Supporting Information

Highly Porous Composite Aerogel Based Triboelectric Nanogenerators for High Performance Energy Generation and Versatile Self-Powered Sensing

Hao-Yang Mi\textsuperscript{a,b,d}, Xin Jing\textsuperscript{a,b,d}, Zhiyong Cai\textsuperscript{e}, Yuejun Liu\textsuperscript{a}, Lih-Sheng Turng\textsuperscript{b,d,*}, and Shaoqin Gong\textsuperscript{b,c,*}

\textsuperscript{a} School of Packaging and Materials Engineering, Hunan University of Technology, Zhuzhou, 412007, China
\textsuperscript{b} Wisconsin Institutes for Discovery, University of Wisconsin–Madison, Madison, WI 53715, USA
\textsuperscript{c} Department of Biomedical Engineering, University of Wisconsin–Madison, Madison, WI 53706, USA
\textsuperscript{d} Department of Mechanical Engineering, University of Wisconsin–Madison, Madison, WI 53706, USA
\textsuperscript{e} Forest Product Laboratory, USDA, Madison, WI 53726, USA

Footnotes:
Corresponding Authors:
L.S. Turng: turng@engr.wisc.edu; and S. Gong: shaoqingong@wisc.edu

The first and second authors contribute equally to this work.
1. Experimental Details

1.1 Preparation of CNF Solution

CNF was prepared in the Forest Products Laboratory according to the following procedure. Commercially supplied bleached eucalyptus Kraft pulp (Aracruz Cellulose, Brazil) was used as the raw material. The pulp was pre-treated with 2 wt% NaClO₂ solution (pH = 2) by pulping the fibers and soaking overnight at 2 wt% solids. The pre-treated fibers were carboxylated using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), sodium chlorite, and sodium hypochlorite at 60 °C for 3 days. TEMPO-oxidized pulp fibers were then washed thoroughly using reverse osmosis-purified (RO) water and homogenized in a disk refiner to break apart the fibril bundles. Obtained fiber slurry was diluted and centrifuged at 12,000 rpm to facilitate the separation of coarse and fine fractions, and the upper clear solution was collected. A final clarification step was performed in which the nanofiber suspension was passed once through an M-110EH-30 microfluidizer (Microfluidics, Newton, MA) with 200- and 87-μm chambers in series. The resulted CNF solution has a concentration of 1 wt.% in water.

1.2 Fabrication of CNF and CNF Composite Aerogel films

Silica fiber (SF) was prepared by self-assembly electrospinning of a tetraethyl orthosilicate (TEOS)/polyvinyl alcohol (PVA) solution followed by calcination according to our previous works. [1-3] Human hair (HH) (black, straight) was donated by the author. Rabbit fur (RF) (faint-yellow) was purchased from Amazon. HH and RF were cut into 2~3 mm in length and sonicated in 50% ethanol followed by sufficient drying in air. SF, HH, and RF fillers were mixed in a CNF solution at a 1:1 weight ratio to CNF, yielding a 2% solid-content solution. To prepare 1% solid-content solution, an equal volume of water was added to the above solution. The solution was mixed via mechanical stirring at 100 rpm for 30 min. The 2% CNF solution was obtained by rotational evaporation at 80 °C with a rotatory evaporator.
(Buchi R-210). Freshly prepared solutions were pre-cooled at 4 °C and poured into aluminum dishes, followed by freezing in a dry-ice/acetone bath (−78 °C) and then freeze-drying using a freeze dryer (Labconco) at −83 °C and 0.04 mBar for 3 days The resulting aerogels were then compressed at a pressure of 1.0 MPa using a universal mechanical property test instrument (Instron) to obtain the corresponding aerogel films.

1.3 Fabrication of PI Aerogel Films

The PI aerogel films were synthesized by crosslinking biphenyl-3,3’,4,4’-tetracarboxylic dianhydride (BPDA) with 50% 2,2’-dimethylbenzidine (DMBZ) and 50% 4,4’-oxydianiline (ODA), followed by supercritical fluid extraction using CO₂, according to previously reported procedures.[4]

1.4 HEF1 Human Fibroblasts Culture

HEF1 fibroblast cells differentiated from the human embryonic stem cell line WA09 (WiCell Research Institute) were used for the cell culture studies on the prepared aerogel films. The cells were cultured in a medium comprised of 80% knockout Dulbecco's modified Eagle's medium (KO-DMEM) (Invitrogen, Carlsbad, CA), 1 mM L-glutamine, 0.1 mM b-mercaptopethanol, 20% fetal bovine serum (FBS) (Hyclone, Logan, UT), and 1% non-essential amino acids. The outgrowth culture was passaged by incubation in TrypLE (Invitrogen) for 5 min.

Prior to cell seeding, all aerogel films were washed 3 times with PBS and then sterilized with ultraviolet (UV) light for 30 min. HEF1 cells were seeded onto the aerogel films at a density of 1×10⁴ cells per well and cultured at incubator settings of 5% CO₂ and 37 °C. Cells were fed with HEF1 media every two days.
1.5 Characterization of Biological Properties

Cell viability was determined after culturing for 3 days and 10 days. Viability was assessed via a live/dead viability/cytotoxicity kit (Life Technologies). Green fluorescent calcein-AM was used to target esterase activity within the cytoplasm of living cells, while red fluorescence ethidium homodimer-1(EthD-1) was used to indicate cell death. Stained cells were imaged with a Nikon A1RSi inverted confocal microscope system.

Cell proliferation was assessed at day 3 and day 10 by MTS assay using the CellTiter 96 Aqueous One Solution kit (Promega Life Sciences). Cells were first treated with media containing a 20% MTS solution and allowed to incubate for 1 h. After incubation, 100 µL of spent media were transferred into a clear 96-well plate. The absorbance of the plates at the 450 nm wavelength was read with a Glomax-Multi+Multiplate Reader (Promega). The subsequent number of cells was determined relative to the negative control.

The shape and cytoskeleton organization of the cells were determined by phalloidin–tetramethylrhodamine B isothiocyanate (phalloidin–TMRho, Sigma) staining. For this assay, cells were fixed following the same procedure in the cell attachment assay. They were then treated with 0.3 µM of phalloidin–TMRho with DAPI for 1 hour at room temperature. Next, samples were washed with PBS and imaged using the same confocal microscope.

References

2. Supporting Figures

**Figure S1.** Schematic showing the self-assembly electrospinning of tetraethyl orthosilicate (TEOS)/polyvinyl alcohol (PVA) fibers. Inset image shows the collected 3D fibers.

**Figure S2.** (A) TEM image of as prepared CNF. (B) SEM images of the surface morphology of CNF aerogel prepared from 1% solution.
Figure S3. SEM images of the surface morphology of (A) CNF aerogel, (B) CNF/SF aerogel, (C) CNF/HH aerogel, and (D) CNF/RF aerogel prepared from 2% solutions.

Figure S4. Fluorescence images of a live/dead assay of HEF1 human fibroblasts cultured on CNF and CNF-based composite aerogels for 10 days.
Figure S5. (A) Cell viability and (B) cell proliferation statistical results of HEF1 human fibroblasts cultured on CNF and CNF-based composite aerogels for 3 and 10 days.

Figure S6. XPS survey scans and the corresponding atom percentages of (A) silica fiber, (B) human hair, and (C) rabbit fur.
Figure S7. (A) Open circuit voltage and (B) short circuit current results of TENG assembled with different CNF and CNF composite aerogels prepared from 2% solutions against PI aerogels.

Figure S8. Comparison of (A) open circuit voltage and (B) short circuit current for TENGs based on CNF, CNF/SF, CNF/HH, and CNF/RF aerogels that were prepared with solutions with 1% and 2% concentrations.
Figure S9. Current density and power density of (A) CNF, (B) CNF/SF, and (C) CNF/HH aerogel-based TENGs on external loads with resistances ranging from 1 kΩ to 10 MΩ.

Figure S10. SEM images of the surface morphology of (A) CNF/RF aerogel, and (B) PI aerogel from the TENG after operating for 30 min.
Figure S11. Enlarged signal of (A) one water droplet dropped on the PCTENG sensor and (B) a single knock on the bench that the PCTENG sensor was attached to.
3. Supporting Media

Movie 1: Thirty-two LEDs with different colors were instantly lit by a porous composite TENG (PCTENG).

Movie 2: Sixty blue LEDs were instantly lit by a PCTENG.

Movie 3: Two blue LEDs were continuously lit by the energy harvested through a PCTENG.

Movie 4: A timer powered by the energy harvested through a PCTENG.

Movie 5: A motor with a fan powered by the energy harvested through a PCTENG.

Movie 6: Self-powered sensing of a finger tap with a PCTENG.

Movie 7: Self-powered sensing of falling water droplets with a PCTENG.

Movie 8: Self-powered sensing performance of a PCTENG in detecting vibrations of the substrate it was attached to.

Movie 9: Voltage output signals of PCTENG when subjected to bending.

Movie 10: Monitoring human walking pace with a PCTENG.