129.
(6) Cheng, X.; Zhang, Y. Micro/Nanoscale 3D Assembly by Rolling, Folding, Curving, and Buckling Approaches. *Adv. Mater.* **2019**, *31*, No. 1901895.
(7) Liu, H.; Xiang, Y.; Lu, Y.; Crooks, R. M. J. A. C. I. E. Aptamer-Based Origami Paper Analytical Device for Electrochemical Detection of Adenosine. *Angew. Chem., Int. Ed.* **2012**, *51*, 6925−6928.
(8) Yang, P. K.; Lin, Z. H.; Pradel, K. C.; Lin, L.; Li, X. H.; Wen, X. N.; He, J. H.; Wang, Z. L. Paper-Based Origami Triboelectric Nanogenerators and Self-Powered Pressure Sensors. *ACS Nano* **2015**, *9*, 901−907.
(9) Lin, C. H.; Tsai, D. S.; Wei, T. C.; Lien, D. H.; Ke, J. J.; Su, C. H.; Sun, J. Y.; Liao, Y. C.; He, J. H. Highly Deformable Origami Paper Photodetector Arrays. *ACS Nano* **2017**, *11*, 10230−10235.
(10) Nogi, M.; Komoda, N.; Otsuka, K.; Suganuma, K. J. N. Foldable Nanopaper Antennas for Origami Electronics. *Nanoscale* **2013**, *5*, 4395−4399.
(11) Song, Z.; Ma, T.; Tang, R.; Cheng, Q.; Wang, X.; Krishnaraju, D.; Panat, R.; Chan, C. K.; Yu, H.; Jiang, H. J. N. C. Origami Lithium-Ion Batteries. *Nat. Commun.* **2014**, *5*, No. 3140.
(12) Li, J.; Bao, R.; Tao, J.; Peng, Y.; Pan, C. Recent Progress in Flexible Pressure Sensor Arrays: From Design to Applications. *J. Mater. Chem. C* **2018**, *6*, 11878−11892.
(13) Li, S.; Pan, N.; Zhu, Z.; Li, R.; Li, B.; Chu, J.; Li, G.; Chang, Y.; Pan, T. All-in-One Iontronic Sensing Paper. *Adv. Funct. Mater.* **2019**, *29*, No. 1807343.
(14) Qin, Y. H.; Pan, S.; Howlader, M. M. R.; Ghosh, R.; Hu, N. X.; Deen, M. J. Paper-Based, Hand-Drawn Free Chlorine Sensor with Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate). *Anal. Chem.* **2016**, *88*, 10384−10389.
(15) Zhan, Z. Y.; Lin, R. Z.; Tran, V. T.; An, J. N.; Wei, Y. F.; Du, H. J.; Tran, T.; Lu, W. Paper/Carbon Nanotube-Based Wearable Pressure Sensor for Physiological Signal Acquisition and Soft Robotic Skin. *ACS Appl. Mater. Interfaces* **2017**, *9*, 37921−37928.
(16) Mazzeo, A. D.; Kalb, W. B.; Chan, L.; Killian, M. G.; Bloch, J. F.; Mazzeo, B. A.; Whitesides, G. M. J. A. M. Paper-Based, Capacitive Touch Pads. *Adv. Mater.* **2012**, *24*, 2850−2856.
(17) Li, W.; Xiong, L.; Pu, Y. M.; Quan, Y.; Li, S. B. High-Performance Paper-Based Capacitive Flexible Pressure Sensor and Its Application in Human-Related Measurement. *Nanoscale Res. Lett.* **2019**, *14*, 183.
(18) Tao, L. Q.; Zhang, K. N.; Tian, H.; Liu, Y.; Wang, D. Y.; Chen, Y. Q.; Yang, Y.; Ren, T. L. Graphene-Paper Pressure Sensor for Detecting Human Motions. *ACS Nano* **2017**, *11*, 8790−8795.
(19) Yu, Z. Z.; Tang, Y.; Cai, G. N.; Ren, R. R.; Tang, D. P. Paper Electrode-Based Flexible Pressure Sensor for Point-of-Care Immunoassay with Digital Multimeter. *Anal. Chem.* **2019**, *91*, 1222−1226.
(20) Heikenfeld, J.; Jajack, A.; Rogers, J.; Gutruf, P.; Tian, L.; Pan, T.; Li, R.; Khine, M.; Kim, J.; Wang, J.; Kim, J. Wearable Sensors: Modalities, Challenges, and Prospects. *Lab Chip* **2018**, *18*, 217−248.
(21) Nie, B.; Li, R.; Cao, J.; Brandt, J. D.; Pan, T. J. A. M. Flexible Transparent Iontronic Film for Interfacial Capacitive Pressure Sensing. *Adv. Mater.* **2015**, *27*, 6055−6062.
(22) Nie, B.; Li, R.; Brandt, J. D.; Pan, T. Iontronic Microdroplet Array for Flexible Ultrasensitive Tactile Sensing. *Lab Chip* **2014**, *14*, 1107−1116.
(23) Nie, B.; Xing, S.; Brandt, J. D.; Pan, T. Droplet-Based Interfacial Capacitive Sensing. *Lab Chip* **2012**, *12*, 1110−1118.
(24) Li, R.; Si, Y.; Zhu, Z.; Guo, Y.; Zhang, Y.; Pan, N.; Sun, G.; Pan, T. J. A. M. Supercapacitive Iontronic Nanofabric Sensing. *Adv. Mater.* **2017**, *29*, No. 1700253.
(25) Zhu, Z.; Li, R.; Pan, T. J. A. M. Imperceptible Epidermal−Iontronic Interface for Wearable Sensing. *Adv. Mater.* **2018**, *30*, No. 1705122.
(26) Siegel, A. C.; Phillips, S. T.; Dickey, M. D.; Lu, N.; Suo, Z.; Whitesides, G. M. Foldable Printed Circuit Boards on Paper Substrates. *Adv. Funct. Mater.* **2010**, *20*, 28−35.
(27) Yuan, L. Y.; Xiao, X.; Ding, T. P.; Zhong, J. W.; Zhang, X. H.; Shen, Y.; Hu, B.; Huang, Y. H.; Zhou, J.; Wang, Z. L. Paper-Based Supercapacitors for Self-Powered Nanosystems. *Angew. Chem., Int. Ed.* **2012**, *51*, 4934−4938.
(28) Qin, Y.; Alam, A. U.; Howlader, M. M.; Hu, N. X.; Deen, M. J. Inkjet Printing of a Highly Loaded Palladium Ink for Integrated, Low-Cost pH Sensors. *Adv. Funct. Mater.* **2016**, *26*, 4923−4933.
(29) Tortorich, R. P.; Shamkhalichenar, H.; Choi, J. W. Inkjet-Printed and Paper-Based Electrochemical Sensors. *Appl. Sci.* **2018**, *8*, 288.
(30) Li, X.; Scida, K.; Crooks, R. M. Detection of Hepatitis B Virus DNA with a Paper Electrochemical Sensor. *Anal. Chem.* **2015**, *87*, 9009−9015.
(31) Kim, W.; Lee, J. C.; Shin, J. H.; Jin, K. H.; Park, H. K.; Choi, S. Instrument-Free Synthesizable Fabrication of Label-Free Optical Biosensing Paper Strips for the Early Detection of Infectious Keratoconjunctivitides. *Anal. Chem.* **2016**, *88*, 5531−5537.
(32) Li, Z.; Liu, H.; Ouyang, C.; Hong Wee, W.; Cui, X.; Jian Lu, T.; Pingguan-Murphy, B.; Li, F.; Xu, F. Recent Advances in Pen-Based Writing Electronics and their Emerging Applications. *Adv. Funct. Mater.* **2016**, *26*, 165−180.
(33) Kurra, N.; Kulkarni, G. U. Pencil-on-Paper: Electronic Devices. *Lab Chip* **2013**, *13*, 2866−2873.
(34) Bandodkar, A. J.; Jia, W.; Ramírez, J.; Wang, J. Biocompatible Enzymatic Roller Pens for Direct Writing of Biocatalytic Materials:"Do-it-Yourself" Electrochemical Biosensors. *Adv. Healthcare Mater.* **2015**, *4*, 1215−1224.
(35) Kim, S. S.; Na, S. I.; Jo, J.; Tae, G.; Kim, D. Y. Efficient Polymer Solar Cells Fabricated by Simple Brush Painting. *Adv. Mater.* **2007**, *19*, 4410−4415.
(36) Wang, Y.; Zhou, H. To Draw an Air Electrode of a Li−Air Battery by Pencil. *Energy Environ. Sci.* **2011**, *4*, 1704−1707.
(37) Hu, J. *Structure and Mechanics of Woven Fabrics*; Elsevier, 2004.
(38) Pan, N. Analytical Characterization of the Anisotropy and Local Heterogeneity of Short Fiber Composites: Fiber Fraction as a Variable. *J. Compos. Mater.* **1994**, *28*, 1500−1531.
(39) Çaykara, T.; Özyürek, C.; Kantoğlu, Ö.; Güven, O. Influence of Gel Composition on the Solubility Parameter of Poly (2-hydroxyethyl methacrylate-itaconic acid) Hydrogels. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 1995−2003.
(40) Faúndez, C. A.; Barrientos, L. A.; Valderrama, J. O. Modeling and Thermodynamic Consistency of Solubility Data of Refrigerants in Ionic Liquids. *Int. J. Refrig.* **2013**, *36*, 2242−2250.
(41) Vig, J. R.; Walls, F. L. In *A Review of Sensor Sensitivity and Stability*, Proceedings of the 2000 IEEE/EIA International Frequency Control Symposium and Exhibition (Cat. No. 00CH37052); IEEE: 2000; pp 30−33.
(42) Grahame, D. C. The Electrical Double Layer and the Theory of Electrocapillarity. *Chem. Rev.* **1947**, *41*, 441−501.
(43) Li, B. Q.; Fan, J. Z.; Li, J. N.; Chu, J. R.; Pan, T. R. Piezoelectric-driven droplet impact printing with an interchangeable microfluidic cartridge. *Biomicrofluidics* **2015**, *9*, No. 054101.
(44) Edmondson, B. J.; Bowen, L. A.; Grames, C. L.; Magleby, S. P.; Howell, L. L.; Bateman, T. C. In *Oriceps: Origami-Inspired Forceps*, ASME 2013 Conference on Smart Materials, Adaptive Structures and Intelligent Systems; American Society of Mechanical Engineers, 2013.
(45) Kim, M.; Moon, B.-U.; Hidrovo, C. H. Enhancement of the Thermo-Mechanical Properties of PDMS Molds for the Hot Embossing of PMMA Microfluidic Devices. *J. Micromech. Microeng.* **2013**, *23*, No. 095024.
(46) Mosadegh, B.; Mazzeo, A. D.; Shepherd, R. F.; Morin, S. A.; Gupta, U.; Sani, I. Z.; Lai, D.; Takayama, S.; Whitesides, G. M. Control of Soft Machines Using Actuators Operated by a Braille Display. *Lab Chip* **2014**, *14*, 189−199.
(47) Dahiya, R. S.; Valle, M. *Robotic Tactile Sensing: Technologies and System*; Springer Science & Business Media, 2012.