UC Davis

UC Davis Previously Published Works

Title

Conductive Polymer Protonated Nanocellulose Aerogels for Tunable and Linearly Responsive Strain Sensors.

Permalink

<https://escholarship.org/uc/item/7ht641qm>

Journal

ACS applied materials & interfaces, 10(33)

ISSN

1944-8244

Authors

Zhou, Jian
Hsieh, You-Lo

Publication Date

2018-08-01

DOI

10.1021/acsami.8b10239

Peer reviewed

Conductive Polymer Protonated Nanocellulose Aerogels for Tunable and Linearly Responsive Strain Sensors

Jian Zhou¹ and You-Lo Hsieh^{1*}

Fiber and Polymer Science, University of California, Davis, California 95616, United States

Supporting Information

ABSTRACT: Strong and highly conductive aerogels have been assembled from cellulose nanofibrils (CNFs) protonated with conductive poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) complex at equal mass or less. Protonating CNF surface carboxylates and hydrogen-bonding CNF surface carboxyls with PSS in PEDOT/PSS generated PEDOT/PSS/CNF aerogels that were up to ten times stronger while as conductive as neat PEDOT/PSS aerogel, attributed to the transformation of PEDOT benzoid structure to the more electron transfer-preferred quinoid structure. Ethylene glycol vapor annealing further increased the conductivity of PEDOT/PSS/CNF aerogels by 2 orders of magnitude. The poly(dimethylsiloxane) (PDMS)-infused conductive PEDOT/PSS/CNF aerogel (70 wt % CNF) transform a resistance-insensitive PDMS-infused PEDOT/PSS aerogel (gauge factor of 1.1×10^{-4}) into a stretchable, sensitive, and linearly responsive strain sensor (gauge factor of 14.8 at 95% strain).

KEYWORDS: nanocellulose, PEDOT/PSS, aerogel, strain sensor, sensitivity, stretchability

1. INTRODUCTION

Strain sensors have continued to grab extensive interests because of their potential applications in a variety of areas including artificial e-skins and health monitoring/diagnosis.^{1–7} Among the major performance criteria for strain sensors, i.e., sensitivity, stretchability, linearity over strain, and stability over time,^{1,3} the relative change in resistance over applied strain, or sensitivity, at the microstrain (less than 1%) levels is particularly vital. Common metallic foil mechanical gauges are limited by not only their ability to detect small deformations (<5%)^{8,9} but also their easy deformation from use. Next-generation mechanical sensors that are highly sensitive, responsive to wider range of mechanical deformation, and yet highly resilient for repetitive use are therefore desirable.

Highly porous and flexible cellulose aerogels that contain conductive nanomaterials like carbon nanotubes (CNTs), graphene, and conductive polymer nanoparticles have shown to possess dual compressive flexibilities and electric conductivities to emerge as promising choices for piezoresistive sensors.^{10–15} Dual temperature- and pressure-sensing aerogels were fabricated by mixing nanofibrillated cellulose (NFC) produced by high-pressure homogenization with polysilane and poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS),^{11,12} but the interplay between NFC and PEDOT/PSS was not elucidated. Unidirectional freeze-drying 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-cellulose nanofibril (CNF) derived from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation mixed with reduced graphene oxide produced aerogels capable of

detecting gas pressure drop perpendicular to the freezing direction.¹³ Conductive aerogels produced from CNT dispersed in cellulose dissolved in aqueous alkaline–urea followed by freeze and freeze-drying exhibited relative resistance change with imposed nitrogen gas pressure.¹⁵ Although compression- and pressure-sensing have been demonstrated, conductive aerogels as stretchable strain sensors have yet to be explored. The challenge lies in the non-conductive nature and low dry compressive strength of nanocellulose aerogel that must be overcome by a strong interplay between the conductive species and the nanocellulose.

Previously, we have shown that protonating the surface C6 carboxylates of TEMPO–CNFs with hydrochloric acid could induce more extensive self-assembly of CNFs into less-water-absorbing film with improved thermal stability.¹⁶ To enhance the CNF self-assembly by protonation with large cationic polymers has not been exploited, yet it has the potential to improve the mechanical strength of self-assembled CNF structures, such as aerogels. The hygroscopic, acidic, and conductivity-tunable nature of PEDOT/PSS^{17–19} makes it a good candidate for protonating CNF while providing high conductivity. Moreover, the carbonyl and hydroxyl double dipoles of the abundant CNF surface carboxyls are capable of hydrogen bonding with the SO₃H groups in PSS. The protonating capability of and strong interaction between

Received: June 20, 2018

Accepted: July 26, 2018

Published: August 9, 2018

Figure 1. Conductive PEDOT/PSS/CNF aerogels: (a) protonation of CNF surface carboxylates and their hydrogen bonding with PEDOT/PSS; (b) schematic of protonation, freezing/lyophilization, and EG vapor annealing processes; and (c) photographs of CNF and PEDOT/PSS/CNF aerogels on top of California poppy and cylindrical PEDOT/PSS/CNF aerogels in different diameters.

conducting PEDOT/PSS and strong CNFs are thought to lead to strong aerogels with highly conductive networks that may meet the requirements for strain sensors.

Here, we report such an approach to synthesize conductive and robust nanocellulose aerogels by protonating TEMPO–CNF with conductive PEDOT/PSS and further infuse these aerogels with an elastomer to produce stretchable high-performance strain sensors. Conducting PEDOT/PSS/CNF aerogels were fabricated by incorporating varying levels of TEMPO–CNF followed by lyophilization and ethylene glycol (EG) vapor annealing. The protonation of TEMPO–CNF with PEDOT/PSS and the effects of CNF loading on the conductivity and strength of PEDOT/PSS/CNF aerogels were investigated. These PEDOT/PSS/CNF aerogels were further infused with an elastomer precursor and cured to produce stretchable strain sensors. The microstructure and electrical and mechanical performances of these elastomer-infused PEDOT/PSS/CNF aerogels were then characterized to relate to their sensing mechanism.

2. MATERIALS AND METHODS

2.1. Materials. Aqueous poly(3,4-ethylene dioxithiophene)/poly(styrene sulfonate) (1:2.5 PEDOT/PSS w/w ratio) dispersion (Clevios PH 1000) was purchased from HC Starck, Inc. Poly(dimethylsiloxane) (PDMS, SYLGARD 184) was purchased from Sigma-Aldrich. Ethylene glycol (EG, purity > 99.8 wt %) was purchased from Fisher Scientific. Cellulose nanofibrils (CNFs) were isolated from pure rice straw cellulose via TEMPO-mediated oxidation followed by mechanical blending, as reported previously.^{20,21} Briefly, 1.0 g of rice straw cellulose was oxidized in an aqueous solution containing 0.016 g of TEMPO, 0.1 g of NaBr, and 5 mmol NaClO at pH 10.0. After centrifugation and dialysis, TEMPO-oxidized cellulose was blended (Vitamix 5200, Vitamix Corporation) at 37 000 rpm for 30 min and centrifuged (5000 rpm, 15 min) to collect the supernatant. Then, the supernatant was concentrated using a rotary evaporator (Buchi Rotavapor R-114) to 0.7 wt % and stored at 4 °C for preparation of films and aerogels.

2.2. Preparation of PEDOT/PSS/CNF Films. To investigate the effect of CNF loading to the conductivity of PEDOT/PSS, the CNFs were added at seven levels based on dry weight: 0, 5, 10, 25, 50, 60, and 70 w%. Aqueous PEDOT/PSS/CNF solution (200 μ L, 0.7 wt %) was cast on glass slides (2.5 $\times$ 2.5 cm²) pretreated with oxygen plasma

via a Micro-RIE Series 800 (Technics company) for 1 min to remove dust and improve the wettability for more uniform films. All PEDOT/PSS/CNF films were dried at 21 °C for 48 h.

2.3. Preparation of Aerogel. Equal mass (5.5 g) of aq PEDOT/PSS was added to aq CNF, both at 0.7 wt % concentration, and vigorously stirred for 30 min to a homogeneous mixture. Aerogels were prepared as previously reported.²¹ The mixture of PEDOT/PSS and CNF (solid weight ratio 1:1) was loaded into polypropylene tubes with inner diameter of 2.6 cm and glass tubes with inner diameter of 4 and 2.5 mm and frozen (−20 °C, 15 h), then lyophilized (−50 °C, 4 days, Free Zone 1.0 L Benchtop Freeze Dry System, Labconco, Kansas City, MO) to yield PEDOT/PSS/CNF aerogels. For comparison, CNF and PEDOT/PSS aerogels were also prepared the same way, each with 0.7 wt % aqueous dispersions. All the aerogels were dried at 70 °C for 2 h to remove residual moisture. By using different containers, aerogels with different diameters (20.0 $\pm$ 2, 3.0 $\pm$ 0.3, 2.1 $\pm$ 0.2 mm) were obtained (Figure 1c). To improve the conductivities, PEDOT/PSS and PEDOT/PSS/CNF aerogels were placed in a closed glass jar containing 500 μ L EG heated at 150 °C under vacuum for 30 min. After EG vapor annealing, these aerogels were placed at 150 °C for 30 min to remove the EG residue. PEDOT/PSS/CNF aerogels with CNF loading at 25, 50, 60, and 70% were prepared and designated as PEDOT/PSS/CNF25, PEDOT/PSS/CNF50, PEDOT/PSS/CNF60, and PEDOT/PSS/CNF70, respectively.

2.4. Encapsulation of Conductive Aerogels for Strain Sensors. The PDMS precursor (4.3 g, the weight ratio of base to curing agent was 10:1) was poured into a 10 cm diameter Petri dish and cured at 70 °C for 12 min to form a 0.4 mm thick base layer. Then, either PEDOT/PSS or PEDOT/PSS/CNF aerogel was placed on top of the PDMS base layer with two ends connected to copper wires and painted with silver epoxy and covered with PDMS precursor (20 g) as the top layer for 2 h at room temperature and then cured at 70 °C for 2 h. The effective length of the aerogels between the silver paste was about 4 $\pm$ 0.2 cm.

2.5. Characterizations. The ionic conductivity and pH values of aqueous CNF or PEDOT/PSS/CNF suspensions were measured using OAKTON pH/CON 510 series meter with ionic conductivity and pH probes, respectively. Scanning electron microscopy (SEM) of aerogels and PDMS-infused aerogels placed on a conductive carbon tape was performed using an XL30 SEM (FEI Company). The PDMS-infused aerogels were sliced into 28 mm $\times$ 4 mm $\times$ 1 mm dimension and mounted to a small mechanical frame with a gauge length of 20 mm (Figure S4), on which the tensile loading was applied to the sample under SEM at 0 and 50% strain. Raman spectra

Figure 2. Microstructure of PEDOT/PSS and PEDOT/PSS/CNF aerogels: SEM images of (a, b) PEDOT/PSS and (c, d) PEDOT/PSS/CNF aerogels, arrow in (d) shows traces of CNF bundles embedded in PEDOT/PSS on pore wall surfaces; and AFM height images of (e, f) pristine PEDOT/PSS and (g, h) PEDOT/PSS/CNF50 films. The images in (e, g) are $20\ \mu\text{m} \times 20\ \mu\text{m}$ and those in (f, h) are $5\ \mu\text{m} \times 5\ \mu\text{m}$.

were collected using an RM1000 Raman spectrometer (Renishaw plc) on aerogels using a 514.5 nm Argon ion laser. The aerogel with diameter of about 3 mm were compressed into $90 \pm 20\ \mu\text{m}$ thick sheets between two glass slides for Raman measurements.

Sheet resistances (R_s) of the casted films were measured via a four-probe device under a constant current of $45.3\ \mu\text{A}$ supplied by Harrison 6205 dual DC power source. The voltage was measured with a multimeter. On each sample, R_s was measured at 10 different locations and averaged value reported. Film thicknesses, t , was measured using a Dektak XT profilometer (Bruker Corporation). The electrical conductivity (σ) of the films was calculated as $\sigma = 1/(tR_s)$.^{17,22}

Wide-angle X-ray diffraction (XRD) was performed on an aerogel with diameter of about 3 mm compressed into of $90 \pm 20\ \mu\text{m}$ thick sheets between the glass slides and scanned from 2 to 36° in a continuous mode using a PANalytical X-ray diffractometer (Malvern Panalytical), with Cu K α radiation ($\lambda = 1.54\ \text{\AA}$) at 40 kV and 40 mA.

The mechanical behavior of CNF, PEDOT/PSS, and PEDOT/PSS/CNF aerogels were measured by a 5566 Instron universal testing machine at a constant $5\% \text{ min}^{-1}$ strain rate. Cylindrical aerogel samples of 3 cm length and either 3.8 ± 0.2 or 3.0 ± 0.3 mm diameters were coated with epoxy adhesive at each end to protect the aerogel from damage during clamping. The tensile strength, Young's modulus, and elongation were collected from at least 5 samples for each formulation, and their average and standard deviation reported.

The setup for electromechanical testing of the specimen is shown in Figure S3b. The loading/unloading of the sample is controlled by a 5566 Instron machine. The dog-bone-shaped specimen was glued to two metal plates that were clamped by the Instron machine. The distance between the metal plates was 8 mm, which was the effective sample length. The change in electrical resistance was monitored by a U1252B digital multimeter. The incremental, cyclic stretching and relaxing program were applied to initiate the fragmentation of the sample. The program was set to an incremental strain of 25%, starting at 0% and continuing until 100%, at a speed of $2.4\ \text{mm min}^{-1}$. Then, the incremental cyclic test was repeated once, and a cyclic stretching/relaxing program was applied to the sample with maximum strains of 50% at each cycle. The strain-sensing stability of PDMS-infused PEDOT/PSS/CNF70 aerogel was tested under stretching and relaxing cycles from 0 to 50% strain at a rate of $4\ \text{mm min}^{-1}$ for more than 4000 cycles. The resistance data were recorded every 1 s during the test. Stretching/relaxing of the sensor was captured by a video camera. The gauge factor (GF) of the strain sensors was defined as $\text{GF} = (\Delta R/R_0)/\epsilon$, where R_0 is the initial resistance, $\Delta R/R_0$ is the relative change in resistance, and ϵ is the applied strain.

3. RESULTS AND DISCUSSION

3.1. Conductive Nanocellulose Aerogels. TEMPO-mediated reaction oxidizes the C6 hydroxyls into carboxylic acid (COOH) that ionizes into C6 sodium carboxylates (COONa) on CNF surfaces at pH 10. Upon neutralization to pH 7 to end the reaction, approximately 86% sodium carboxylates remain, keeping the majority of negatively charges to facilitate the subsequent mechanical defibrillation into highly aqueously dispersed individual CNFs.^{16,20} The aqueous CNF at 0.7 wt % has a pH value of 5.7, close to that of deionized water in the air (5.5 pH due to the dissolution of CO_2),¹⁹ as well as the high ionic conductivity of $0.38\ \text{mS cm}^{-1}$ that is consistent with the highly dissociated COO^-Na^+ ions.

In PEDOT/PSS, the PSS benzene rings carry both neutral SO_3H and anionic SO_3^- (Figure 1a), with the latter ionically bonding with the cationic PEDOT thiophene rings into the PEDOT/PSS ionomer structure.¹⁹ The dominant PSS ionomer causes PEDOT/PSS complexes to be more anionic, providing electrostatic repulsion to repel each other as well as the negatively charged CNFs. Therefore, the negatively charged PSS serves as both dopant and dispersant for the cationic PEDOT particles. The dissociated $\text{SO}_3^- \text{H}^+$ in PSS also makes PEDOT/PSS dispersion highly acidic with a pH of 1.9 at 0.7 wt %, thus highly effective in protonating the negatively charged sodium carboxylated on the CNF surfaces. Upon adding the dark blue aqueous PEDOT/PSS dispersion to the clear aqueous CNF at 1:1 w/w CNF/PEDOT/PSS and mixing for 30 min, the CNF/PEDOT/PSS mixture turned lighter blue (Figures 1b and S1). The ionic conductivity increased from $0.38\ \text{mS cm}^{-1}$ of the aq CNF to $1.07\ \text{mS cm}^{-1}$ of the 1:1 w/w CNF/PEDOT/PSS mixture, whereas the pH value reduced from 5.7 to 2.7. Aqueous CNF, PEDOT/PSS, and well-mixed PEDOT/PSS/CNF dispersions, all at 0.7 wt %, were frozen at $-20\ ^\circ\text{C}$ for 15 h and then slowly freeze-dried ($-50\ ^\circ\text{C}$, 0.05 mbar, 4 days) to produce aerogels. Cylindrical (2 cm diameter, 4 cm length) CNF and PEDOT/PSS/CNF aerogels weighed 14.6 and 14.1 mg or had calculated densities of 11.6 and $11.2\ \text{mg cm}^{-3}$, respectively. California poppy can support them without deforming their structures. Aerogels with different diameters (20.0 ± 2 , 3.0 ± 0.3 , $2.1 \pm 0.2\ \text{mm}$) could be fabricated simply by using different sizes of containers (Figure 1c).

Figure 3. Characteristics of conductive PEDOT/PSS/CNF aerogels: (a) CNF loading and EG vapor annealing on conductivity; (b) CNF loading on conductivity of cast films of comparable compositions to aerogels; (c) Fourier-transform infrared spectroscopy (FTIR) spectra of CNF, PEDOT/PSS, and PEDOT/PSS/CNF aerogels; and (d) a schematic of benzoid and quinoid structure of PEDOT chains. (e) XRD patterns of CNF, PEDOT/PSS, and PEDOT/PSS/CNF50 aerogels; (f) Raman spectra of pristine PEDOT/PSS, PEDOT/PSS/CNF50, and EG vapor-annealed aerogels at an excitation wavelength of 514.5 nm, showing benzoid to quinoid structural transformation of PEDOT chain (as shown in (d)) from mixing with CNF and EG vapor annealing.

Whereas the CNF aerogel retains the same volume as the original aqueous suspension, both PEDOT/PSS aerogels with or without CNF decreased in volumes with more noticeable shrinkage of PEDOT/PSS/CNF aerogel than of PEDOT/PSS aerogel (Figure S1a). This more pronounced volume reduction in PEDOT/PSS/CNF aerogel is ascribed to the protonation of the CNF by PEDOT/PSS and their closer association, reinforcing the PEDOT/PSS network. Indeed, the 2.4 ± 0.7 kPa tensile strength and 32.8 ± 5.3 kPa Young's modulus of PEDOT/PSS aerogel was increased by ca. 1 order of magnitude to 25.0 ± 4.1 and 282.3 ± 78.5 kPa, respectively, for PEDOT/PSS/CNF aerogel (Figure S1). The tensile strength and Young's modulus of the conductive aerogel are not at par with the CNF aerogel's respective 36.2 ± 5.3 and 510.4 ± 95.3 kPa, as expected from the reduced self-assembling of the CNFs as a result of their protonation with PEDOT/PSS. Thus, the enhancement in the strength and Young's modulus of PEDOT/PSS aerogel by CNF is mainly ascribed to the reinforcing effect of CNFs, but the breaking strain of PEDOT/PSS/CNF aerogel was reduced to 3.5 from 18% of PEDOT/PSS, also consistent with the reinforcement.

Both PEDOT/PSS and PEDOT/PSS/CNF aerogels are highly porous, containing pores in widely varied sizes of one to tens of micrometers (Figure 2a,c). The thin cellular walls of PEDOT/PSS aerogels appeared smooth, whereas those of PEDOT/PSS/CNF contained some micrometer-wide fibrils (Figure 2b,d), indicating self-assembly of CNFs into thicker bundles and embedding in PEDOT/PSS thin walls. Whereas PEDOT/PSS aerogel disassembled and dispersed in water into a blue slurry within 5 min, PEDOT/PSS/CNF aerogel remains

intact in water for several days, showing excellent wet resiliency (Figure S2), similar to CNF aerogels reported previously.²¹ This observation shows that, in the presence of PEDOT/PSS, CNFs self-assembled into coherent fibrous network that behave similarly to those pristine CNF aerogels. PEDOT/PSS/CNF aerogel is also similarly hydrophilic as CNF aerogel, absorbing 76 times of distilled water as compared with the 83 times of the CNF aerogel. Therefore, even in the presence of the dominant anionic PSS, self-assembly of CNFs may be aided by their protonation with PEDOT/PSS and lowered repulsion among CNFs. Although wet resilient, PEDOT/PSS/CNF aerogel lost 8.5% mass when immersed in water for 10 min. The increased ionic conductivity of the surrounding water from 2.35 to $9.82 \mu\text{S cm}^{-1}$ supports the leaching of unbonded PSS that changed PEDOT/PSS/CNF weight ratio from the original 1:2.5:3.5 to 1:1.9:3.5, losing approximately one-quarter of PSS. The remaining hygroscopic PSS is thought to be either tightly associated with PEDOT or strongly hydrogen bonded with CNFs through the neutral SO_3H , thus insoluble.

The association between CNF and PEDOT/PSS and their morphology was further elucidated by atomic force microscope (AFM) evaluation of films cast with and without CNF (Figure 2e–h). PEDOT/PSS thin film appeared relatively smooth with a root-mean-square (rms) roughness of 4.74 nm, whereas that containing CNF showed self-assembled CNF bundles of several hundred nm width embedded in PEDOT/PSS matrix (Figure 2e,g), resulting in increased rms roughness of 12.52 nm. A closer examination of PEDOT/PSS film showed connecting nanograins with an averaged width of 75.1 ± 14.3 nm (Figure 2f). These nanograins are consistent with the

Figure 4. Cross-sectional images of the PDMS-infused conductive aerogels: (a) PEDOT/PSS and (b) PEDOT/PSS/CNF50.

previous report of thin-layer PSS-coated and bonded PEDOT nanocrystals.¹⁸ The higher magnification image of PEDOT/PSS/CNF film (Figure 2h) showed further details of 48.5 ± 5.7 nm wide PEDOT/PSS nanograins covering the CNF bundles, a clear evidence of a strong CNF/PEDOT/PSS interaction among the coexisting PEDOT nanocrystals and the self-assembled CNF bundles. The more segregated nanograins in PEDOT/PSS/CNF film is similar to EG doping effect of PEDOT/PSS films or fibers,^{18,23} consistent with the reduced electrostatic interactions between PEDOT and PSS in the presence of CNFs.

The electrical conductivity of PEDOT/PSS aerogel is low at 0.05 S m^{-1} , overly underpredicted based on their chemical compositions due to the highly porous aerogel structure, and increased with CNF loadings to reach 0.12 S m^{-1} with 50 wt % CNF. The increased conductivity indicates a microstructural change in PEDOT/PSS is likely induced by the nonconductive CNF and will be explained in later sections. To further investigate the effect of CNF loading to PEDOT/PSS, the conductivity of the films cast in the same compositions as the aerogels was measured to show similar levels of increase from 18.8 ± 2.1 to $40.8 \pm 5.0 \text{ S m}^{-1}$ at 0 to 50 wt % CNF loadings, i.e., more than doubling. The conductivities of both aerogels and casted films, however, decreased with higher CNF loadings of 60 and 70 wt %, suggesting that protonating the excessive, nonconductive CNF with PSS may interfere with the electrostatic interaction of PEDOT and PSS and the conductive pathway in either composite. Annealing the highly porous aerogels in EG vapor (150°C , 30 min) further reduced the resistance of PEDOT/PSS/CNF50 aerogel to $29.7 \pm 4.0 \text{ } \Omega \text{ cm}^{-1}$ (from $9.1 \pm 1.3 \text{ k} \Omega \text{ cm}^{-1}$ for the unannealed), corresponding to significantly increased conductivity from 0.12 ± 0.03 to $136 \pm 33 \text{ S m}^{-1}$, an impressive 1133 times increase (Figures 3a and S2). It should be noted that annealing by immersing in EG bath was not feasible as the aerogel collapses upon removing excess EG by heating at 150°C . Thus, EG vapor annealing was proven to be not only far more effective but also more desirable in that only minute quantity was applied and no extra cleaning was necessary, thus a greener process than liquid EG immersion.

The interaction between CNF and PEDOT/PSS was further delineated by FTIR spectroscopy (Figure 3c), specifically the carbonyl stretching in COOH (1740 cm^{-1}) and $\text{COO}^- \text{Na}^+$ (1610 cm^{-1}). CNF showed a sharp peak at 1610 cm^{-1} , indicative of the dominant $\text{COO}^- \text{Na}^+$ that is responsible for the high conductivity and acidic pH mentioned above. PEDOT/PSS/CNF aerogel exhibited a new peak at 1740 cm^{-1} , whereas the one at 1610 cm^{-1} almost completely diminished, indicating significant $\text{COO}^- \text{Na}^+$ to COOH conversion and confirming the protonation of CNFs. The

apparent broadening of the CNF hydroxyl band in PEDOT/PSS/CNF aerogel as compared to pure CNF aerogel indicates increased hydrogen bonding interactions between the CNF surface carboxyl and PSS. Most significantly, the 1523 cm^{-1} peak identified as the ring stretching of C=C bonds in the quinoid structure of thiophene backbone of PEDOT²⁴ sharpened and significantly intensified in PEDOT/PSS/CNF aerogel. The planar quinoid structure presents the preferred conjugated backbone (Figure 3d) that explains the higher conductivity of PEDOT/PSS/CNF aerogels. The absorbed water in PEDOT/PSS/CNF aerogel was shown by the appearance of the OH deformation peak at 1640 cm^{-1} and the shifting of the CNF hydroxyl peak at $3380\text{--}3442 \text{ cm}^{-1}$.

The planar PEDOT quinoid structure in PEDOT/PSS/CNF50 aerogel was further verified by XRD (Figure 3e). The CNF aerogel exhibited the typical peaks at 16.8 and 22.7° , corresponding to monoclinic $d(110)$ and $d(200)$ crystallographic lattice planes of cellulose I β , respectively, as reported on TEMPO–CNF derived from rice straw cellulose.¹³ PEDOT/PSS aerogel presented two characteristic peaks at 6.1 and 25.9° , corresponding to the lamella stacking distance, $d(100)$, of alternating PEDOT and PSS in the plane and the interchain planar $\pi\text{--}\pi$ stacking distance $d(010)$ of PEDOT, respectively. Another peak at 17.3° is indicative of the amorphous halo of PSS chains.^{18,19,23} PEDOT/PSS/CNF aerogel showed a significantly intensified 6.1° peak, confirming that the interaction with CNFs strongly enhanced the planar PEDOT/PSS lamella stacking, which promotes the self-organization of PEDOT chains, consistent with planarization of thiophene into the planar quinoid structure (Figure 3d).

To further explain the significantly improved electrical properties from protonation and EG vapor annealing, conjugated PEDOT molecular structure was analyzed by Raman microscopy. Pristine PEDOT/PSS aerogel had a sharp peak at 1433 cm^{-1} (Figure 3f), assigned to the symmetric $\text{C}_\alpha = \text{C}_\beta$ stretching deformation in the PEDOT aromatic thiophene ring. The shoulder peak at 1454 cm^{-1} was assigned to the breathing of benzoid structure of the thiophene ring, representing a coil conformation structure associated with a low conductive state.^{17,18,23} This benzoid band reduced with CNF loading, consistent with the benzoid-to-quinoid structural transformation. Such preferred linear or expanded-coil conformation facilitates electron transfer. This transformation agrees with the FTIR and XRD results (Figure 3c,e), providing structural evidence on the effect of CNFs on changing the PEDOT structure from a low conductive state to a high conductive state. The benzoid-associated peak at 1454 cm^{-1} further reduced after EG vapor annealing. Moreover, the position of the symmetric $\text{C}_\alpha = \text{C}_\beta$ peak is 4 cm^{-1} lower than the 1433 cm^{-1} for pristine PEDOT/PSS and PEDOT/PSS/

Figure 5. Strain sensing of PDMS-infused PEDOT/PSS/CNF conducting aerogels as determined by relative electrical resistance change $\Delta R/R_0$: (a) $\Delta R/R_0$ under incremental increasing strains of cyclic loading and unloading and (b) strain effects of PDMS-infused PEDOT/PSS/CNF70 and PEDOT/PSS aerogels. The blue line represents the fitting line for the applied strain from 0 to 95% (with the linearity of 0.98); (c) dynamic response to five repetitive loading and unloading cycles at 50% strain; (d) effects of CNF loadings; (e) dynamic response of the PDMS-infused PEDOT/PSS/CNF70 aerogel to 0 to 50% stretching and relaxing cycles at a rate of 4 mm min⁻¹, showing long-term repeatability of the sensor after 4005 cycles; (f–h) repeatability of the sensor at cycles 500–505, 2000–2005, and 4000–4005, respectively.

CNF aerogels, consistent with the dominant thiophene quinoid structure over benzoid or planarization of the thiophene rings on PEDOT from EG vapor annealing (Figure 3d). EG vapor annealing was advantageous and significant to not only dramatically improve the conductivity of the aerogel by 2 orders of magnitude but also preserve the integrity of the aerogel.

3.2. Strain Sensing Based on Conductive Nanocellulose Aerogels. The highly porous structure of PEDOT/PSS/CNF aerogels was infused with PDMS (Figure S3a). PEDOT/PSS/CNF50 and PEDOT/PSS/CNF70 aerogels (4 cm long) infused with PDMS precursor showed only slight increase in resistance from 98 to 108 Ω and 4.1 to 4.3 k Ω , respectively, and then further increase to 208 Ω and 15 k Ω , respectively, from curing, ascribed mainly to the release of residue stress in PDMS. The scanning electron microscopy (SEM) of the cross sections of PEDOT/PSS–PDMS or PEDOT/PSS/CNF–PDMS composite materials showed completely PDMS-infused aerogels (Figure 4).

The relative change in the electrical resistance, $\Delta R/R_0$ (ΔR is the resistance change, R_0 is the initial resistance), of the PDMS-infused conductive PEDOT/PSS aerogel was minimum from 0 to 100% strain, reaching only 0.019 at 100% (Figure 5a). The little change in resistance indicates that the conductive pathway of PEDOT/PSS network was not altered by elastic PDMS filling. In contrast, CNF loadings at 50 and 60 wt % caused noticeable changes in the resistance in these PDMS-infused PEDOT/PSS/CNF conducting aerogels. Over incrementally increased strains, $\Delta R/R_0$ first increased at low strain (<20%), attributed to the disconnecting of the conductive networks in PEDOT/PSS/CNF aerogel, and then plateaued from 20 to 100% strain range. PEDOT/PSS/CNF

aerogels are not as elastic as PEDOT/PSS aerogels (Figure S1, stress–strain curve), forming cracks to disconnect the conductive network with increasing strain at up to 20% strain. The resistance then plateaued or became insensitive to strain from 20 to 100%, suggesting maximum cracks density may have reached at around 20% strain. The conductive pathway becomes elastic from 20 to 100% strain. The different response of the aerogel to mechanical strain levels may offer different sensing mechanism for these PDMS-infused strain sensors.

At 70 wt % CNF loading, no $\Delta R/R_0$ plateaus were observed as seen at lower CNF loadings. On the contrary, $\Delta R/R_0$ dramatically increased to 14.7 at 100% strain, and the trend of $\Delta R/R_0$ vs strain was completely reversible following each incremental step of increasing applied strains. The relative changes in the resistance ($\Delta R/R_0$) of PDMS-infused PEDOT/PSS and PEDOT/PSS/CNF70 aerogels were plotted over strain levels to show high linearity of 0.98 from 0 to 95% strain and a very high gauge factor (GF) = 14.8 at 95% strain. The GF value is 5 orders of magnitude higher than the 1.1×10^{-4} GF of the insensitive PDMS-infused PEDOT/PSS aerogel. The value is also over 7 times higher than that of conventional metal gauges, typically with GF around 2.0 at low strain ($\epsilon < 5\%$).⁹ Nonlinearity is one of the main drawbacks of most of the piezoresistive-type strain sensors.³ Typical strain sensors based on conductive nanomaterials, e.g., metal nanoparticles, CNT networks, as the sensing components exhibit either nonlinear or two linear regions.^{3–7} The single and extended linear regions of the PDMS-infused PEDOT/PSS/CNF70 sensor simplify the calibration process and ensure accurate measurements through the whole range of applied strains. Whereas PDMS-infused PEDOT/PSS aerogels can be used as resistance-insensitive materials at large strains, PDMS-infused

Figure 6. Microstructural change of conductive aerogel composites under tensile strains: (a, b) PDMS-infused PEDOT/PSS aerogel at 0 and 50% strains, respectively; (c, d) PDMS-infused PEDOT/PSS/CNF70 aerogel at 0 and 50% strains, respectively; (e, f) incremental cyclic loading and unloading tests on PDMS-infused PEDOT/PSS aerogel and PDMS-infused PEDOT/PSS/CNF70 aerogel from 0 to 100% strain at a rate of 2.4 mm min⁻¹; and (g, h) schematic illustrations of the proposed microstructural change of the aerogel network under an applied tensile strain.

PEDOT/PSS/CNF aerogels can be applied as highly stretchable, strain-sensitive sensors.

Dynamic $\Delta R/R_0$ responses of PDMS-infused PEDOT/PSS/CNF aerogels over five cycles of a strain from 0 to 50% was also showed to be highly reversible and stable at all CNF loadings, with very little hysteresis. For the sensor loaded with 70 wt % CNF, $\Delta R/R_0$ follows the evolution of the applied strain closely. This $\Delta R/R_0$ vs strain relationship shows that the sensing behaviors of PEDOT/PSS/CNF aerogels are tunable by changing the CNF loading and are sensitive to detect subtle strain change with a wide strain detection range. Figure 5d further confirms the impact of CNF loading on $\Delta R/R_0$, proving the nonconductive CNF could replace a significant portion (up to 70 wt %) of PEDOT/PSS in the aerogel while dramatically improving the sensitivity of the strain sensor. Figure 5e–h shows that PDMS-infused PEDOT/PSS/CNF70 aerogel has good durability and repeatability, which are crucial for long-term use. After 4005 cycles of loading and unloading from 0 to 50% strain, the performance of the strain sensor remained repeatable. The good repeatability of the sensor was confirmed at cycles 500–505, 2000–2005, and 4000–4005 (Figure 5f–h).

To explore the strain-sensing mechanism, both PDMS-infused aerogels were sliced to expose the aerogel network and mounted on a small mechanical frame (Figure S4), on which tensile strain can be applied under SEM. PDMS-infused PEDOT/PSS aerogel showed no obvious microstructure changes when stretched from 0 to 50% strain, which is ascribed to the elastic nature of PEDOT/PSS aerogel (Figure 6a,b). In contrast, PDMS-infused PEDOT/PSS/CNF70 aerogel network exhibited noticeable detachment between PDMS and the aerogel, with an average opening distance of $23.6 \pm 8.5 \mu\text{m}$, under tensile strain (Figure 6c,d).

The microstructural change in aerogel/PDMS composites under loading motivated further investigation of degradation in their mechanical properties by incremental cyclic stretching/unstretching (Figure 6e,f), a classical damage mechanics approach.²³ The highly linear and parallel loading/unloading curve showed very minor change in Young's modulus at different cycle number (Figure 6e), suggesting an elastic behavior of PDMS-infused PEDOT/PSS aerogels across the overall strain range (0 to 100%). It is important to note that this macroscopic elastic behavior is a result of the elastic network of PEDOT/PSS aerogel and the elastic PDMS matrix. In comparison, PDMS-infused PEDOT/PSS/CNF70 aerogel

displayed clear decrease in Young's modulus with increasing number of cycles. PEDOT/PSS/CNF aerogel had a 9-fold increase in Young's modulus than PEDOT/PSS aerogel (Figure S1), ascribed mainly to the increased stiffness from the significant CNF incorporation. The CNF loadings help to resist strain to a large extent by forming cracks. Thus, the degradation of Young's modulus is ascribed to the formation of cracks.

By analyzing the SEM images at different strains and incremental cyclic loading/unloading, some insights into the sensing mechanism of the PDMS-infused aerogels are illustrated in Figure 6g,h. The load transfer from PDMS to PEDOT/PSS aerogel leads to the deformation and elongation of the conductive network in the tensile direction without degradation. The deformed conductive network maintains the conductive pathway with the help of elastic PDMS around (Figure 6g), displaying resistance-insensitive behavior upon stretching. On the other hand, with high CNF loadings into PEDOT/PSS, the load transfer from PDMS to PEDOT/PSS/CNF leads to cracks. This disconnection of conductive paths upon stretching is responsible for the sensor's resistance-sensitive behavior (Figure 6h). The most relevant comparison to the stretchable sensors described here in this study is based on PDMS-infused graphene oxide aerogels, which demonstrate high strain sensitivity ($GF = 61.3$) but limited stretchability of only 19% and nonlinear sensing behavior.²⁵

Other stretchable strain sensors were based on the application of fragmentation strategy to carbon nanomaterials, e.g., CNT and graphene, to achieve a combination of high sensitivity, high stretchability, and linearity.^{4–7} However, a low initial resistance of the sensing component in these sensors required large quantities of these hydrophobic carbon nanomaterials whose aqueous dispersion could only be met by strong acid, surfactants, or sonication. Therefore, significant advantages of using PEDOT/PSS as the sensing component in this study are (1) aqueous PEDOT/PSS dispersions are fully compatible and readily mixed with aqueous CNF dispersions without needing any surfactant or sonication; (2) CNF is biologically derived and PEDOT/PSS is environmental friendly in contrast to carbon nanomaterials; (3) the initial resistance of PEDOT/PSS aerogel can be enhanced with a green vapor annealing process, which is a key to increasing the final sensitivity; and (4) high CNF loading replaces a significant portion of PEDOT/PSS to reduce the cost of sensing component, thus being economically favorable. This is not likely to happen for carbon nanomaterials.

In PDMS-infused PEDOT/PSS/CNF aerogels, CNF plays several roles and has many merits. First, CNF strengthens and increases the stiffness to improve the integrity of such aerogels to be handled. CNF also transforms the resistance-insensitive PEDOT/PSS aerogels into a highly strain-sensitive PEDOT/PSS/CNF sensors to exhibit high linearity in relative electrical resistance change $\Delta R/R_0$ in comparison to other piezoresistive strain sensors. Economically, high CNF loading replaces a significant portion of the pricey PEDOT/PSS to reduce the overall cost. To the best of our knowledge, this is the first report on conductive nanocellulose aerogel strain sensors that are highly stretchable (up to 100% strain) and sensitive ($GF = 14.8$) with high linearity. Furthermore, this represents novel use biomass-derived nanoconductive CNFs as the building blocks in creating light, strong, stretchable, and conductive strain sensors.

4. CONCLUSIONS

Rice straw cellulose-derived TEMPO–CNF has shown to be effectively protonated and hydrogen bonded with a conductive PEDOT/PSS polymer complex to generate strong and conductive PEDOT/PSS/CNF aerogels. This approach has several merits. Most significantly, the dual interactions between CNF surface carboxylate/carboxyl groups with PSS in PEDOT/PSS complex transformed the PEDOT benzoid into a more favorable electron conductive planar quinoid structure. As the nonconductive CNF loadings increased from 0 to 50 wt %, the conductivity of the aerogel was in fact increased from 0.05 to 0.12 S m⁻¹. The protonation of the CNF surface carboxylates into carboxyls, which hydrogen bond with PSS, significantly improved the tensile stress and Young's modulus of PEDOT/PSS/CNF aerogels. When infused with PDMS elastomer, CNF transformed a resistance-insensitive PDMS-infused PEDOT/PSS aerogel into strain sensors with high sensitivity and high linearity. The approach to protonate CNF surface carboxylates with PSS in the conductive PEDOT/PSS and their hydrogen bonding with carboxyls is robust, producing not only ultralight and strong, water-insoluble conductive aerogels but, when infused with an elastomer, also sensitive, stretchable, and linearly responsive strain sensors with tunable sensitivity. These findings demonstrate the potential of nonconductive nanocelluloses as the building blocks to design and optimize the strain sensors with a specific piezoresistive behavior.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b10239.

Mechanical properties of aerogels, additional characterizations of conductive PEDOT/PSS/CNF dispersions and aerogels, preparation and characterization of PDMS-infused aerogel strain sensors (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ylhsieh@ucdavis.edu.

ORCID

Jian Zhou: 0000-0003-0144-5901

You-Lo Hsieh: 0000-0003-4795-260X

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors appreciate the funding support from the California Rice Research Board.

■ REFERENCES

- (1) Trung, T. Q.; Lee, N. Flexible and Stretchable Physical Sensor Integrated Platforms for Wearable Human-Activity Monitoring and Personal Healthcare. *Adv. Mater.* **2016**, 28, 4338–4372.
- (2) Lipomi, D. J.; Vosgueritchian, M.; Tee, B. C. K.; Hellstrom, S. L.; Lee, J. A.; Fox, C. H.; Bao, Z. N. Skin-Like Pressure and Strain Sensors Based on Transparent Elastic Films of Carbon Nanotubes. *Nat. Nanotechnol.* **2011**, 6, 788–792.
- (3) Amjadi, M.; Kyung, K.; Park, I.; Sitti, M. Stretchable, Skin-Mountable, and Wearable Strain Sensors and Their Potential Applications: A Review. *Adv. Funct. Mater.* **2016**, 26, 1678–1698.

- (4) Zhou, J.; Xu, X.; Hu, Y.; Lubineau, G. Deformable and Wearable Carbon Nanotube Microwire-based Sensors for Ultrasensitive Monitoring of Strain, Pressure and Torsion. *Nanoscale* **2017**, *9*, 604–612.
- (5) Xin, Y.; Zhou, J.; Xu, G. X.; Lubineau, G. Laser-Engraved Carbon Nanotube Paper for Instilling High Sensitivity, High Stretchability, and High Linearity in Strain Sensors. *Nanoscale* **2017**, *9*, 10897–10905.
- (6) Zhou, J.; Hu, Y.; Xu, X.; Han, F.; Lubineau, G. Fragmented Carbon Nanotube Papers for Ultrasensitive, Stretchable Strain Sensors. *ACS Appl. Mater. Interfaces* **2017**, *9*, 4835–4842.
- (7) Zhou, J.; Xu, X.; Xin, Y.; Lubineau, G. Coaxial Thermoplastic Elastomer-Wrapped Carbon Nanotube Fibers for Deformable and Wearable Strain Sensors. *Adv. Funct. Mater.* **2018**, *28*, No. 1705591.
- (8) Yamada, T.; Hayamizu, Y.; Yamamoto, Y.; Yomogida, Y.; Izadi-Najafabadi, A.; Futaba, D. N.; Hata, K. A Stretchable Carbon Nanotube Strain Sensor for Human-Motion Detection. *Nat. Nanotechnol.* **2011**, *6*, 296–301.
- (9) Park, J.; You, I.; Shin, S.; Jeong, U. Material Approaches to Stretchable Strain Sensors. *ChemPhysChem* **2015**, *16*, 1155–1163.
- (10) Wang, M.; Anoshkin, I. V.; Nasibulin, A. G.; Korhonen, J. T.; Seitsonen, J.; Pere, J.; Kauppinen, E. I.; Ras, R. H. A.; Ikkala, O. Modifying Native Nanocellulose Aerogels with Carbon Nanotubes for Mechanoresponsive Conductivity and Pressure Sensing. *Adv. Mater.* **2013**, *25*, 2428–2432.
- (11) Khan, Z. U.; Edberg, J.; Hamed, M. M.; Gabrielsson, R.; Granberg, H.; Wagberg, L.; Engquist, I.; Berggren, M.; Crispin, X. Thermoelectric Polymers and their Elastic Aerogels. *Adv. Mater.* **2016**, *28*, 4556–4562.
- (12) Han, S.; Khan, Z. U.; Edberg, J.; Fabiano, S.; Crispin, X.; Jiao, F. Thermoelectric Polymer Aerogels for Pressure-Temperature Sensing Applications. *Adv. Funct. Mater.* **2017**, *27*, No. 1703549.
- (13) Pan, Z. Z.; Nishihara, H.; Iwamura, S.; Sekiguchi, T.; Sato, A.; Isogai, A.; Kang, F. Y.; Kyotani, T.; Yang, Q. H. Cellulose Nanofiber as a Distinct Structure-Directing Agent for Xylem-like Micro-honeycomb Monoliths by Unidirectional Freeze-Drying. *ACS Nano* **2016**, *10*, 10689–10697.
- (14) Huang, Z.-M.; Liu, X.-Y.; Wu, W.-G.; Wang, H.; Li, Y.-Q. Highly Elastic and Conductive Graphene/Carboxymethylcellulose Aerogels for Flexible Strain-Sensing Materials. *J. Mater. Sci.* **2017**, *52*, 12540–12552.
- (15) Qi, H. S.; Mader, E.; Liu, J. W. Electrically Conductive Aerogels Composed of Cellulose and Carbon Nanotubes. *J. Mater. Chem. A* **2013**, *1*, 9714–9720.
- (16) Jiang, F.; Hsieh, Y. L. Self-assembling of TEMPO Oxidized Cellulose Nanofibrils As Affected by Protonation of Surface Carboxyls and Drying Methods. *ACS Sustainable Chem. Eng.* **2016**, *4*, 1041–1049.
- (17) Zhou, J.; Lubineau, G. Improving the Electrical Conductivity in Polycarbonate Nanocomposites Using Highly Conductive PEDOT/PSS Coated MWCNTs. *ACS Appl. Mater. Interfaces* **2013**, *5*, 6189–6200.
- (18) Zhou, J.; Anjum, D. H.; Li, E. Q.; Lubineau, G.; Thoroddsen, S. T. Unraveling the Order and Disorder in Poly (3,4-ethylene dioxathiophene)/ Poly (styrene sulfonate) Nanofilms. *Macromolecules* **2015**, *48*, 5688–5696.
- (19) Zhou, J.; Anjum, D.; Chen, L.; Xu, X.; Ventura, I.; Jiang, L.; Lubineau, G. The Temperature-Dependent Microstructure of PEDOT/PSS Films: Insights from Morphological, Mechanical and Electrical Analyses. *J. Mater. Chem. C* **2014**, *2*, 9903–9910.
- (20) Jiang, F.; Hsieh, Y. L. Chemically and Mechanically Isolated Nanocellulose and Their Self-Assembled Structures. *Carbohydr. Polym.* **2013**, *95*, 32–40.
- (21) Jiang, F.; Hsieh, Y. L. Amphiphilic Superabsorbent Cellulose Nanofibril Aerogels. *J. Mater. Chem. A* **2014**, *2*, 6337–6342.
- (22) Schroder, D. K. *Semiconductor Material and Device Characterization*, 3rd ed.; IEEE Press: Hoboken, NJ, 2006; Chapter 1, pp 3–9.
- (23) Zhou, J.; Li, E. Q.; Li, R.; Xu, X.; Aguilar Ventura, I.; Moussawi, A.; Anjum, D.; Hedhili, M. N.; Smilgies, D.; Lubineau, G.; Thoroddsen, S. T. Semi-metallic, Strong and Stretchable Conjugated Polymer Fibers. *J. Mater. Chem. C* **2015**, *3*, 2528–2538.
- (24) Zhang, X. T.; Chang, D. W.; Liu, J. R.; Luo, Y. J. Conducting Polymer Aerogels from Supercritical CO₂ Drying PEDOT-PSS Hydrogels. *J. Mater. Chem.* **2010**, *20*, 5080–5085.
- (25) Wu, S.; Ladani, R. B.; Zhang, J.; Ghorbani, K.; Zhang, X.; Mouritz, A. P.; Kinloch, A. J.; Wang, C. H. Strain Sensors with Adjustable Sensitivity by Tailoring the Microstructure of Graphene Aerogel/PDMS Nanocomposites. *ACS Appl. Mater. Interfaces* **2016**, *8*, 24853–24861.