Fracture-Induced Mechanoelectrical Sensitivities of Paper-Based Nanocomposites

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Nanostructured composites built with microporous cellulose fibers and carbon nanotubes (CNTs) have potential impacts in the fields of energy storage, sensors, and flexible electronics. Few results have been shown for high mechanoelectrical sensitivity of CNT-paper composite because of numerous current paths in the network. Here, CNT-paper-based nanostructured composite sensors whose sensitivities are generated by controlled tensile fracture of the composite are presented. Under uniaxial load, the cellulose fibers in the paper experience straightening, stiffening, and fracture. The cellulose fibers originally parallel to the tension are fractured while those inclined and perpendicular to the tension are reorganized to form crossbar junctions in the vicinity of a crack. The cross junctions exhibit resistive and capacitive sensitivity to the out-of-plane force by the compression of the junctions. Such piezoresistive and piezocapacitive sensitivities are characterized and evaluated for human behavior monitoring.

Nanostructured composites using cellulose fiber templates have been studied for developing light-weight and inexpensive devices. Cellulose fibers extracted from wood pulp offer large surface area facilitating energy, sensing, and electronic applications. Since the porous and hydrophilic nature of cellulose fibers enhances adhesion, various nanomaterials have been used to modify the surface properties of cellulose fibers for multifunctionality. Carbon nanotubes (CNTs) are versatile filler materials to create electrical and thermal conductivity. When a CNT-paper composite (CPC) is fabricated, it promises novel applications, such as flexible electronics, energy devices, and sensors. However, the random network of CNTs in a cellulose fiber matrix limits the mechanoelectrical sensitivity due to the numerous current paths in the matrix. We present a fracture-induced mechanoelectrical sensitivity of a CPC for wearable sensing applications. With precise control of the applied strain under uniaxial load to a CPC, the tensile directional fibers coated with CNTs are fractured, and the cellulose fibers inclined or orthogonal to the tension are reoriented to form crossbar junctions near a crack. The junctions create highly sensitive resistive and capacitive responses for measuring strain, force, and noncontact displacement. The novel manufacturing process allows the integration of flexible sensors in low-cost tissue paper, which is easily adapted to human body for behavior monitoring.

Figure 1a shows the fabrication method of a CPC sensor. A 100 µm thick porous paper (KimWipes) was used as a template. An aqueous solution of multiwall CNTs (MWCNTs) (5 mg mL$^{-1}$) was deposited onto porous paper. When MWCNT solution was introduced to a cellulose fiber matrix, MWCNTs were bound on fibers and spanned between fibers by capillary action. Silver paste was applied to both ends of the paper strip and cured to fabricate electrodes. The composite was stretched to induce a crack due to the fracture of the tensional directional fibers. The fractured composite was attached on a double-sided adhesive tape and sealed by sticky tape to fabricate a prototype sensor. As illustrated in Figure 1b, the proposed sensor can be designed and fabricated to exploit different sensing mechanisms by the magnitude of applied prestrain (i.e., in-plane strain sensor, out-of-plane piezoresistive sensor, and capacitive sensor in stage II, III, and IV, respectively). The stress–strain relationship shows three different stages in terms of the mechanical and electrical behavior. The electrical resistance at the initial stage ($I_0$) increases linearly at the elastic region (stage II in Figure 1b) by unidirectional strain. With the application of larger strain, a crack is initiated and propagated along the orthogonal direction to the tension, which significantly reduces the mechanical stiffness of composite (stage III in Figure 1b). The electrical resistance increases drastically because of the fracture of MWCNT-coated cellulose fibers. Near the crack, the untangled cellulose fibers...
form crossbar junctions where the coated MWCNTs exhibit out-of-plane piezoresistivity. With larger strain, the increased stress near the crack tip terminates the composite electrically (resistance $> 500$ MΩ) (stage IV in Figure 1b), although the composite is still connected by untangled fibers. The stress concentration of cellulose fibers along the crack edge increases the local strain and the deposited MWCNTs along the edge are disconnected. The numerous junctions create an out-of-plane piezocapacitive sensor.

In mechanoelectrical characterization, the composites deposited with 0, 3, 10, and 20 times of MWCNTs were prepared to vary electrical paths. The number of depositions was limited to 20 at which the cellulose fiber matrix was fully saturated with MWCNTs. The sheet resistance of the CPC decreased as the number of MWCNT depositions increased (Figure S1, Supporting Information). The composite resistance in the stretching direction was slightly lower than that of the orthogonal direction. In this study, the tension direction is defined as 0° ("parallel") and the direction orthogonal to tension is 90° ("perpendicular").

We characterized the mechanical strength and electrical resistance change of a CPC under the uniaxial load according to the deposition numbers (Figure 1c). The paper was composed of randomly oriented cellulose fibers as shown in the histogram of Figure 1d. The stretching direction was perpendicular to the dominant fiber orientation at stage $I_0$. The stretching parallel to the orientation of the dominant fibers was not considered in our further test because the stress–strain relationship was not consistent (Figure S2, Supporting Information). The perpendicular wrinkles that were generated during the manufacturing of the tissue paper resulted in the unpredictable strain at the ultimate strength for the parallel stretching (Figure S3, Supporting Information).

In Figure 1c (left), regardless of the deposition numbers, the ultimate strength and its strain were in the range of $1.47 \pm 0.12$ MPa and $0.053 \pm 0.0056$ mm mm$^{-1}$, respectively. The stiffness became larger with the increase of the deposition numbers (Figure S4, Supporting Information). Based on the scanning electron microscopy (SEM), cellulose fibers were bridged and coated with the deposited MWCNTs (Figure S5, Supporting Information), which increased the composite stiffness. When the electrical resistance was measured under tension, the inflection point of the resistance change was clearly lagged from the strain of $0.06–0.08$ mm mm$^{-1}$ as the deposition number increased from 3 to 20 (Figure 1c, right). The inflection point was where the resistance change deviated the initial
linear slope by 5%. As the more cellulose fibers were bundled with more depositions of MWCNTs, the significantly increasing point of the resistance was delayed.

The electrical resistance increased with a power law, which agreed with the percolation theory.10 The effective resistivity of a composite network can be expressed as \( \rho = \rho_f (1 - f) + \rho_c f^t \), where \( \rho_f \) is the resistivity of fiber, \( f \) is the conductor volume fraction, \( f^t \) is the critical conductor volume fraction, and \( t \) is an exponent. Since the fiber network in our composite is degenerated with stretching, the resistance change ratio \( (R/R_0) \) can be expressed with strain (\( \varepsilon \)) as \( \frac{\Delta R}{R_0} = a \varepsilon^t \), where \( R_0 \) is the initial resistance, \( \Delta R \) is the resistance change \( (R - R_0) \), and \( a \) and \( b \) are the parameters that are determined by the MWCNTs depositions. The estimated \( a \) and \( b \) for 3, 10, and 20 depositions were 1.82 \( \times \) 10^2, 4.49 \( \times \) 10^2, 1.67 \( \times \) 10^2, and 39.0, 4.0, 4.0, respectively. The more MWCNTs were deposited, \( a \) and \( b \) were smaller because the bundled MWCNTs lagged the inflection point of the resistance change.

Figure 1d shows the structural change of the cellulose fibers and MWCNTs under tension based on optical and SEM study. A CPC with 3 times of MWCNT depositions was used for this study because more than 10 depositions could hamper reorganization of fibers. The resistance change for 3 times-MWCNT deposited CPC during the tensile test was relatively uniform as shown in Figure S6 (Supporting Information). The creation of piezosensitivity stems from the realignment and fracture of CPC network under tensile loading. The bottom graphs of Figure 1d show the percentile histogram of the fiber orientations in stage of I 0, II, III, and IV. According to the SEM observation, the fiber orientations in the area of 1 \( \times \) 1 mm^2 were divided into three ranges of 0° to \( \pm 30^\circ \), \( \pm 30^\circ \) to \( \pm 60^\circ \), and \( \pm 60^\circ \) to \( \pm 90^\circ \). In the original paper template (stage I 0), 26% of the fibers were in 0° to \( \pm 30^\circ \), 23% in \( \pm 30^\circ \) to \( \pm 60^\circ \), and 51% in \( \pm 60^\circ \) to \( \pm 90^\circ \). Therefore, the dominant orientation in the initial composite was \( \pm 60^\circ \) to \( \pm 90^\circ \). Here 0° and 90° imply parallel and perpendicular directions to the loading.

In stage II (0 \( \leq \varepsilon \leq 0.06 \)), the parallel fibers were straightened and stiffened by tension. The resistance increase was resulted from the breakdown of the MWCNT bridges spanning neighboring cellulose fibers. Although a CPC was stretched in an elastic range, the resistance was not recovered to the original value due to the broken MWCNT bridges (Figure S7, Supporting Information).

In the strain of 0.06–0.16 (stage III), most parallel fibers were fractured at ultimate strength. Both inclined and perpendicular fibers were oriented to the tensile direction, which changed the dominant orientation of fibers into \( \pm 0^\circ \) to \( \pm 30^\circ \) (see the histogram in Figure 1d and Figure S8, Supporting Information). Both spanning and coated MWCNTs on fibers were broken. The reorganized fibers (green and blue fibers in Figure 1d) formed numerous cross-shaped junctions (Figure S9, Supporting Information). Electrical resistance was significantly increased as the MWCNT network among the fractured fibers was broken.

Although cellulose fibers were deformed, buckled, and fractured in the stage, MWCNTs were not delaminated or separated from the fibers. According to our SEM study, the diameter of the cellulose fibers ranged from 10 to 30 \( \mu \)m, and the curvature radius of the cellulose fibers was larger than 100 \( \mu \)m. The diameter and the length of the MWCNTs were 8–15 nm and 0.5–2 \( \mu \)m, respectively. Compared with the MWCNT dimensions, the fiber dimensions were significantly larger than the cellulose fibers. In CPC, MWCNTs were tightly bonded on cellulose fibers by hydrogen, ionic, and nonspecific bondings in conjunction with capillary action in the deposition process.

At the stage where the strain was greater than 0.16 (stage IV), all the electrical connections were broken by extreme stretching. The composite was electrically terminated along the crack edge, which was clearly observed from the bright and dark contrast in the SEM image (Figure 1d). The high contrast indicated that electrons could not flow through the crack edge. In the orientation graph, the fraction of the parallel and inclined fibers (0° to \( \pm 30^\circ \) and \( \pm 30^\circ \) to \( \pm 60^\circ \)) became 80%, forming crossbar junctions. Since the resistance became infinite, pure capacitance of the MWCNTs could be measured through the dielectric media of air and fibers.

By the control over the applied strain to the CPC, different sensors (a strain sensor, a piezoresistive sensor, and a piezoelectric sensor) can be designed in the stages II, III, and IV, respectively. To demonstrate this, a series of prototypes were fabricated in stages II–IV. The CPC prestrained at the stage II by applying 0, 0.02, 0.04, and 0.06 of strains was prepared and attached to a polydimethylsiloxane (PDMS) cantilever beam for the sensor evaluation (Figure 2a). With the bending of the cantilever, the top surface of the beam was stretched, which linearly increased the sensor resistance (Figure 2b). As the prestrain increased from 0 to 0.06, a gauge factor \( \frac{\Delta R/R_0}{\Delta \varepsilon} \) increased.

Figure 2. Evaluation of the strain sensor in stage II. a) Schematics of the strain sensor design and calibration. b) Normalized resistance change according to the applied strain by bending (prestrain: 0.04 mm mm^{-1}; 3 \times MWCNT depositions). c) Gauge factor according to the prestrain that is applied for a CPC.
from 2 to 13 (Figure 2c). The operation range of the strain sensor was below 0.01. If the applied strain exceeded 0.01, the gauge factor could be changed as tested. The initial resistances of the four specimens at the strains of 0, 0.02, 0.04, and 0.06 were 83, 87, 93, and 100 kΩ, respectively. The increase of the gauge factor in the elastic region was caused by the breakage of the MWCNT bridges among the intact cellulose fibers. Therefore, a prestrain could partially remove the electron paths spanning cellulose fibers, which increased the sensitivity.

In stage III, the reoriented cellulose fibers in the crack generated a sensitivity for out-of-plane directional force. The sensing performance was evaluated by recording the electrical resistance change with respect to the applied force. An elastic finger was fabricated using PDMS to mimic a human finger (Figure 3a). To calibrate the applied force, a force sensor (LCFD-1KG, Omega Engineering, Norwalk, CT) was attached under the sensor substrate. As the force was applied on the cracked area of the composite, the untangled crossed fibers generated in the fracture were compressed to increase the contact area, which decreased the resistance in proportion to the force (Figure S10, Supporting information).

The piezoresistive sensitivity was defined as \( \frac{\Delta R}{R_0 \Delta F} \), where \( \Delta R \) was the resistance change of the sensor, \( R_0 \) was the initial resistance of the sensor, and \( \Delta F \) was the change of the applied force. The sensitivity was increased by larger prestrain (Figure 3b). As the prestrain increased from 0.06 to 0.13, the sensitivity rapidly increased from 0.002 to 0.003 N\(^{-1}\). The response of the resistance change to the applied force for the 3 times MWCNT deposited CPC is shown for the prestrain of 0.06, 0.08, 0.10, and 0.12 (Figure S11, Supporting information). Without the prestrain, the piezosensitivity was close to 0 because the cellulose fibers were firmly bonded with numerous MWCNT network. To validate if the sensitivity was created by a crack, the forcing point was moved from a crack tip (0 mm) to 8 mm by a 2 mm step along the longitudinal direction. The sensitivity was continuously reduced from 0.022 to 0.001 N\(^{-1}\) as the distance \( d \) in Figure 3c) from the crack tip increased (Figure 3c). When the distance from the crack was greater than 8 mm, the composite was not sensitive to an out-of-plane force. To test the reproducibility and the MWCNT deposition effect, the composites deposited with 3, 10, and 20 times were stretched by prestrain of 0.12 mm mm\(^{-1}\). The sensitivity was reduced as the deposition numbers increased because more bundled fibers by MWCNTs limited the structural change under tension (Figure 3d). With more depositions, fewer junctions were created to lag the increase of the resistance, thus the sensitivity.

When a step force input was applied to a composite with a 0.12-prestrain, the response time was less than 50 ms, which was significantly smaller than other polymer sensors (Figure 3e). However, the resistance offset was continuously reduced for 100 s. Under the force, the cellulose fibers continuously slipped and crept, which caused the continuous decrease of the resistance. When a cyclic loading (frequency: 0.3 Hz) was applied between 0 to 5.5 N, the resistance changed periodically, and the resistance offset reached a steady state after 300 s (Figure 3f). The response of the sensor pressed by a human finger was relatively reliable for 500 cycles (Figure S12, Supporting information).

In stage IV, a capacitive sensor could be created. Since the final fracture of the composite was not predictable, the applied prestrain was stopped when the resistance became larger than 500 MΩ. Similar to the piezoresistive sensor, junctions...
were created by the crossed structure of cellulose fibers. Due to the large surface areas of cellulose fibers and MWCNTs, intrinsic capacitance without parasitic capacitance was so large as $0.5 \pm 0.04 \, \text{pF}$ ($N = 6$). The capacitance sensor could detect conductive objects by contact and noncontact modes, and nonconductive objects by a contact mode using the setup in Figure 4a. Note that the composites deposited with 10 and 20 times MWCNTs could not be used to create a capacitive sensor because the bundled fibers by MWCNTs made the CPC electrically conductive till the complete fracture.

When a conductive finger (PDMS finger coated with aluminum) was forced on a crack, the capacitance increased with a sensitivity of $0.036 \, \text{N}^{-1}$ (Figure 4b). The sensitivity for the same test using a nonconductive finger was reduced to $0.004 \, \text{N}^{-1}$. When a step input was applied, the time constant was less than 50 ms (Figure 4c). For the noncontact sensing mode, when a conductive object was withdrawn from the crack surface of the capacitive sensor, the capacitance was first rapidly reduced by the decrease of parallel capacitance (sensitivity: $-0.068 \, \text{mm}^{-1}$), and subsequently, increased by the reduction of charge dissipation (sensitivity: $0.0048 \, \text{mm}^{-1}$) (Figure 4d). Here, the sensitivity for the noncontact distance sensor was $\frac{\Delta C}{\Delta D}$, where $\Delta D$ was the distance change between the sensor and the object surface. For the capacitance increase, the characteristic length between the sensor and the conductor became greater than that of the capacitance sensor, which increased the capacitance by decreasing the current dissipation to the conductor. At the $-0.068 \, \text{mm}^{-1}$ sensitivity region, the $8 \, \mu\text{m}$ displacement of a piezoactuator could be measured (Figure 4e).

Using resistive and capacitive sensors, human behaviors could be monitored. Both sensors could be used to measure heartbeats on wrist (Figure 5a,b). The offset change of the heartbeat signal might be generated from the cardiac impulse during the heartbeat. In comparison to other results, the offset fluctuation was in an acceptable range. In the measurement, a CPC sensor on a both-side sticky tape was attached on the wrist. When a piezoresistive sensor was attached on a finger of a glove, cyclic gripping motion could be detected (Figure 5c). When a sensor was attached on a finger joint, the resistance change could be measured for the angle change between $0^\circ$ and $135^\circ$ (Figure 5d). A noncontact capacitive sensor was installed on an eyeglass to detect the eyeball movement (Figure 5e). The up/down and the open/close movement of an eye could be detected because the distance from the sensor to the eye surface was changed.

Figure 4. Evaluation of a capacitive sensor in stage IV. a) Schematics of piezocapacitive force sensor calibration. Force and capacitance are recorded when the cracked surface of the sensor is pressed. b) Normalized capacitance change for both conductive and nonconductive object for CPC of 3× MWCNT depositions. c) Capacitance response to a step force input of 8 N. Inset: closeup of the response time. d) Capacitance change of noncontact displacement as a function of the distance between the sensor and a conductive object. e) Capacitive response of a noncontact displacement sensor to cyclic displacement by a piezoactuator ($8 \, \mu\text{m}$). f) Capacitive change of a conductive PDMS finger for a cyclic force. Inset: closeup of the capacitive change between 500 and 520 s.
To date, various mechanisms and materials have been studied for wearable applications to monitor physical, chemical, and biological activities.\(^\text{[9,10]}\) Among the methods, fracture-induced methods have been developed to fabricate wearable sensors.\(^\text{[11]}\) A composite made of polymer-coated graphene was stretched to induce a crack, which generated a sensitivity.\(^\text{[12]}\) A platinum film was bent to create a crack, which showed a high sensitivity.\(^\text{[13]}\) Compression-induced internal cracks generated piezoresistive sensitivity.\(^\text{[14]}\) In our study, the composite of MWCNTs and tissue paper was fractured to form crossbar junctions in a crack, which could generate piezoresistive and piezocapacitive sensors.

The three different types of sensors were demonstrated by controlling the applied prestrain to CPC. Since one specific sensor was fabricated by a prestrain value, it could function only in the designed sensing mode, without transforming the sensing mode into another in the sensing process. The fabricated sensor made of a fractured CPC could be fragile. In the paper, the sensor was fixed on surface by a tape, which will be improved by infiltrating polymer or other filler materials in our future work.

In summary, we presented a low cost, flexible, and highly sensitive sensor whose sensitivity was induced by controlled fracture on an MWCNTs-paper composite. By prestraining, three different sensors were demonstrated as resistive strain sensor, resistive force sensor, and capacitive force and displacement sensors. The piezoresistive and capacitive sensors could be fabricated by the reorganized crossing junctions of MWCNT-coated cellulose fibers. The calibration of each sensor showed reliability and repeatability. The sensors attached onto flexible surface such as human skin were sensitive enough to monitor heart beats, grabbing force, finger motion, and eye movement. The inexpensive and disposable sensors can be useful to monitor human behaviors with reliable performance.

**Experimental Section**

**Fabrication of Composite:** An aqueous solution of MWCNTs (Nano structured & Amorphous Materials, Inc.) was prepared by using 1% SDS in deionized water. After 2 h sonication, the solution was deposited on a suspended paper using a pipette. The CPC was cut into pieces \((10 \times 30 \text{ mm}^2)\). For electrodes, silver epoxy (MG chemical #8330s-21G) was pasted onto both ends of the composite for a \(10 \times 10 \text{ mm}^2\) area. The CPC was cured in an oven at 65 °C.

**Mechanical and Electrical Tests:** The nanocomposites were tested by using a custom-made uniaxial tensile test bed that was controlled by using LabView interface. The force and displacement were recorded for stress–strain relationship. Real-time, high-resolution video was used to observe the nanocomposite’s behavior as well as its morphologies and failures under mechanical loading. The resolutions of the force and displacement sensors were 3 mN and 1 \(\mu\text{m}\), respectively. The resistance was measured by using a reference resistor as shown in Figure 3a.

**Prestraining for Sensor Fabrication:** The composite was stretched on the uniaxial tensile stage until the required strain value or resistance reached. At a controlled value, the stage was stopped for 1 min for structural stability of a composite. After the prestraining, the composite was carefully unloaded from the setup and used for measurement.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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have been tested by de-identified volunteers. Among the testing results from multiple volunteers, a randomly chosen secondary data set is demonstrated for performance evaluation.

Conflict of Interest
The authors declare no conflict of interest.

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fracture, multiwall carbon nanotubes, nanocomposites, paper, wearable sensors

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