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Trends in Carbohydrate Research

Advanced Applications of Cellulose in Mechanical Energy Harvesting and Sensing

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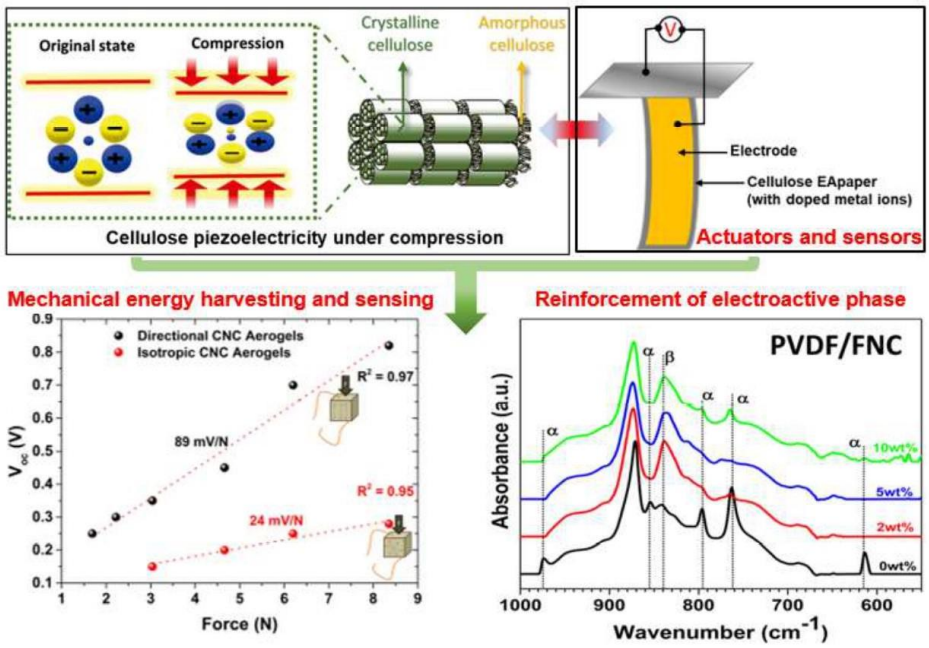
Graphical Abstract



Abstract

Environmental concerns and depleting fossil resources have led to tremendous research interest in sustainable polymeric materials. Cellulose occupies a unique place among the various polymers that have been widely explored as sustainable alternatives to fossil-derived polymers. It is incredible to see new and exciting developments involving cellulose, a ubiquitous polymer that has been known to humankind for millions of years. Mechanical energy harvesting and sensing is one such emerging application of cellulose. The inherent piezoelectric properties of this polysaccharide and its ability to strengthen the piezoelectric properties of other polymers have captivated a lot of research interest in recent years. This minireview attempts to capture some of the recent developments on cellulose-based piezoelectric materials with a particular focus on nanogenerator device fabrication and characterization. The review is not intended to be comprehensive. It is only an effort to showcase the potential of cellulose as piezoelectric sensors and actuators, mechanical energy harvesters, and as a reinforcing agent for piezoelectric composites.

Keywords: Mechanical energy harvesting; Sensors and actuators; Cellulose; Piezoelectric; Sustainable polymer material.

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1. Introduction

Cellulose, the most popular member of the polysaccharide family, is a naturally abundant biopolymer that is renewable, biodegradable and non-toxic. The unique physical and chemical properties of cellulose have rendered its use in a wide range of applications including but not limited to textiles, paper, furniture and explosives. Cellulose is a linear polysaccharide with β-1,4-linked D-glucose repeat units. Numerous hydroxyl groups in cellulose facilitate the formation of strong inter- and intramolecular hydrogen bonds between polymeric chains. The macromolecular cellulose chains further stack into fibrils of 3-5 nm width and a few hundred nanometers in length. Hemicelluloses and lignin bind several such fibrils to form microfibrils having widths of 10-30 nm. This hierarchical structure is characteristic of cellulose fibers derived from plants.[1] The development of new processes to convert cellulosic biomass into nanometer dimensions has further expanded the range of applications for this biopolymer.[2]

Nanocellulose refers to two different nanomaterials: short, low aspect ratio cellulose nanocrystals or cellulose nanowhiskers (CNC or CNW) and long, high aspect ratio cellulose nanofibrils (CNF). CNC or CNW is typically produced through a sequence of chemical treatments, including acid hydrolysis. This removes most of the hemicellulose, lignin and amorphous portions of cellulose, leaving behind short nanocellulose crystals (CNC) (5-10 nm diameter, 50-200 nm length) with a surface charge that depends on the chemical processing. CNCs are attractive as mechanical reinforcements and rheology modifiers. While it helps to obtain functionalized nanocellulose suitable for unique applications, the yield is low when chemical methods are used for producing nanocellulose. Cellulose nanofibrils can be obtained from bleached cellulose pulp by mechanical methods such as homogenizing, ball milling, grinding etc. This is a relatively high throughput process (1-30 Kg/day) and yields thin nanofibrils (5-50 nm diameter, 3-10 microns length). Bacterial nanocellulose (BNC) is another type of nanocellulose produced by a bottom-up approach using bacteria cultures. BNC is highly crystalline and pure, having unique water-absorbing properties. Cellulose has low density, high mechanical strength, thermal stability and biocompatibility.[3] In the last two decades, nanocellulose has been explored in various functional materials, including stimuli-responsive mechanically dynamic nanocomposites,[45,6] gels,[7] shape memory composites,[8] optoelectronic devices,[9] electrochemical energy storage devices,[10] nanogenerators,[1] flexible sensors,[11] and biomimetic electronic skins.[12]

Cellulose-based nanogenerators have gained tremendous research interest in recent years. These nanogenerators, leveraging the piezoelectric property of cellulose, are becoming prominent candidates for low power applications such as sensors, miniature electronic devices etc. The piezoelectric effect refers to the electromechanical transduction property of certain materials by which mechanical deformation can be converted into electric charge and vice-versa. Bazhenov discovered the direct piezoelectric effect (mechanical force to electrical charge) in wood in 1950.[13] In 1955 Fukada showed that wood also exhibits converse piezoelectric effect (electrical field to mechanical deformation).[14] Cellulose shows the highest piezoelectric effect[15] among other natural piezoelectric polymeric materials such as chitosan,[16] collagen,[17] and silk.[18] Cellulose exists as a semicrystalline polymer. Based on the chain orientation in crystalline domains, cellulose can be classified as cellulose I (chains are parallelly aligned) or cellulose II (chains are anti-parallelly aligned and usually found in regenerated cellulose).[19] Cellulose I, also known as native crystalline cellulose, exists in two crystalline forms, I_α and I_β. These I_α and I_β allomorphs, consisting of non-centrosymmetric triclinic and monoclinic crystal units, are responsible for the piezoelectricity in cellulose-I.[17, 20] The origin of piezoelectricity is also attributed to the net dipole moment arising from non-centrosymmetrically arranged hydroxyl groups.[21] This was later on supported with a computational simulation study, where it was established that the piezoelectricity of cellulose-I_β 2D crystal is due to inter- and intralayer hydrogen bonds between these hydroxyl groups. [20] Frka-Petesic et al.[22] reported the first experimental proof of permanent dipole moment of 4400 ± 400 Debye along the long axis of CNCs.

The piezoelectric performance of a material is defined by piezoelectric coefficients, which define the amount of charge generated per unit force (pC/N) or the extent of actuation per unit applied electric field (pm/V). Based on the direction of the external force and the direction in which charge is harvested, piezoelectric coefficients are classified as transverse piezoelectric constant (d_{31}), the longitudinal piezoelectric constant (d_{33}), and the shear piezoelectric constant (e.g., d_{14}). In earlier studies, the shear piezoelectric constant (d_{14}) of wood was reported, where the applied shear force and the resultant polarization are induced in the same direction 1(x-axis). This d_{14} equals $-d_{25}$, where the applied shear force and the resultant polarization

are induced in direction 2 (y-axis). Shear piezoelectric constant was reported in cellulose I, e.g., Japanese cypress (0.1 pC/N),[23] hinoki wood untreated (0.03 pC/N),[24] ramie bundle (−0.27 pC/N, −0.21 pm/V), rayon bundle (−0.026 pC/N, −0.026 pm/V),[25] in cellulose II, e.g., NaOH treated hinoki wood (0.1 pC/N), and in cellulose III, e.g., NH_3 treated hinoki wood (0.12 pC/N).[24] Hirai et al. reported another shear piezoelectric constant d_{36} in the softwood and hardwood, where the applied shear force and the resultant polarization are induced in direction 3 (z-axis). In the same study, two more new piezoelectric constants (d_{mn} = d_{31}, d_{32}) of cellulose I in softwood and hardwood were reported, where m defines the direction in which charges are being collected/generated (here it is in direction 3 (z-axis)) and n defines the direction in which the mechanical force is applied. The presence of d_{31} and d_{32} suggests the parallel orientations of the cellulose chains in cellulose I.[23] Mahadeva et al. reported another piezoelectric constant (d_{33}) of cellulose paper made from softwood pulp, which was found to be ~0.4 pC/N.[26] Although the longitudinal piezoelectric coefficient d_{33} of natural cellulose (0.4 pC/N) is lower than that of the widely explored synthetic piezoelectric polymer PVDF (d_{33} = 21-30 pC/N), the renewable and biodegradable nature of cellulose has spurred the interest in cellulose-based mechanical energy harvester and sensors.

Efforts to enhance the piezoelectric output of cellulose have mainly focused on cellulose or nanocellulose films. For example, Csoka et al. reported the shear piezoelectric constant (d_{25}) of the ultrathin polarized film of aligned CNC to be around 211 pm/V. The high response was accredited to the collective contribution from the asymmetric crystalline structure of the cellulose crystals.[27] In a recent report, Wang et al. fabricated a vertically aligned CNC film in a confinement cell (**Figure 1a**), where the film exhibited a piezoelectric constant (d_{33}) comparable to the PVDF. The alignment of CNC was induced by high interfacial energy between poly(tetrafluoroethylene) (PTFE) surface and CNC suspension. It was further assisted by torque-induced shear force, which led to the alignment of the CNC upon solvent evaporation, as shown in **Figures 1a** and **1b**. Further, the dipoles were aligned in the thickness direction by the application of the electrical field (E), as shown in **Figure 1c**, where permanent dipoles were created due to inter- and intramolecular hydrogen bonds in CNC (**Figure 1d**). The alignment of CNCs was confirmed with wide-angle x-ray scattering (**Figure 1e**) and scanning electron microscopic (SEM) images (**Figure 1f** and **1g**). Finally, piezoelectric constant (d_{33}) was measured by piezoresponse force microscopy (PFM) and found to be 19.3 ± 2.9 pm/V, which was comparable to poly(vinylidene difluoride) (PVDF) (20–30 pm/V).[28] This makes cellulose a promising candidate for mechanical energy harvesting and sensing applications.

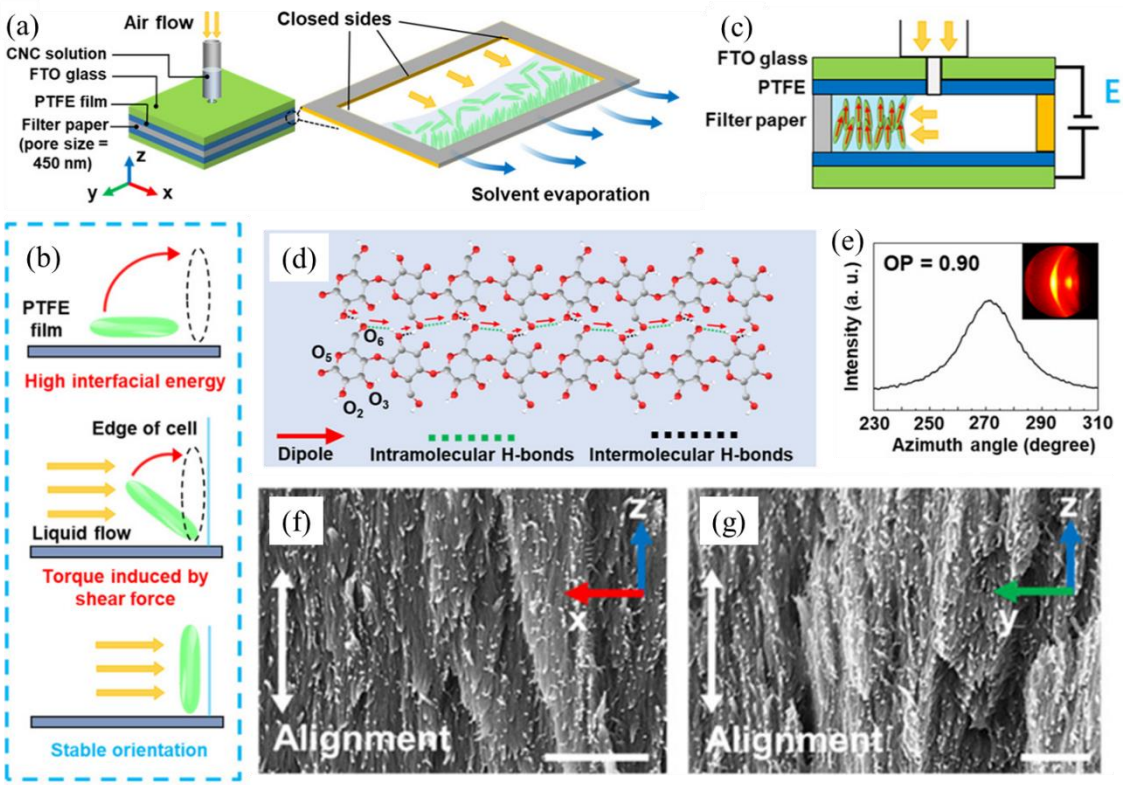

Figure 1. (a) Schematic of a confinement cell and the alignment process, (b) illustration of the mechanism of the vertical alignment, (c) electrical field-assisted dipole alignment in vertical CNC films, (d) hydrogen bonds

networks in cellulose Iβ, where the inter- and intramolecular hydrogen bonds induce a permanent dipole moment in CNCs. (e) Azimuthal integrated intensity distribution curve and 2D WAXS patterns of a vertically aligned CNC film. SEM images of a vertically aligned CNC film (scale bare 500 nm) in a different plane with respect to the alignments, (f) from the z–x plane and (g) from the z–y plane. (Reproduced with permission from reference 28, Copyright, American Chemical Society)

A comprehensive review of cellulose-based nanogenerators has been published recently.[29] This minireview highlights only the recent progress in cellulose-based piezoelectric materials and their applications in mechanical energy harvesting and sensing. The entire discussion is categorized into three topics; 1) Cellulose-based piezoelectric sensors and actuators, 2) Cellulose-based mechanical energy harvesters, and 3) Cellulose as a reinforcing agent for piezoelectric composites. The discussion concludes with the scientific and technological challenges in this emerging field and future outlook.

2. Cellulose-based piezoelectric sensors and actuators:

Cellulosic films have been used as sensors or actuating materials. Piezoelectric sensors respond to applied force, pressure, stress, strain or other types of mechanical deformation and result in electrical polarization, measured as charge, voltage, current or power. Tuukkanen's group developed various cellulose-based piezoelectric sensors. For example, a piezoelectric sensor was fabricated from cellulose nanofiber film.[30] The film exhibited a ferroelectric-like behavior, and characteristic polarization-voltage (P-V) loop features were observed between 40-50 V/μm with a maximum polarization of 0.15 μC/cm^2 at 50 V/μm applied field. The film was further evaluated for the piezosensitivity (charges per unit force) at various places, which was 4.7 ± 0.9 pC/N. In another report, CNC[31] and bacterial cellulose[32] film-based piezoelectric sensors were fabricated, which resulted in a piezosensitivity of 7.3 ± 2.5 and 5-20 pC/N, respectively. The CNC and CNF were added to the chitosan to fabricate a chitosan/nanocellulose nanocomposite-based sensor. However, this led to a decrease in their piezosensitivity values.[33,34]

Piezoelectric actuators respond to an electrical signal and result in mechanical deformation or actuation. The cellulose-based actuators referred to as electroactive paper (EApap) were first reported by Kim et al.[35] An EApap was fabricated from regenerated cellulose paper by applying two thin electrodes on either side. When voltage was applied across the electrodes, it resulted in a bending deformation. This is termed as EApap, which has many potential applications ranging from soft-robotics to artificial muscles.[36] Based on the working mechanism, these EApaps are of three types, ionic, piezoelectric and hybrid EApap. In this section, we will discuss the working mechanism of piezoelectric and hybrid EApaps. The origin of the electroactive nature of EApap was attributed to the ordered and disordered region with doped ions and hydroxyl-bound water in cellulose paper (**Figure 2a**).

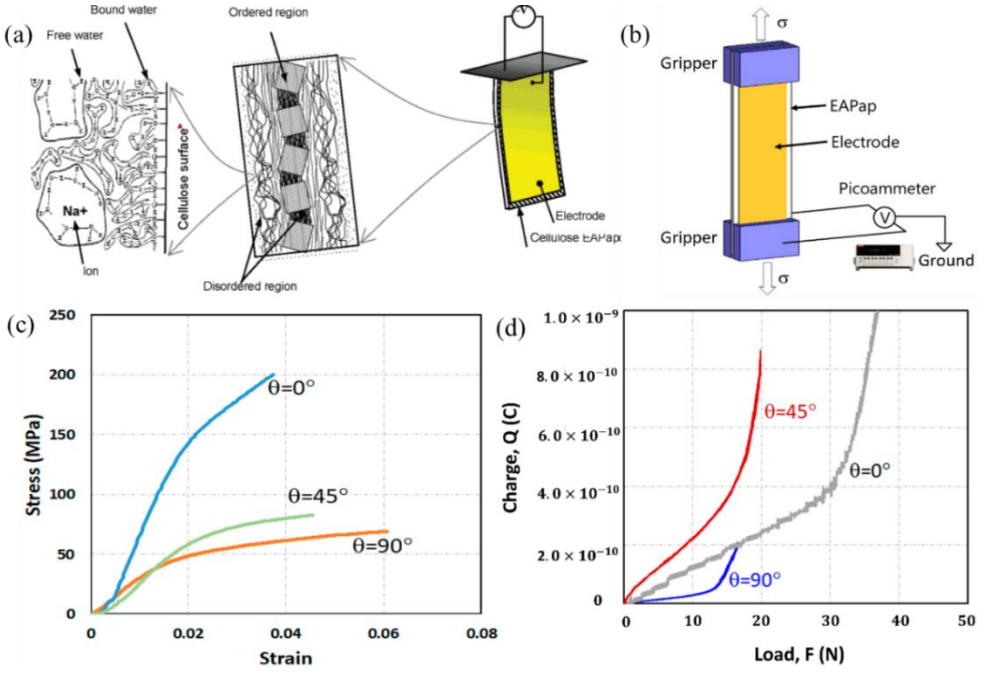

Figure 2. (a) Schematic illustration of working mechanism of the EApap. (Reproduced with permission from reference 37, Copyright the American Chemical Society). (b) Schematic representation of measurement of piezoelectric charge constant. (c) Stress–strain curves of stretched EAPap with the orientation of 0°, 45°, and 90° and (d) Charges as a function of strain of load of EAPap. (Reproduced with permission from reference 40 under Creative Commons Attribution License, Copyright the authors and publisher MDPI.)

Under applied electrical potential, these ions with free water move towards the anode, resulting in volumetric change, leading to bending. It is greatly affected by humidity and has a positive correlation with the bending of paper. Additionally, under the applied electrical potential, the ordered and disordered regions of paper behave differently. The disordered region creates a local state associated with hydrogen bonding, enhancing the charge transfer process and increasing the dipolar orientation. This led to the generation of a permanent dipole by stabilizing other dipoles, and the paper exhibits the piezoelectric behavior.[37]

The piezoelectric behavior of EApap is characterized by measuring charge per unit area per unit applied force (termed as piezoelectric constant-d_{31}). A schematic illustration is shown in the **Figure 2b**, where EApap is gripped between tensile test gripper and charges were measured using a picoammeter. The d_{31} increased with the applied electrical field,[38] and it was further enhanced in mechanically stretched and aligned films.[39] For example,[40] Yoon et al. fabricated an EApap by dissolving cotton pulp in LiCl/ N, N-dimethylacetamide and casting a film. This was wet drawn in different directions. The stretching in the machine direction was labeled as 0° orientation angle, and the other directions were 45 and 90° orientation angle to the machine direction. The different stretching directions resulted in different orientations of cellulose chains in the film. This also resulted in differential mechanical properties of the film, as shown in **Figure 2c**, where tensile strength was highest when the cellulose chains were oriented in longitudinal ($\theta = 0°$) and lowest in the transverse direction ($\theta = 90°$). **Figure 2d** shows the charge as a function of load, and the piezoelectric charge constant was calculated from the linear elastic region. An EApap was fabricated from the film with a stretching ratio of 1.6, whose d_{31} values for 0,45 and 90° were 7.3, 12 and 1.5 pC/N. The highest d_{31} with orientation in 45° degree is attributed to the strong shear effect.[41] In the past few decades, several reports have focused on fabricating electroactive paper for sensor and actuator applications.[42,43,37,44,] For example, as acoustic wave generators,[45] as speakers,[46] as a mechanical energy harvester,[47] and as a vibration sensor.[48]

3. Cellulose-based mechanical energy harvesters:

Piezoelectric materials can be used to harvest mechanical energy. A mechanical energy harvester or piezoelectric nanogenerator is fabricated by sandwiching active material between two electrodes, and then a set of wires is soldered for output measurement. Finally, the device is protected in an insulating matrix to avoid static effects and ensure mechanical robustness. Cellulose-based materials and their composites have been extensively explored for mechanical energy harvesting.

Sun et al.[49] reported mechanical energy harvesting from delignified balsa wood aerogels. Delignification results in increased cellulose content and improved wood compressibility, leading to enhanced energy generation with an output voltage of 0.84 V under 22.2 kPa stress. Further enhancement of the piezoelectric property was achieved through the fungal decay of wood.[50] Fungal treatment destroyed the cell walls by selective removal of lignin and hemicellulose, which increased elastic compressibility, as shown in schematic **Figure 3a**. The piezoelectric output in wood originates from crystalline cellulose, as shown in **Figure 3a**. With different fungal treatment times, the weight loss was different. All the fungal treated wood samples were compressible, as shown in **Figure 3b**, and compressibility increased with weight loss. The fungal-treated wood with 45% weight loss was compressed for 100 cycles at 25% strain. From the 1st to 100th cycle, the energy loss coefficient decreased from 0.34 to 0.26, which was attributed to the good mechanical stability of the fungal-treated wood. The fungal treated wood-based mechanical energy harvester resulted in an output voltage of 0.085, 0.33, 0.59 and 0.87 V at 10 N force (45 kPa) stress with 15, 25, 35 and 45% weight loss, as shown in **Figure 3d**. The native wood device only resulted in an output voltage of 0.015V.

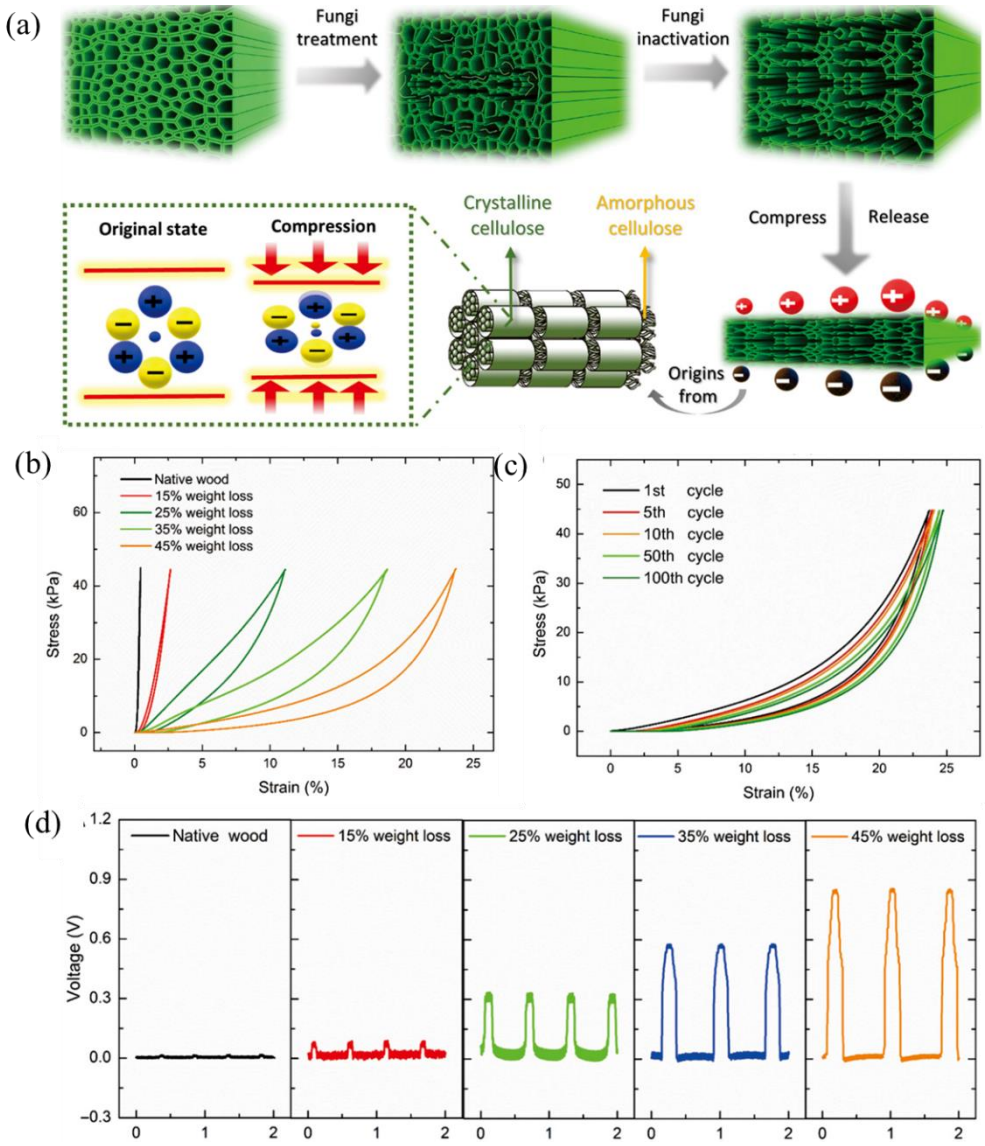

Figure 3. (a) Schematic illustration fungal treatment assisted structural evaluation of wood and its mechanism of piezoelectricity. (b) Stress-strain curves of the decayed wood with different weight losses and (c) cyclic compression of 45% weight loss wood at a stress of 45 kPa. (d) The output voltage of the decayed wood with different weight loss. (Reproduced with permission from reference 50 under Creative Commons Attribution-NonCommercial license, Copyright the authors and published by American Association for the Advancement of Science).

In a bottom-up approach, Ram et al.[51] prepared highly compressible and elastic composite aerogels from cellulose nanocrystals. Nanocellulose can be used to prepare low-density aerogels using the freeze-drying process. However, due to their moderate compressibility and weak elastic recovery, the practical application of these aerogels has been very limited. This has been successfully addressed using a modified ice-templating process, as reported elsewhere.[52] In brief, the process involves combining aqueous CNC dispersion, polyethylene glycol-diepoxide crosslinker and 1M NaOH and vortex mixing them for 120 s. After cooling this mixture in an ice bath for 20 min, it is combined with an ice-cold polyethylene imine solution and vortex mixed for 120 s. Directional aerogels are prepared using a directional cooling stage as described earlier.[52] CNC dispersion is placed on a surface maintained at -15 °C, and the top surface of the dispersion is exposed to ambient temperature (25 °C). The CNC dispersion experiences a unidirectional temperature gradient. This drives the ice crystals to grow in one direction, upwards along the direction of the temperature gradient. After about 25 min, the frozen sample is refrigerated at -18 °C for 24 h to complete the crosslinking reaction. Isotropic aerogels are prepared by directly placing the CNC dispersions at -18 °C in the refrigerator and

then following the same protocol. Finally, the aerogels are obtained by freeze-drying (-83 °C temperature and 0.120 mbar pressure) for 24 h to sublimate the ice crystal templates and obtain a three-dimensional interconnected macroporous aerogel (**Figure 4**).

Interestingly, these aerogels have a porosity of ~85-87% and recover completely after repeated compression to 50 % strain. When these aerogels were converted into piezoelectric devices and

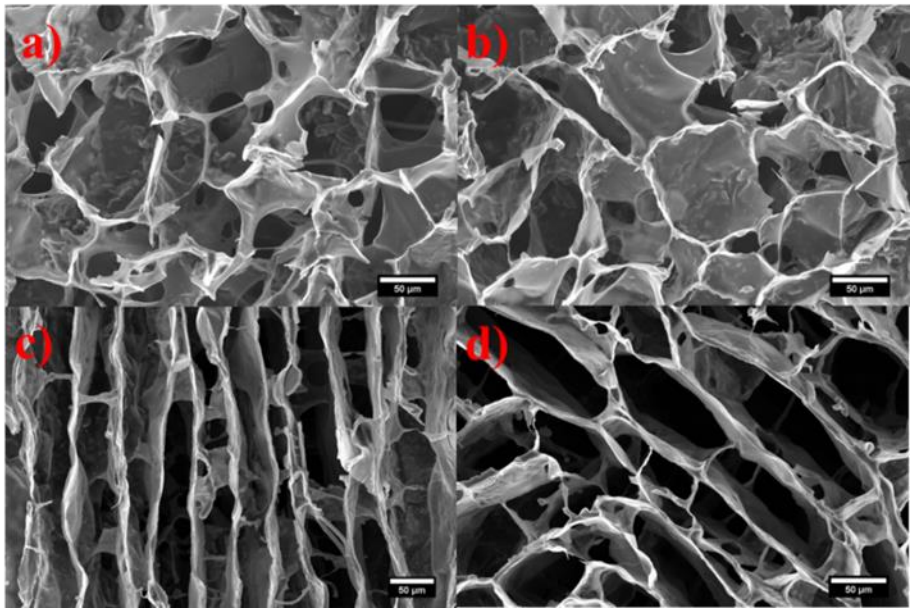

Figure 4: FESEM images of isotropic cellulose aerogels, a) vertical and b) horizontal section. and anisotropic aerogels, c) vertical and d) horizontal sections. (Reproduced with permission from reference 51, copyright Springer Nature).

subjected to an impact load of ~8N, the anisotropic aerogels yielded a piezoelectric output of 840 mV (when force was applied in the pore orientation direction) compared to 320 mV of isotropic CNC aerogels as shown in **Figure 5a** and **5b**. The enhanced piezoelectric effect is attributed to the confinement of the CNCs within the aligned pore walls, which leads to more active piezoelectric material in the direction of applied force. The anisotropy in voltage out was observed in the case of directionally frozen aerogels. It resulted in an output voltage of ~280 mV when a force was applied to the perpendicular direction to the oriented pores (**Figure 5c**). This was comparable

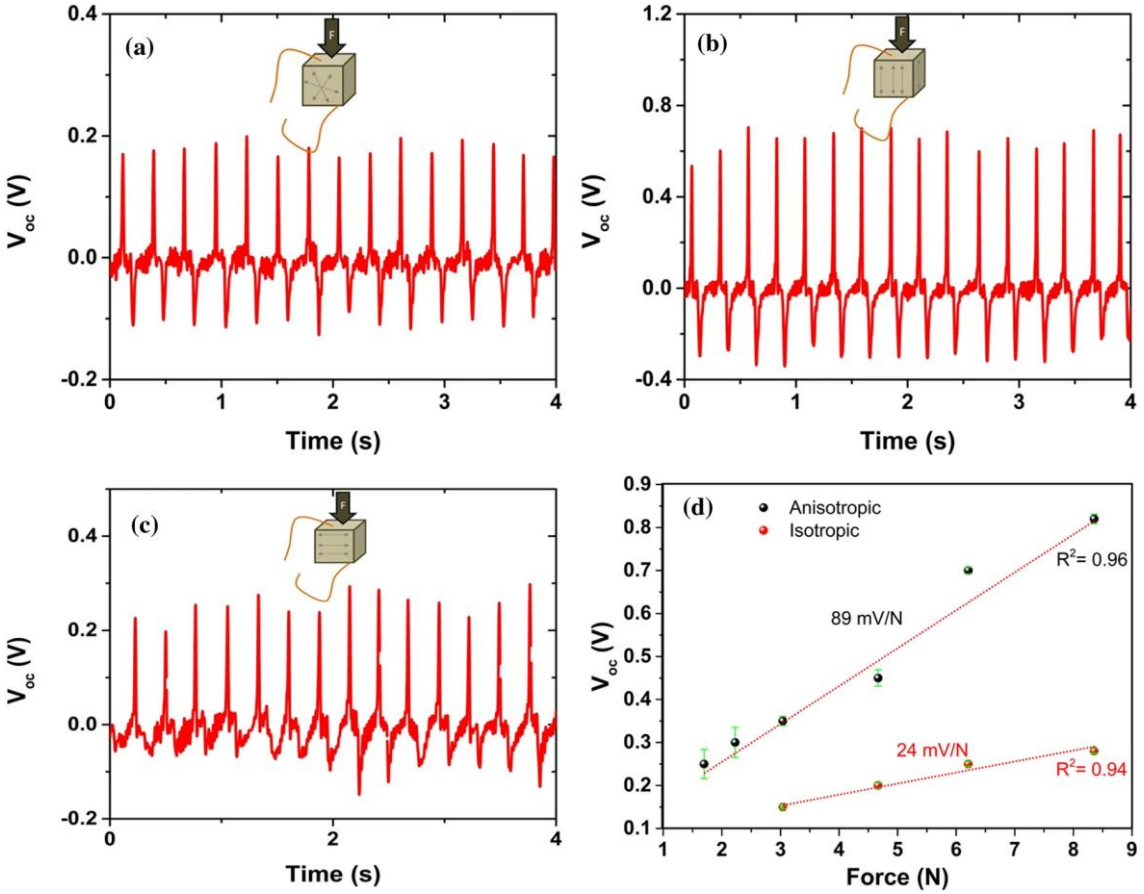

Figure 5: a) Voltage output from CNC-PEI aerogels, (a) isotropic, (b) anisotropic (force applied to oriented pore direction) and (c) force applied to perpendicular to oriented pores. (d) voltage output as a function of the applied load. (Reproduced with permission from reference 51, copyright Springer Nature.

to the output from isotropic aerogel, and it was attributed to the reduced piezo-active material in this direction. As shown in **Figure 5d**, the aerogel PENG output voltages scaled up with the applied load, which suggested that these aerogels PENGs could also be used as a force sensor. The anisotropic aerogel PENGs have a higher sensitivity of 89 mV/N than the isotropic aerogel PENGs with a sensitivity of 24mV/N. The force sensitivity of anisotropic aerogels was also 3.7 times

higher than that of isotropic aerogels. Such highly compressible and elastic anisotropic CNC aerogels have potential applications as pressure sensors, impact detectors and microenergy harvesters for powering small electronic devices.

In yet another approach, cellulose was incorporated in poly(dimethylsiloxane) (PDMS) matrix. The output voltage was improved due to the homolytic dissociation of Si-O- Si bonds in PDMS and their interaction with cellulose. Further, a conductive filler was added to improve the output power density.[53,54] For example, Pusty et al.[55] reported Au NPs-CNF/PDMS nanogenerators for mechanical energy harvesting. The mechanical energy harvester fabricated from Au NPs- CNF/PDMS composite resulted in an output voltage of 6V (**Figure 6a**), whereas a neat CNF/PDMS device resulted in an output voltage of ~1V. The enhanced output was attributed to the formation of new dipoles between Au-NPs and CNF, as shown in **Figure 6b**. In addition, the incorporation of CNF enhanced the dielectric constant, and the addition of Au NPs reduced the dielectric loss. The device resulted in output current and power density of 700 nA and 8.34 mWm^{-2}, respectively. The device was further used for charging a capacitor, where it charged a 10uF capacitor to 6.3 V in 677s (**Figure 5c**). The mechanical energy harvesting performance was constant under 3 h of continuous measurement, which demonstrated the durability of the device (**Figure 6d**).

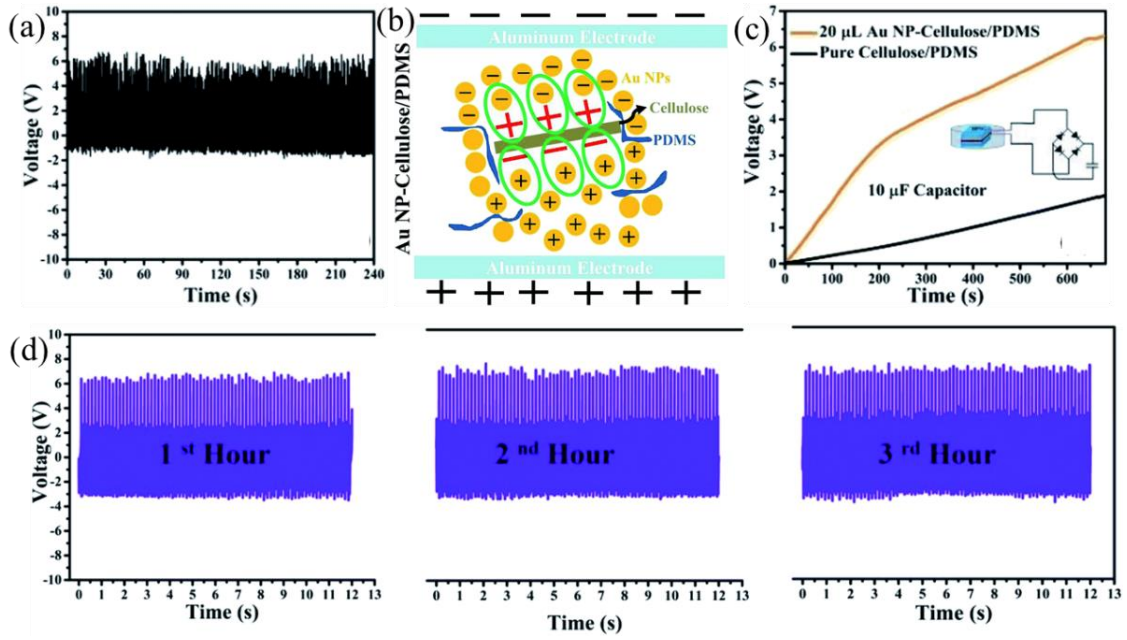

Figure 6. Piezoelectric performances of PENG fabricated from 20 µL Au NP–cellulose/PDMS (a) voltage output, (b) schematic of the formation of new dipoles between Au NP–cellulose under stress, (c) charging of a 10 µF capacitor and comparison with pure cellulose/PDMS, and (d) stability of the PENG when tested for continuous 3h. (Reproduced with permission from reference 55 under Creative Commons Attribution 3.0 Unported Licence, copyright authors and publisher Royal Society of Chemistry).

4. Nanocellulose reinforced composite piezoelectric materials

Organic piezoelectric and ferroelectric materials have elicited tremendous interest in recent years owing to many advantages such as ease of processing, lightweight and low cost as compared to traditional inorganic ferroelectric materials. Poly(vinylidene fluoride) (PVDF) is a well-known ferroelectric polymer exhibiting many crystal phases, of which the β phase is the most ferroelectric. However, PVDF melts generally crystallize into the nonpolar α phase since it is the thermodynamically favored phase. Special conditions such as mechanical stretching, high-pressure treatment, the addition of inorganic fillers etc., are known to favor β phase formation. Nonetheless, these strategies have their own limitations. Though some copolymers of PVDF can readily crystallize into the β phase, they are very expensive. Ram et al.[56] have shown that incorporating 2-5 wt % surface fluorinated cellulose nanocrystals (FNC) enhances the polar β/γ-phase crystallization in PVDF, which does not happen with the addition of unmodified cellulose nanocrystals (**Figure 7**). Energy harvesting devices fabricated from PVDF/FNC nanocomposites were shown to charge a 4.7 µF capacitor relatively faster than PVDF films, and the accumulated voltage on the capacitor was 3.8 times more than that of neat PVDF (**Figure 8**). This significant increase in energy harvesting properties of PVDF/FNC nanocomposites could be attributed to the tailored surface chemistry of nanocellulose. This leads to strong interfacial interactions between PVDF and surface fluorinated cellulose nanocrystals and enhanced polar β/γ-phase crystallization in PVDF. PVDF/FNC nanocomposites also show remarkable flexibility, with a strain at break of 10− 15%, suggesting their use as flexible piezoelectric composites for powering portable electronic devices, wireless sensors, and implantable biomedical devices materials.

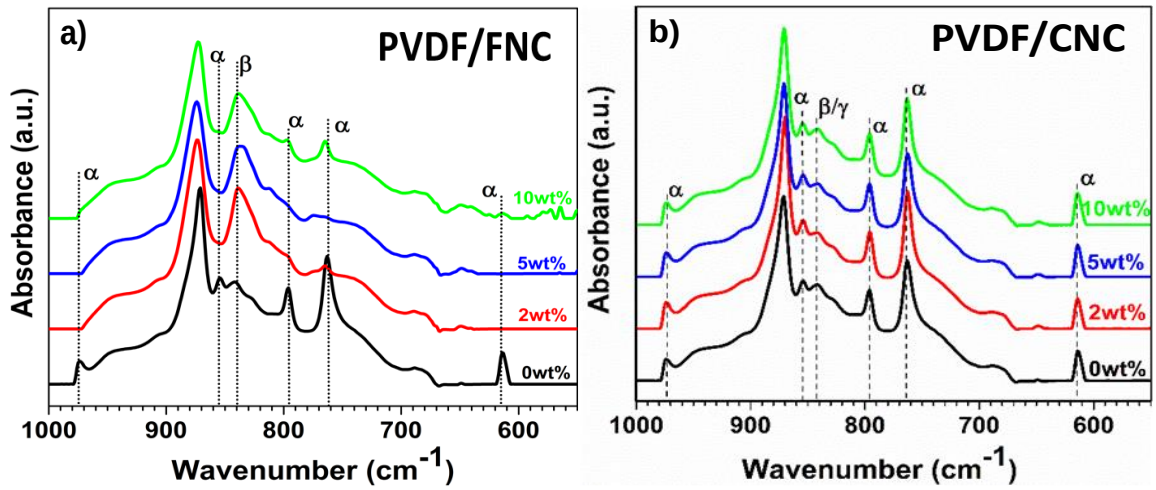

Figure 7: ATR-FTIR analysis of (a) PVDF/FNC and (b) PVDF/CNC composite films shows that there is no significant influence on the electroactive phase when unmodified nanocellulose is used. (Reproduced with permission from reference 56, copyright American Chemical Society).

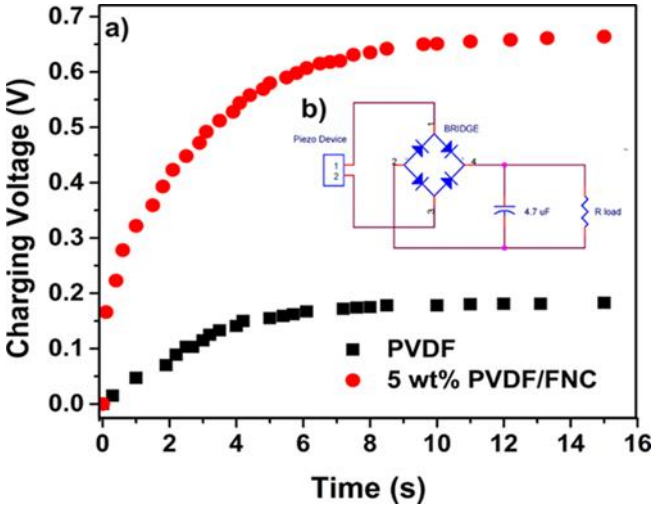

Figure 8: (a) Capacitor charging comparison of PVDF and 5 wt% PVDF/FNC composite film and (b) bridge rectifier circuit. (Reproduced with permission from reference 56, copyright American Chemical Society).

Ram et al.[57] have also shown that this facile and straightforward approach of using cellulose nanocrystals to enhance the polar crystal formation is broadly applicable to other polymers with hydrogen bonding groups. For example, Nylon 11 belonging to the family of odd nylons with molecular repeat unit –HN-(CH2)2nCO- is another synthetic polymer exhibiting weak piezoelectric behavior. Herein, the hydrogen bonding is maximized by the favorable placement of carbonyl and amine groups in two adjacent chains. This leads to the preferred alignment of dipoles and maximum net polarization.[58] In the even-numbered nylons, the adjacent chains pack in such a way that the dipole moment associated with hydrogen bonds is canceled. Odd nylons such as Nylon 11 exhibit at least three stable crystal polymorphs, *i.e.*, triclinic α form, pseudohexagonal γ form and hexagonal δ form. Among these, the γ form is the most polar. Although several reports are available on nylon 11 composites with additives such as PZT[59], $BaTiO_3$,[60] $CaCu_3Ti_4O_{12}$,[61] and $NaNbO_3$,[62] etc., no crystal phase change in nylon 11 has been observed or reported. However, a recent report[57] has shown that cellulose nanocrystals could be used to enhance the electroactive γ or δ' phase in nylon 11 and lead to high piezoelectric performance. In this report, carboxylated cellulose nanocrystals (CNC) have been prepared by TEMPO-mediated oxidation. The incorporation of 2-5 wt% CNC in nylon 11 resulted in an almost complete transition of α-phase to polar γ-phase. This could probably be attributed to the strong hydrogen bonding interactions between CNC and amide groups in nylon 11. Piezoelectric devices

prepared from 5 wt% nylon 11/CNC films resulted in 2.6 times higher output voltage (6.95 V) as compared to neat nylon 11 devices (2.68 V) under an impact load of ~23 N measured using a Flexiforce sensor (Teckscan A450). This performance was durable over 800 cycles and also after three months of storage of the films (**Figure 9**). 5 wt% nylon 11/CNC devices charged a 10 µF polarized capacitor up to 3.78 V in 90 seconds, which is 2.8 times higher than nylon 11 devices. It was also shown that large area composite films of nylon 11/CNC could be prepared by a simple solution casting approach, and the brittleness of films can be reduced by adding 5 wt% glycerol.

Composite films of PVDF or Nylon 11, despite having polar crystal phases, have randomly oriented dipoles and require electrical poling to align the dipoles. Electrospinning of piezoelectric polymers, wherein the polymer solution is extruded from a nozzle under a high electric field and collected on a metallic collector, facilitates the alignment of dipoles during the fiber spinning process. This eliminates the need for a separate electrical poling process.[63] Ram et al.,[64] have shown that nanocellulose, a relatively easy to access nanomaterial as compared to graphene oxide or CNTs, can be used to significantly enhance the piezoelectric performance and sensitivity of composite PVDF nanofibers.

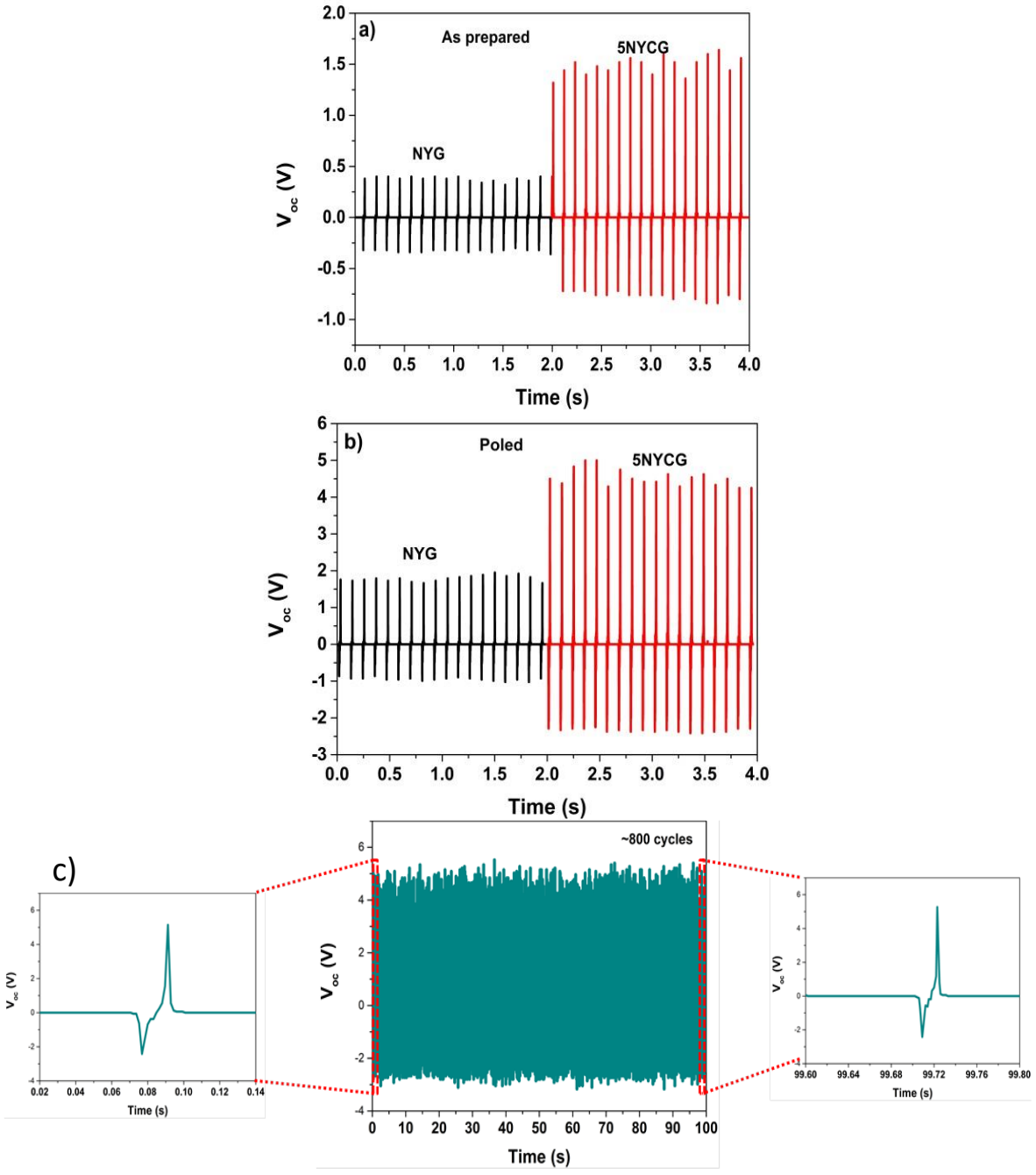

Figure 9: Open circuit voltage (V_{oc}) output of of flexible films based PENG, (a) nylon 11 films, (b) 5 wt% nylon 11/CNC films and (c) durability test of 5 wt% nylon 11/CNC films. (Reproduced with permission from reference 57, copyright American Chemical Society).

In this work, surface fluorinated cellulose nanocrystal (FNC) dispersed in DMF was mixed with PVDF/DMF solution and electrospun at 15 kV field and a flow rate of 0.5 mL/h. The electrospun fibers were collected on a steel plate fixed at 15 cm from the needle tip. These composite nanofibers containing only 2 wt% FNC, when subjected to varied pressure, showed a significantly higher pressure sensitivity of upto 18.36 mV/kPa and also a low detectable pressure limit of 10 Pa (**Figure 10a** and **10b**). The sensitivity of the composite PENGs to forced steady-state vibrations

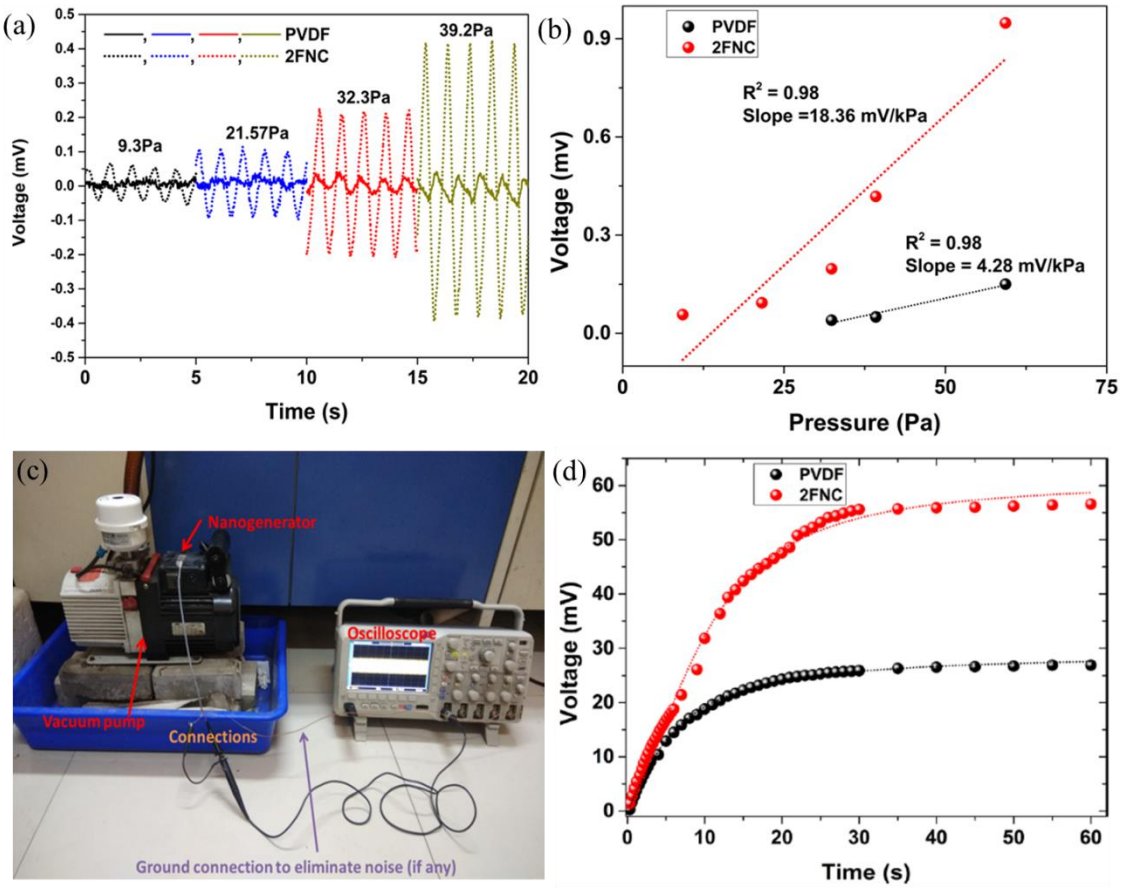

Figure 10. (a) Comparison of pressure sensing ability of PVDF and 2FNC PVDF, and (b) pressure sensitivity of PVDF and 2FNC PVDF. Energy harvesting from the vacuum pump vibrations: (c) setup and (d) capacitor charging performance of PVDF and 2FNC PVDF (right). (Reproduced with permission from reference 64, copyright American Chemical Society).

was also determined using a parallel plate set up in dynamic strain mode. The applied strain was varied from 0.1 to 1% at a fixed frequency of 1 Hz. While the output signal from PVDF nanofibers at 0.2 % applied strain for a sample of 100 µm thickness was within the noise level, the 2FNC/PVDF composites resulted in order of magnitude higher voltage response.[64] For a practical demonstration of vibrational energy harvesting capability, the composite PENG device was mounted on a vacuum pump (**Figure 10c** and **10d**). 2FNC/PVDF composite devices led to ~3.8 times enhanced voltage output over neat PVDF devices and quickly charged a capacitor. The enhanced piezoelectric performance of PVDF/FNC nanofibers was attributed to the compatible interface between PVDF and nanocellulose and enhanced polarizability.

5. Summary and Future Outlook

The piezoelectric properties of cellulose have garnered tremendous interest in recent years. In this

review, certain recent developments on cellulose-based piezoelectric materials have been highlighted. Although the piezoelectric behavior of wood and other natural polymers such as silk, collagen, chitosan etc. has been known for several decades, efforts to leverage this property for energy harvesting and sensing have been minimal. This is partly due to the weak piezoelectric performance of these natural polymers. Advancements in the chemical processing of wood and other cellulosic biomass have led researchers to revisit the piezoelectric properties of cellulose and create a unique class of materials termed cellulose nanogenerators. For example, the recent report on the preparation of wood nanogenerators using a simple delignification process of balsa wood has uncovered the potential for many innovations on cellulose-based mechanical energy harvesters. On a different note, the ability to process cellulosic biomass into nanometer-sized fibrils and whiskers has further expanded the scope of applications for cellulose, which was traditionally known for its use in textiles, paper and furniture. The ice-templated process to convert cellulose nanocrystals into highly compressible anisotropic aerogels that completely recover themselves to their original size adds a new direction to research on cellulose-based piezoelectric materials. These exciting new developments highlight that cellulose, although a polymer known for centuries, is still an excellent source for exciting innovations, and we have hardly scratched the surface.

Conflicts of interest: None

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Dr. Farsa Ram received his doctorate from the Academy of Scientific and Innovative Research, Ghaziabad, India, based on his research at the Council of Scientific and Industrial Research-National Chemical Laboratory, Pune, India. There he worked with Dr. Kadhiravan Shanmuganathan on nanocellulose based composite materials for energy applications. He joined Prof. Lars Berglund's group as a postdoctoral researcher in July 2020 in the Wallenberg Wood Science Center, and Fibre and Polymer Technology Department at KTH Royal Institute of Technology, Sweden. His is currently working on functionalization of wood materials for energy and sensing applications.

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