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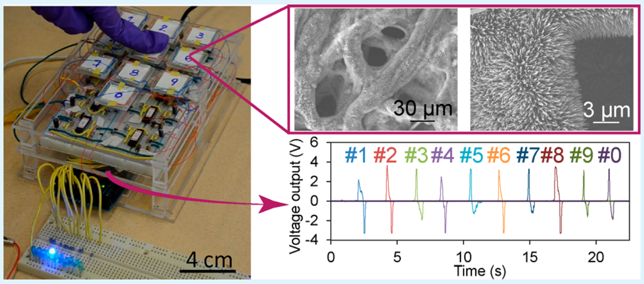
Paper-Based Piezoelectric Touch Pads with Hydrothermally Grown Zinc Oxide Nanowires

Xiao Li,[‡] Yu-Hsuan Wang,[‡] Chen Zhao, and Xinyu Liu*

Department of Mechanical Engineering, McGill University, 817 Sherbrooke Street West, MD270, H3A 0C3, Montreal, Quebec Canada

Supporting Information

ABSTRACT: This paper describes a new type of paper-based piezoelectric touch pad integrating zinc oxide nanowires (ZnO NWs), which can serve as user interfaces in paper-based electronics. The sensing functionality of these touch pads is enabled by the piezoelectric property of ZnO NWs grown on paper using a simple, cost-efficient hydrothermal method. A piece of ZnO-NW paper with two screen-printed silver electrodes forms a touch button, and touch-induced electric charges from the button are converted into a voltage output using a charge amplifier circuit. A touch pad consisting of an array of buttons can be readily integrated into paper-based electronic devices, allowing user input of information for various purposes such as programming, identification checking, and gaming. This novel design features ease of fabrication, low cost, ultrathin structure, and good compatibility with techniques in printed electronics, and further enriches the available technologies of paper-based electronics.



KEYWORDS: *paper-based electronics, touch pad, user interface, zinc oxide nanowires, hydrothermal growth, piezoelectricity*

INTRODUCTION

Paper, as a ubiquitous material in everyday life, has recently emerged as flexible substrates for electronics. It offers the ground to functional electronic modules with advantages of low cost, ease of fabrication, good printability, high flexibility, and light weight. Researchers have fabricated functional electronic components on paper and paperlike substrates such as diodes,[1] transistors,[2] capacitors,[3] and so forth. Through layout design and integration of these components, paper-based electronic devices have achieved a variety of functionalities including flexible display,[4] energy harvesting and storage,[5,6] and "smart" packaging,[7] to name just a few. Beyond electronics, other electrically enabled functions were also realized on paper, as seen in the research and development of paper-based electrochemical biosensors[8−14] and paper-based microelectromechanical systems (MEMS).[15] Considering those remarkable efforts and advances, it is reasonable to predict wider applications of functional paper-based electronic devices in the future.

One type of integral component in many paper-based electronic devices is the human−device interface that allows users to input information, through finger touching, for various purposes such as programming, unlocking, and gaming. It would be desirable to realize these touch-based interfaces directly on paper to form monolithic devices. Despite recent advances in paper-based electronics,[16] few efforts have been made to invent paper-based user interfaces. Conventional piezoresistive, piezoelectric, and capacitive sensing mechanisms have all been applied to developing flexible touch sensors on plastic and polymer substrates; however, implementing them onto paper platforms requires special functionalization and structural designs of paper substrates and is less explored in the context of paper-based electronics. The first attempt to developing paper-based touch pads was reported recently,[17] and the design was based on capacitive sensing and employed commercially available metallized paper to construct touch-sensitive touch buttons. In this research, we seek a simple chemical approach to render the paper piezoelectric and therefore realize piezoelectric touch sensing on single-layer paper substrates.

It is a natural choice to resort to nanomaterials to add new electronic functionalities to paper. The synthesis of zinc oxide (ZnO) nanostructures with different morphologies (e.g., nanowires, nanorods, and nanoflowers) has sparked significant research interests because of their extraordinary semiconductive and piezoelectric properties. These ZnO nanostructures have been used for constructing a variety of functional devices such as solar cells,[18] biosensors,[19] electrical generators,[20] and physical sensors.[21] Another unique merit of ZnO nanostructures is the ease of chemical synthesis using solution-based methods at relatively low temperatures.[22] These synthesis methods are completely compatible with most of the paper substrates, making it possible to integrate piezoelectric ZnO nanostructures onto paper in a cost-efficient fashion.[23,24]

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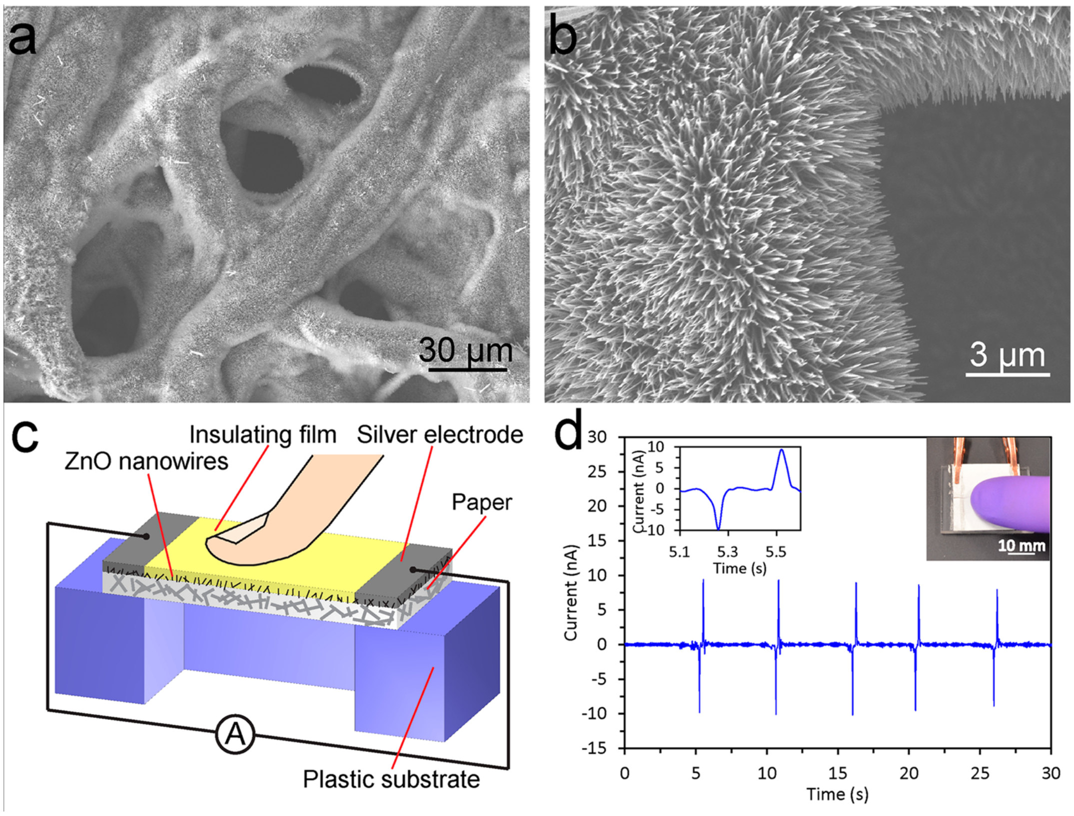

Figure 1. A paper-based piezoelectric touch button with hydrothermally grown ZnO NWs. (a) SEM image of ZnO NWs grown on paper. (b) Zoomed-in SEM image of ZnO NWs grown on cellulose fiber. (c) Schematic view of the touch button. (d) Typical current response of the touch button upon repeated finger presses. (insets) A close look at the first pair of peaks and a photo of the device.

Here, we report a new type of paper-based piezoelectric touch pad integrating ZnO nanowires (ZnO NWs) as the sensing component. We directly grow ZnO NWs on cellulose paper using a simple hydrothermal approach and fabricate the ZnO-NW-coated paper into single-layer piezoelectric touch buttons. Finger contact of a touch button induces deformation of the ZnO NWs on paper microfibers and the ZnO-NW-coated paper substrate as a whole, resulting in an electric charge output from the button, which is converted into a measurable voltage via a charge amplifier circuit. We investigate the effect of length of ZnO NWs grown on paper on the output of the touch button, and calibrate the button output response. We construct an integrated touch pad consisting of ten buttons as input keys as a demonstration device. The paper-based touch pads presented in this work are inexpensive (CAD $0.03 per pad), easy-to-fabricate, ultrathin, lightweight, and easily obtainable and disposable; they will further enrich the available technology set of paper-based electronics.

EXPERIMENTAL PROCEDURES

Hydrothermal Growth of ZnO NWs on Cellulose Paper. We grew ZnO NWs on Whatman 3MM chromatography paper (340 μm thick) through a hydrothermal process modified from a previous protocol.[25] We first synthesized ZnO nanoparticles (ZnO NPs) in ethanol and added the ZnO NPs to the paper to form a seeding layer of ZnO NPs for subsequent hydrothermal growth of ZnO NWs. Zinc acetate dihydrate (ZAD) (20 mL, 4 mM) and sodium hydroxide (NaOH) (20 mL, 4 mM) solutions were respectively prepared in ethanol (200 proof) at 70 °C with heavy stirring. Ethanol (20 mL, 200 proof) was then added to the ZAD solution, which was later heated in oven at 70 °C for 30 min. After the ZAD and the NaOH solutions cooled to room temperature, the NaOH solution was slowly added into the ZAD solution with constant stirring, and the mixture was placed in oven at 60 °C for 2 h to crystallize the ZnO NPs and form a colloidal seeding solution. Six pieces (26 mm × 26 mm) of oxygen-plasma-treated paper were immersed in the seeding solution for 3 min and dried at 86 °C for 3 min, and the seeding and drying processes were repeated six times for each paper piece. When drying the paper pieces after dipping, we put them horizontally on a drying rack with small supporting pillars and alternated the surface of paper piece that faced down, so that each surface had equal times of facing down. This leveled out the effect of gravity to draw the seeding solution to the surface facing down during drying. An aqueous solution of zinc nitrate hexahydrate (ZNH) (50 mM) and hexamethylenetetramine (HMTA) (25 mM) was prepared in a 500 mL flask with stopper. For better efficiency of the ZnO-NW growth, ammonium hydroxide (AH) solution (0.372 M) was added to the growth solution to suppress the homogeneous nucleation of ZnO NWs.[26] AH forms $Zn(NH_3)_n^{2+}$ to buffer the supply of Zn^{2+} so that the supersaturation of the ions in the bulk solution could be lowered and the nucleation in bulk solution could be suppressed. This solution was preheated in oven at 86 °C for 15 min. Three pieces of seeded paper were then dipped into 100 mL of growth solution at 86 °C for growth of 1.5−15 h. After growth, the ZnO-NW paper pieces were washed in deionized water and dried in oven at 90 °C.

Fabrication of the Paper-Based Touch Buttons. The three-dimensional cross-section view of a touch button is illustrated in Figure 1c. We selected the Whatman 3 MM chromatography paper, widely used for fabricating microfluidic devices,[27,28] to fabricate the touch buttons, because: (i) its composition of pure cellulose makes the hydrothermal growth of ZnO NWs more reproducible; and (ii) its relatively thick structure (340 μm) is mechanically stable and can hence better withstand pressing-induced deformations. Nevertheless, ZnO NWs can also be readily grown on other common paper substrates (packing paper[29] and plain printing paper[30]), and our touch button design, in principle, can be realized on many other types of paper as long as the paper substrate provides sufficient mechanical strength for finger pressing.

After the growth of ZnO NWs, the paper pieces were screen printed with silver ink (E1660, Ercon) on their top surfaces to form electrodes (3 mm × 26 mm) (Figure 1c) and dried at 80 °C for 1 h. The silver electrodes form Ohmic contact with the ZnO-NW paper (Supporting Information, Figure S1), similar to cases reported elsewhere.[20] We covered a layer of insulating adhesive film (electrical property described in Supporting Information) on the top surface of the paper, and finally attached the paper to an acrylic piece (3 mm thick) with a central square cavity (20 mm × 20 mm) using double-sided tape. On the basis of commercial prices in small quantities, the total material cost of each touch button was calculated to be CAD $0.03.

EXPERIMENTAL RESULTS

Design of Paper-Based Piezoelectric Touch Pads. The working principle of the proposed touch pad design is based on the piezoelectric response of ZnO NWs on paper upon touching, which was confirmed by a series of experiments (see details in the section of "Investigation of Piezoelectric Response of Touch Pads"). Through the hydrothermal process, ZnO NWs were grown on microfibers of cellulose paper. The ZnO NWs, as shown in Figure 1a,b, stand radially outward on the cellulose microfibers at a high density. A piece of ZnO-NW paper suspended over a supporting substrate forms a touch button (Figure 1c and inset of Figure 1d) and can produce electric charges in response to a finger press. For device prototyping, we used an acrylic substrate with a square cavity as the support underneath the ZnO-NW paper, and the acrylic substrate can be replaced by thick cardboard to make the touch button completely paper-made. An adhesive tape covers the button top surface for electrical insulation.

During operation, finger pressing deforms the ZnO-NW paper, thus inducing mechanical stresses/strains and generating electric charges in the ZnO-NW layer on paper surface. Two silver electrodes screen-printed on top of the ZnO-NW paper collect the generated electric charges and feed them into a precision current meter or a charge amplifier circuit. Figure 1d shows the typical current response of a touch button upon repeated finger presses, measured by a precision potentiostat (PGSTAT302N, Metrohm) at a sampling rate of 50 Hz. A negative current peak at the nanoampere level appeared while pressing and then quickly dissipated through the closed circuit loop. Upon finger release, the deformed paper restored and generated a positive current peak.

We attribute the piezoelectric current output to two types of deformations of ZnO NWs on paper: (i) the deformations of ZnO NWs in the touch area of the paper that were induced directly by a finger press; and (ii) the deformations of ZnO NWs in the nontouched area of the paper that were induced by the deformations of the paper fibers they rooted on (which caused the ZnO NWs on them to contact each other and thus get bent). Thus, the presence of a cavity under the touch pad is necessary in our design to allow the paper fibers in the nontouched area to deform and thus produce piezoelectric currents from the ZnO NWs on them. It is also possible to have a design with a ZnO-NW paper button sitting on a solid susbstrate, which we speculate will generate a lower level of current outputs than our design.

To make the applied force and resulting deformation more consistent, in the following experiments to characterize the individual touch buttons, we used a machine-shop-made metal stand with a finger-shaped tip to mimic finger pressing. By changing the deformation depth, we were able to control the force applied to touch button. The details of the setup are available in Supporting Information. The tip of the metal stand that exerted a touch force to the touch button has a flat circular area of 0.785 cm^2 (1 cm in diameter), similar to the size of a finger press. We applied consistent pressing force of 17.6 ± 1.2 N with the metal stand in experiments, and we released the tip right after pressing, unless otherwise specified.

Quality of ZnO NWs Grown on Paper. We synthesized the ZnO NPs and formed seeding layer with it through simple dipping. Because there are abundant −OH groups on the surface of cellulose fibers of paper, these −OH groups can form hydrogen bonds with the surface oxygen atoms of ZnO nanoparticles.[31] The multiple dipping steps helped rearrange the ZnO NPs attached to cellulose fibers to form more uniform layer. Atomic layer deposition could be also used to generate high-quality, texture-controlled seeding layer of ZnO.[32,33] The controlled texture and crystal orientation of the seeding layer could affect the orientation and quality of subsequently grown ZnO NWs.

We analyzed the morphology and crystal structure of the ZnO NWs grown on paper using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and the molecular composition was analyzed with energy dispersive spectroscopy (EDS). As shown in Figure 1a,b, the cellulose microfibers were uniformly covered by the ZnO NWs standing radially outward. After 15 h of growth, the ZnO NWs have an average width of 69.61 ± 9.55 nm and an average density of 30.30 ± 5.40 /μm^2 (n = 20 from five paper samples). From Figure 1a,b, one can observe that a single ZnO NW has relatively uniform width along its length. Clear crystal lattice structures of ZnO NWs were observed via high-resolution TEM imaging (Figure 2a), which shows a 0.264 nm lattice spacing for the (0002) crystal planes. The electron diffraction image of a selected area in Figure 2b indicated the lattice orientation along [0001], which is the *c*-axis of ZnO crystalline. Clear peaks of Zn and O in the spectrum obtained from EDS indicate correct molecular composition of the NWs (Figure 2b).

Investigation of Piezoelectric Response of Touch Pads. We performed a series of experiments to verify that the current output of the touch button is generated from the piezoelectric response of the ZnO-NW paper. First, we performed control experiments of measuring current outputs of touch buttons made from pure cellulose paper and cellulose paper coated with a layer of ZnO NPs. The ZnO-NP paper was prepared before the hydrothermal growth of ZnO NWs, and the ZnO NPs, seeded on cellulose fibers of the paper, form a quasi-film as the starting point for ZnO NW growth (synthesis details in the section of Experimental Procedures). As shown in Figure 3a, the touch button made from pure paper only generated current waveforms with very small peak magnitudes (<0.6 nA) upon finger pressing and releasing, and the current waveforms are less regular and hard to be discerned from the background noise whose average amplitude is close to 0.2 nA. These small current responses most likely came from the weak piezoelectricity in the cellulose paper.[34] The ZnO-NP paper touch button generated current waveforms with slightly higher peak magnitudes (0.6−1.1 nA) than the pure-paper touch button (Figure 3b). However, these peak magnitudes are still just approximately one-tenth of the current peak magnitudes (8−10 nA) generated from the ZnO-NW paper buttons. These measurement data, obtained from the two control materials (pure paper and ZnO-NP paper), confirmed that ZnO NWs

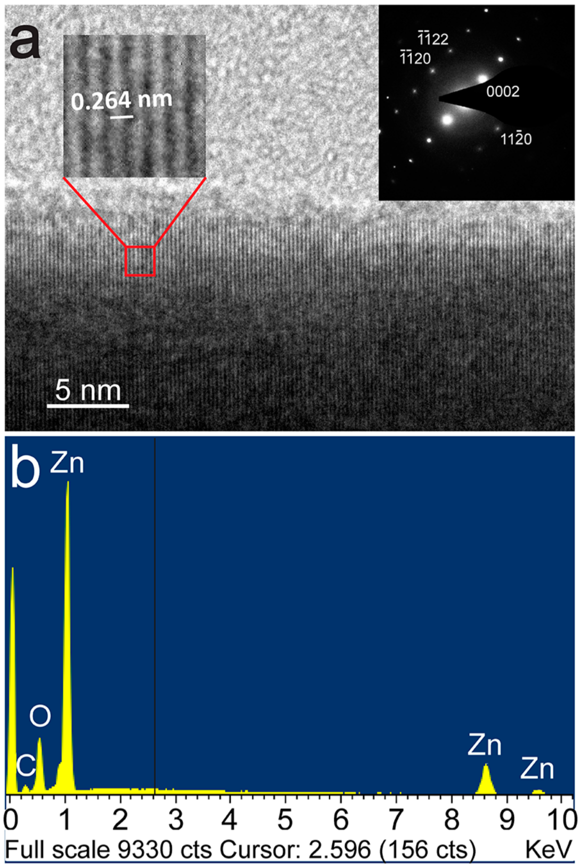

Figure 2. Characterization of ZnO NWs grown on paper. (a) TEM images of a ZnO NW. (inset) An electron diffraction image showing the lattice orientation along [0001]. (b) Chemical analysis of paper surface after ZnO NW growth using EDS.

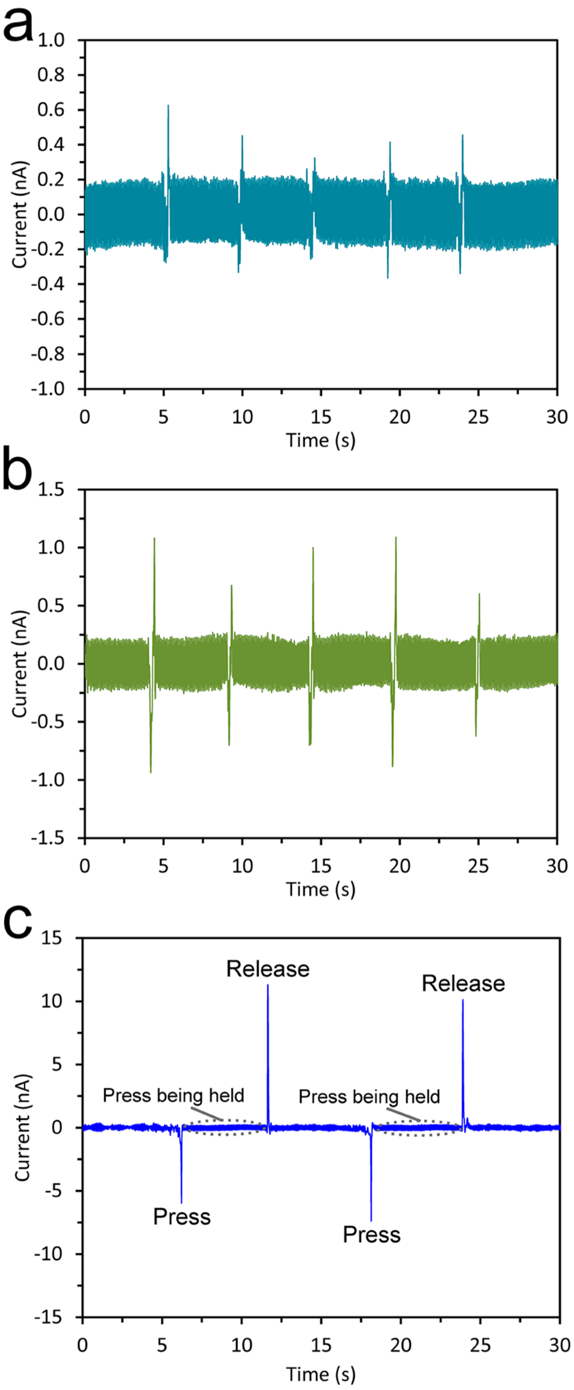

Figure 3. Investigation of piezoelectric response of the touch button. (a) Current response of touch buttons made from pure paper upon repeated finger presses. (b) Current response of touch buttons made from ZnO-NP paper upon repeated finger presses. (c) Current response of a ZnO-NW paper touch button during presses and delayed releases.

are the major source of these repeatable and high-magnitude current waveforms generated from the ZnO-NW paper buttons.

Second, we validated that it is the piezoelectricity rather than the piezoresistivity of ZnO-NW paper that causes the current outputs of the touch buttons. When the ZnO-NW paper is pressed, the ZnO NWs standing radially outward on the cellulose fiber will be bent down and contact with each other, which changes the resistivity of the ZnO-NW paper. This piezoresistive effect was illustrated by the measurement data of the resistance of a ZnO-NW paper button upon finger pressing (Supporting Information, Figure S3). However, we experimentally proved that, under our setup for current output measurement (precision potentiostat; no offset voltage applied during current measurements), the resistance change of the ZnO-NW paper does not induce any current output. We measured the current output of a ZnO-NW paper button upon presses and delayed releases, during which a finger pressed the touch button, held the press for a few seconds, and then released it. As shown in Figure 3c, the current output has only negative peaks upon pressing and only positive peaks upon releasing. During the period of holding the press, the resistance of the ZnO-NW paper changed to a different level (Supporting Information, Figure S3), but there was no obvious change in the current level (Figure 3c). On the basis of this observation, we believe that the piezoresistive effect of the ZnO-NW paper does not induce obvious current output during touch-button operation; thus, the current peaks are generated by the piezoelectric effect of the ZnO-NW paper. During pressing and releasing, the piezoelectric charges were dissipated via current flows through the measurement circuit; thus, the piezoelectric current diminished quickly when the press and releas were completed. As a control experiment, we also used the same experimental setup to measure the press-induced current output of a touch button made from cellulose paper coated with carbon ink (Supporting Information, Figure S4). We have shown previously that carbon ink coated on paper has an obvious piezoresistive effect upon being deformed.[15] The measurement data, as shown in Supporting Information, Figure S3, demonstrates that there were no obvious current peaks induced by the presses. This also proved that the piezoresistive effect of the ZnO-NW paper does not lead to current output of the touch button.

As a further proof of the piezoelectric effect in the ZnO-NW paper, we took time integrations of the current waveforms during pressing (negative peaks) and releasing (positive peaks) of the touch button (Supporting Information, Figure S5), and these integrations quantify the amounts of electric charges generated during pressing and releasing. If we assume elastic deformations of the ZnO-NW paper, the amounts of charges generated during pressing and releasing should be equal. Our calculation results show that the amounts of generated charges for each pair of negative and positive current peaks are fairly close (Supporting Information, Figure S5). This further testifies to the piezoelectric effect in the ZnO-NW paper during touch button operation. The small deviations in the amounts of charges generated during pressing and releasing are possibly due to small unrecovered deformations of the ZnO-NW paper as well as the background noise. We should point out that, although in some current waveforms the negative and positive peaks in a pair have different magnitudes, the time integration results of the current peaks are still very close. The different magnitudes of the positive and negative current peaks are because of the different speeds of finger pressing and releasing.[29]

On the basis of the above experimental validations, we concluded that the current output of a ZnO-NW paper button mainly results from the piezoelectric response of the ZnO NWs grown on paper. The ZnO NWs generate the major portion of the electric charges that form the output currents.[20,29] Since the randomly oriented ZnO NWs on cellulose fibers are bent down and contact each other during pressing, it is possible that a portion of the generated electric charges from different ZnO NWs are neutralized upon contact, since the contact areas from two ZnO NWs may have opposite piezoelectric charges accumulated upon deformation.[35] On the other hand, the press-induced contacts among different ZnO NWs could also provide additional pathways for transporting piezoelectric charges and thus enhance the charge-transfer efficiency.[21]

To fully characterize the piezoelectric properties of the ZnO-NW paper, detailed material characterization will be needed. In regard to mechanical properties, the Young's moduli of ZnO NW and cellulose are expected to be 52 GPa[36] and 130 GPa,[37] respectively. A piece of cellulose paper is a network of interconnected cellulose microfibers with pores, and its effective Young's modulus was measured to be just 2 GPa[15] (assuming homogeneity of cellulose paper). When analyzing the mechanical deformations, note that the system is a multiscale complex structure network involving deformations of structures of different sizes, orientations, and connections. In regard to electrical property, piezoelectric coefficient is an important parameter, and its measurement requires sophisticated experimental setup. We did not measure the piezoelectric coefficient of ZnO NWs we synthesized due to the experimental constraints. According to a previous study on single ZnO NWs, the effective piezoelectric coefficient (d_{33}) of ZnO NW grown in the orientation of [0001] can be estimated as 3−12 nm/V.[38] To scrutinize the deformation of individual ZnO NWs on paper under finger touch, multiscale mechanical modeling of the hierarchical structure of ZnO NWs on cellulose microfiber network is required. The reasons are the nanowires are not well-aligned on randomly woven paper microfibers, and the deformation of individual ZnO NWs varies across the entire piece of paper.

Effect of ZnO-NW Growth Percentage on Device Current Response. It is a common observation that, given extended growth time, ZnO NWs grow longer.[26,39] We measured the weight of paper pieces before and after growth. We defined the growth percentage of ZnO NWs as weight increase of the paper pieces (vs weight before growth) in percentage: 100% × (weight after growth − weight before growth)/weight before growth. We investigated the effect of ZnO-NW growth percentage on the device current output. In our experiments, the paper pieces were weighed in dry form before and after ZnO-NW growth. Similar with other reports,[26,39] we noted that the ZnO NWs grew quickly in the first 3 h, and the growth slowed down after that and almost stopped after 15 h. This growth profile can be explained by the gradual depletion of chemicals in the growth solution. The growth percentages after 1.5, 3, and 15 h are 19.7 ± 0.5%, 30.3 ± 1.2%, and 40.3 ± 0.5%, respectively ($n = 3$). Higher growth percentages can be achieved by carrying out the growth for a longer period of time and refreshing the growth solution constantly.[18]

We measured current outputs of the touch buttons, with ZnO-NW growth percentages of 19.7% (1.5 h of growth), 30.3% (3 h of growth), and 40.3% (15 h of growth). As shown in Figure 4a, the average magnitude of negative current peaks shows an obvious increasing trend with the growth percentage. We opted not to present the data of average current magnitude vs ZnO-NW length, because it is hard to clearly identify the root of ZnO NWs that are grown on non-flat and not-smooth cellulose surface. That is also the major reason we resorted to the parameter, growth percentage, which is more convenient and accurate to indirectly quantify the length of ZnO NWs.

On the basis of the discussions in the section of "Investigation of Piezoelectric Response of Touch Pads", we speculate two possible reasons for the increased current outputs with higher growth percentages. (i) Longer ZnO NWs deflect more under the same pressing force and thus generate more electric charges. (ii) Longer ZnO NWs have higher chance to contact each other when the cellulose fiber they stand on is bent; thus, longer ZnO NWs may gain more electronic pathways for charge transport. Although the results imply that a longer growth time leads to a higher growth percentage and longer ZnO NWs, along with higher current output, note that there are limitations to elevating piezoelectric output by increasing growth time or ZnO-NW length. First, another research has showed there is an optimal ratio of ZnO NW length to width that generates the highest piezoelectric response.[40] Second, over long time growth, ZnO NWs tend to fuse at their tips, which interferes with their growth.

Effect of Pressing Force on Device Current Response. We also investigated the current response of touch buttons at different pressing force levels. Hard and gentle presses deform the ZnO-NW paper at different rates and to different extents, thus resulting in different current outputs. We adjusted the pressing force applied to the touch buttons and measured their current outputs. As shown in Figure 4b, the average magnitude of negative current peaks increases linearly with the pressing force, with a sensitivity of 0.57 nA/N. If a more sensitive response of the touch button is desired, one can choose a thinner and thus more flexible paper substrate and adopt a

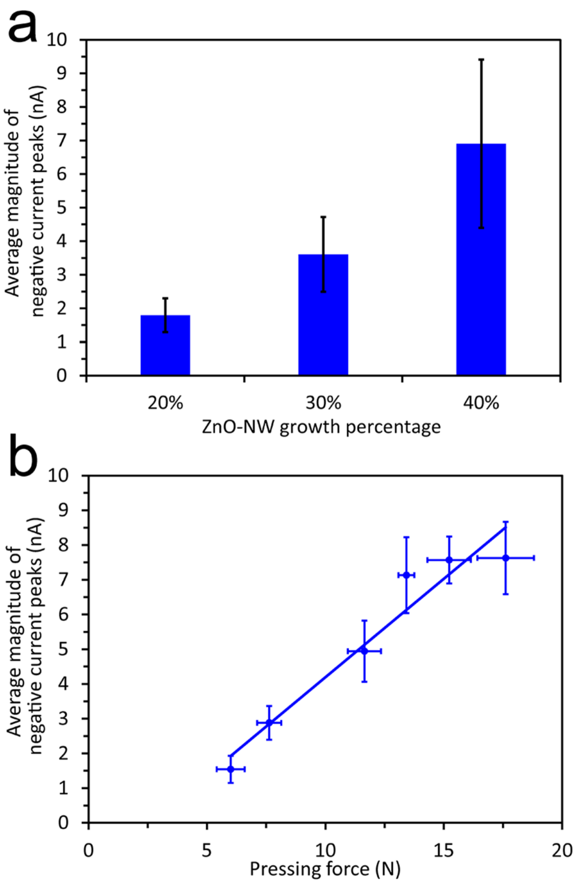

Figure 4. Experimental results of average negative current peaks vs growth percentage and force applied. (a) Experimental results of average negative current peaks vs ZnO-NW growth percentage ($n = 3$ devices). ZnO NWs were grown for 1.5, 3, and 15 h, yielding 20%, 30%, and 40% weight growth, respectively. (b) Experimental results of average negative current peaks vs pressing force ($n = 3$ devices; 10 measurements per deformation), collected from devices with a growth percentage of 40%. Equation of the linear regression: $y = 0.57x - 1.48$, ($R^2 = 0.937$).

higher ZnO-NW growth percentage in device preparation. The linear fitting in Figure 4b shows that an initial force (2.60 N, obtained from the linear fitting equation) is needed before a current output can be measured, which represents the cutoff force value of the device's dead zone. One can reduce this cutoff value by using a thinner piece of paper for constructing the touch button, which is more compliant to deform.

In the experiments, the metal tip on the metal stand we used has a flat circular area (1 mm in diameter) with a similar size with a typical human finger. We experimentally verified that a press by the metal post and a press by a similarly sized human finger, both with the same level of applied force, generated piezoelectric current outputs from the same button with a discrepancy of <10%. It is reasonable to predict that when the area and shape of the metal post change, the amount of deformed ZnO NWs and the stress/strain distribution in the ZnO-NW paper will change accordingly. This will definitely lead to the change in the piezoelectric current outputs. To reduce the experimental complexity, we did not investigate the effect of the contact shape and the area on the touch button output.

Durability Testing. Performance degradation after repeated operations could be a concern if the paper-based touch buttons are designed for long-term use. We tested the device durability through repeated pressing of a touch button made from paper with a ZnO-NW growth percentage of 30.3%. The button was continuously pressed 2000 times using the metal stand at a high force level of 17.6 ± 1.2 N. After every 200 presses, the current output was measured 10 times to calculate the average. As shown in Figure 5, the average magnitude of negative current peaks decreased gradually during the first 600 presses and started to stabilize after that.

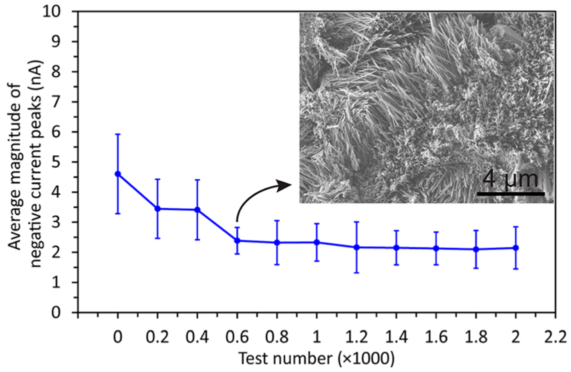

Figure 5. Experimental results of average negative current peak vs number of presses ($n = 10$ measurements every 200 presses). (inset) An SEM image of a touch pad after 600 presses.

We observed two causes associated with the output degradation. (i) Repeated presses resulted in unrecoverable (inelastic) deformation of the paper, which we started to observe after the first 100 presses. This irreversible deformation caused stiffening in the suspended paper structure, decreased the deformation/strain induced by the subsequent presses, and thus lowered the current output. (ii) Repeated presses also permanently bent down the ZnO NWs on paper, making them less stressed in the subsequent presses. This was revealed through SEM imaging of the ZnO NWs after 600 presses (inset in Figure 5). The current output stabilized after 600 presses, possibly because the suspended paper reached the limit of inelastic deformation and mainly underwent elastic deformation afterward. After 2000 presses, the touch button still operated responsively, and no mechanical damage was observed on the paper button. In application scenarios where extended uses are targeted, the paper touch buttons can be preloaded to reach stabilized performance.

Development and Operation of a Ten-Key Touch Pad. After characterization of the touch button, we constructed a touch pad by arraying 10 numbered buttons (Figure 6) on an acrylic frame. The touch pad also includes a 10-channel charge amplifier circuit (Supporting Information, Figure S6; CAD $1.4 per channel) for converting electric charges from the buttons into voltage outputs, a microcontroller circuit (ATxmega32A4, ATMEL) for measuring the voltage outputs, and 11 light-emitting diodes (LEDs; 10 blue and one green) for touch-responsive displays. Figure 6a shows the voltage outputs from the 10 touch buttons when they were pressed sequentially by a human operator. The positive peak amplitudes of the voltage outputs vary across different buttons, which could be attributed to the different levels of pressing and environmental noises coupled into the 10 channels of the charge amplifier circuit. The microcontroller was programmed to recognize finger presses by detecting the positive voltage peaks from the touch buttons based on a threshold value. Upon recognition of finger

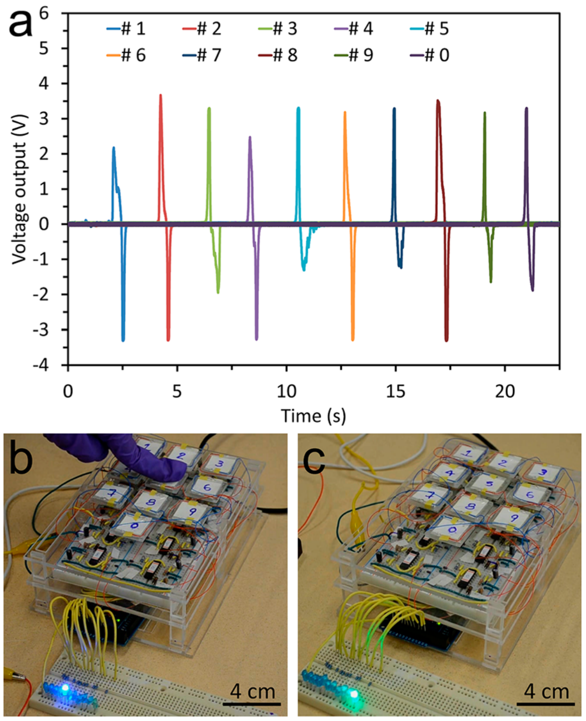

Figure 6. Voltage output and snapshot of key pad. (A)Voltage outputs from 10 number keys while being dialed. (b) The corresponding blue LED lighting when the number key is pressed. (c) The green LED lighting when a preprogrammed password is entered correctly.

pressing on a specific button, a corresponding blue LED was lit by the microcontroller (Figure 6b and the video of Supporting Information, 2). To highlight the potential use of our touch pads in paper-based electronics where input of information is needed, we demonstrated the input of a six-digit numeric code on the touch pad. The microcontroller was programmed to compare the inputted code with the preset one and activate the green LED when there was a match (Figure 6c and the video of Supporting Information, 3).

■ DISCUSSION

Advantages of the Developed Touch Pad. The addition of touch-sensing capabilities to common paper substrates is of primary importance to developing monolithic paper-based electronic devices with touch user interfaces. In this research, we demonstrated a new design of paper-based piezoelectric touch pads that serve as interfaces for user input of information. Our touch pad design has five useful characteristics for uses in paper-based electronics. (i) The piezoelectric sensing principle is, in principle, applicable to most types of paper substrates. The hydrothermal synthesis of ZnO NWs can be performed on virtually any paper substrates with proper mechanical stability, making our design useful for many paper-based electronic devices involving different paper substrates. (ii) The design just needs a single layer of paper, which simplifies the device assembly. (iii) The device is simple-to-fabricate, fairly low-cost (CAD $0.03 per button), and does not require sophisticated microfabrication facilities. (iv) The device fabrication process is compatible with existing techniques for constructing electronic circuits on paper substrates (e.g., inkjet and screening printing). The hydrothermal growth of ZnO NWs is performed in a moderate chemical solution at relatively low temperatures (50–100 °C), which does not substantially change the chemical and mechanical properties of the paper substrate and hence permits subsequent fabrication of electronic components on the same paper substrate. (v) The hydrothermal synthesis of ZnO-NWs is highly selective and spatially guided by the seeding layer of ZnO NPs. One can easily pattern the seeding layer via inkjet printing of the ZnO-NP solution and conduct selective growth of ZnO NWs on paper with micrometer resolution (determined by the resolution of inkjet printing). This will potentially lead to more versatile designs of paper-based touch sensors.

Advantages of Using Paper as Electronic Substrate. It is possible to hydrothermally grow ZnO NWs on plastic substrates,[41] which represents another type of common materials for constructing flexible electronic devices. Compared to plastics, paper has the following advantages for use as an electronic substrate. (i) Paper is biodegradable, readily disposable by incineration, and thus more environmentally friendly than plastics. (ii) According to a previous comparison,[16] paper has lower cost (~EUR €0.001 per dm^2) than most plastics (e.g., polyethylene terephthalate: ~EUR €0.02 per dm^2; polyimide: ~EUR €0.3 per dm^2). (iii) There exist mature mass-production techniques for manufacturing paper materials (e.g., printing, folding, and cutting) that could be adapted to manufacturing paper-based electronic products. (iv) As a substrate for growing ZnO NWs, the porous structure of cellulose paper provides a higher surface-to-volume ratio than plastic substrates, which allows the growth of more ZnO NWs per unit area of substrate.

New Contributions of the Presented Work. Although previous work has demonstrated the use of ZnO-NW paper for energy harvesting,[29] we believe this research is distinct in several important aspects. First, this work is aimed toward inventing a new type of user touch interface for paper-based electronics, which is a different application from the previous work.[29] Our research is the first demonstration of paper-based piezoelectric touch sensor. Second, the procedures of growing ZnO NWs on paper in this research are different from those of previous work.[29] For example, the previous work[29] sputtered ZnO NPs on paper, while we prepared ZnO-NP colloidal solution and dipped paper into it for seeding, which does not require sophisticated equipment. For hydrothermal synthesis of ZnO NWs, we utilized ammonium hydroxide as an assistant chemical to suppress the homogeneous nucleation of ZnO in solution, which leads to thinner ZnO NWs (69.61 nm after 15 h of growth) than that (100–200 nm after 3 h of growth) in the previous work.[29] Third, the form of deformation of the ZnO-NW paper is different in our work than that of previous work.[29] The previous design[29] used a piece of paper as a strain gauge (attached to a plastic cantilever beam), which experienced tensile or compressive strains during operation. We formed a touch button from a suspended ZnO-NW paper, and the finger touching induced both bending and stretching of the paper. This difference in form of deformation led to different quantitative relationships of the current output versus the applied load. Fourth, we undertook a series of investigations on the piezoelectric sensing mechanism of ZnO-NW paper, which are new technical contributions. We calibrated the current output as a function of the amount of ZnO NWs grown on paper (reflected by the growth weight percentage), which provides guidelines for device design. We tested the performance degradation of the touch button upon repeated pressing, which is a necessary test for constructing reliable paper-based sensors. We also developed a simple charge amplifier circuit for converting the piezoelectric charge output into a measurable voltage output.

Understanding the Detailed Physical Mechanisms. We dedicated a series of experiments to understand the mechanism of the current responses from the developed touch pads. We obtained the following experimental observations for our current touch pad design: (i) ZnO NWs grown on paper made the major contribution to the output current peaks; (ii) the press-induced piezoresistive effect of ZnO-NW paper did not lead to obvious current response of the touch pad; and (iii) the piezoelectric charges generated during a finger press and subsequent release of the touch button are equal (small deviations exist in experiments due to small uncovered deformations and background noise of the buttons). These observations led to our conclusion that the current outputs from the touch pads arise from the piezoelectric effect of the ZnO NWs on paper. These investigations also reveal a highly interesting research topic to explore in future on theoretical modeling and computational simulation of the mechanical deformation and corresponding piezoelectronics of the hierarchical structure of ZnO NWs on interwoven cellulose microfibers, which will help us better understand the charge generation and transfer in ZnO-NW paper.

Potential Improvements. We developed touch pad prototypes for proof-of-concept demonstrations, and further engineering improvements can be performed to enhance the device performance or extend the functionality. (i) The consistency of output voltages from different touch buttons can be further improved through better control of the ZnO growth consistency and environmental noises coupled into the charge amplifier circuit. (ii) Selective growth of ZnO-NW and corresponding patterning of conductive inks (as electrodes) can be achieved, via techniques such as inkjet printing, to form addressable arrays of touch sensing "pixels" with potentially smaller footprint. This will further increase the level of device integration. The major limitations of reducing the sensing pixel size include the patterning resolution of the hydrothermally grown ZnO NWs (mainly determined by inkjet printing resolution of the seeding solution) and the size-related limitation of the piezoelectric current output of each patterned sensing pixel (the smaller the pixel, the lower the output current). (iii) The whole charge-amplifier circuit can be integrated onto the same paper substrate using existing circuit fabrication techniques in paper-based electronics.[15,16]

Potential Applications. Besides the demonstrated usages of these touch pads, we expect many other interesting applications. For instance, the single-layer touch pad design can be integrated into many interactive electronic paper products such as business and greeting cards, boarding passes, intelligent magazines. Creative cutting and folding of paper patterned with ZnO NWs can make "smart" paper toys that respond to physical interactions from users (e.g., pressing, bending, and accelerating). The piezoelectric mechanism for physical sensing could also enable the development of low-cost disposable force sensors and accelerometers.

■ CONCLUSION

This paper reported a new design of paper-based piezoelectric touch pads integrating ZnO NWs, representing an inexpensive solution to developing novel user interfaces for paper-based electronics. We hydrothermally grew ZnO NWs on cellulose paper and fabricated the ZnO-NW paper into piezoelectric touch buttons. The ZnO-NW paper button is responsive to finger pressing and generates electric charges, which are then converted into a voltage signal using a charge amplifier circuit. We fully characterized the output performance of the touch button and examined the device durability during 2000 cycles of pressing. We constructed an integrated touch pad with 10 touch buttons and demonstrated its potential use in user–device interactions. We believe that this technology has a significant potential for use in paper-based electronic platforms to improve interactive user experience and enable other touch-sensing-based functionalities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures mentioned in the section of "Investigation of Piezoelectric Response of Touch Pads" and videos taken with the ten-key touch pad. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xinyu.liu@mcgill.ca.

Author Contributions

‡These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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