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Nanocrystalline Cellulose for Anisotropic Magnetoelectric Composites

Yan Zong
*University of Wollongong, yz818@uowmail.edu.au*

Zhilian Yue
*University of Wollongong, zyue@uow.edu.au*

Michael J. Higgins
*University of Wollongong, mhiggins@uow.edu.au*

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Abstract
The emergence of piezoelectric polymers in magnetoelectric (ME) composites enables flexible and low-cost device fabrication though notably gives rise to the highest ME output voltages to date. Accordingly, the highest piezoresponsive polymers, poly(vinylidene fluoride) (PVDF) and its copolymers, are exclusively studied despite an inventory of unexplored piezoelectric polymers such as naturally occurring cellulose, that is only recently demonstrated in ME composites. Herein, the development of nanocrystalline cellulose (CNC)-based ME composites is reported on. Two types of CNC, nanospheres and nanowhiskers, are synthesized and incorporated in laminate composite, which exhibit a giant α ME ( > 1 V cm⁻¹ Oe⁻¹ ). By successfully reconstructing the orientated cellulose fibril structures found in natural plants using spinning-induced alignment of CNC nanowhiskers, an anisotropic effect originating from the piezoelectric phase in ME composites is attained. The anisotropic effect produces output voltages an order of magnitude higher than those in current polymer-based particulate ME vector sensing composites with 0-3 configurations.

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Yan Zong, Zhilian Yue and Michael J. Higgins

Y.Zong, Dr. Z. Yue, Assoc. Prof. M. J. Higgins
Address: ARC Centre for Electromaterials Science (ACES), Intelligent Polymer Research Institute/AIIM Faculty, Innovation Campus, Squires Way University of Wollongong, NSW 2522, Australia
E-mail: mhiggins@uow.edu.au

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Abstract

The emergence of piezoelectric polymers in ME composites enables flexible and low-cost device fabrication though notably gives rise to the highest ME output voltages to date. Accordingly, the highest piezoresponsive polymers, poly(vinylidene fluoride) (PVDF) and its copolymers, are exclusively studied despite an inventory of unexplored piezoelectric polymers such as naturally occurring cellulose that was only recently demonstrated in ME composites. Herein, we report on the development of nanocrystalline cellulose (CNC)-based ME composites. Two types of CNC, nanospheres and nanowhiskers, are synthesized and incorporated in laminate composite that exhibit a giant $\alpha_{ME}$ (>1 V cm$^{-1}$ Oe$^{-1}$). By successfully reconstructing the orientated cellulose fibril structures found in natural plants using spinning-induced alignment of CNC nanowhiskers, an anisotropic effect originating from the piezoelectric phase in ME composites is attained. The anisotropic effect produces output voltages an order of magnitude higher than those in current polymer-based particulate ME vector sensing composites with 0-3 configurations.

* Supporting Information is available online from the Wiley Online Library or from the author.
FIGURE FOR ToC
1. Introduction

Magnetoelectric (ME) materials that enable magnetic-to-electrical signal conversion\(^1-^2\) are applied for magnetic sensing\(^3\), energy harvesting\(^4\) and non-volatile memory storing\(^5\) applications. ME composite provides an ease of approach to integrate piezoelectric and magnetostrictive components and the strain mediated ME coupling ensures superior room temperature performance than single phase ME crystals.\(^6-^8\) Polymer-based magnetoelectric (ME) composites are easier to process and more flexible than ME ceramics.\(^7,^9\) Significant enhancement of the ME effect can be achieved through modification of a polymer matrix to improve its piezoelectricity.\(^10-^11\) For example, the highest \(\alpha_{ME}\) reported so far is observed in a polymer ME laminate combining chain-end crosslinking functionalized poly(vinylidene fluoride-co-trifluoroethylene), P(VDF-TrFE), with a high performance magnetostrictive film, Metglas\(^\circledR\),\(^11\) Accordingly, due to their high \(\alpha_{ME}\), PVDF and its copolymers have almost exclusively been used in ME composites and this remains the current situation despite an inventory of unexplored piezoelectric polymers such as naturally occurring biomolecules\(^12-^14\) that were first demonstrated only recently by our group. In this work, regenerated cellulose in ME composites exhibited a giant \(\alpha_{ME} (>1 \text{ V cm}^{-1} \text{ Oe}^{-1})\) under relatively weak magnetic field, leading to the discovery of new fundamental ME properties as well as access to cheap, renewable and degradable materials for development of ME devices.\(^15\) Therefore, despite having lower piezoelectric coefficients, polymers other than PVDF have potential to bring added value properties and functions, and cellulose is no exception in this regard. It is known to come in many different structural forms and degrees of crystallinity, including a wide variety of easily synthesized nano-crystalline cellulose such as nanofibrils, nanowhiskers,\(^16-^18\) and nanospheres\(^19-^20\), which we purport are expected to offer a unique opportunity to manipulate the fabrication and operation of ME devices.
2. Results and Discussion

Herein, we demonstrate the novel use of nanocrystalline cellulose (CNC) to impart new functions in biopolymer-based ME composites. CNC is actually the structural component of cellulose fibrils which coexists with amorphous cellulose in plant tissues.\textsuperscript{[16-17]} High aspect CNC nanowhiskers can be produced by acid hydrolysis of the amorphous cellulose section\textsuperscript{[17-18]} and this unique low dimensional (1D) nano-material can be manipulated to form aligned structures that are sensitive to directional changes, which is effectively confirmed in natural wood sheets showing anisotropic piezoelectricity\textsuperscript{[21]}. We take advantage of aligned CNC nanowhiskers to demonstrate an anisotropic ME effect, which as yet has not been demonstrated \textit{via} the piezoelectric component in polymer-based ME composites and gives rise to significant increases in the output voltage by an order of magnitude for anisotropic ME devices with vector-sensing capability.

2.1 Synthesis and Characterization of CNCs

We synthesise two types of CNC, namely the nanowhiskers and nanospheres to fabricate the ME laminates. Spherical CNC has been reported elsewhere and produced by mixed acid combined with ultrasonic treatment.\textsuperscript{[19-20]} In this study, CNC nanowhiskers (\textbf{Figure 1a}) are obtained from direct acid hydrolysis while a newly introduced pre-swelling treatment before the acid hydrolysis produces the nanospheres (\textbf{Figure 1b}). X-ray diffraction (\textit{Supplementary Fig. 1}) and Fourier transform infrared spectroscopy (\textit{Supplementary Fig. 2}) spectra reveal the nanospheres possess a crystalline II lattice structure in contrast to nanowhiskers and raw material (\(\alpha\)-cellulose) that both show crystalline I lattice structures. In particular, cellulose crystalline I is ubiquitous and widely observed in earlier studies on CNC,\textsuperscript{[16, 19-20]} however, the existence of crystalline II in CNC is a serendipitous finding yet to be reported. A conversion from the crystalline I to II is explained by the prior swelling treatment that weakens the interaction between polymer chains and leads to rearrangement of the cellulose polymeric matrix into spherical-like structures. The piezoelectric property of cellulose is critically
dependent on the degree of crystallinity. One reliable evaluation standard is the crystallinity index (CI) determined by the XRD interference intensity and expressed by the following equation:\[^{22}\]

\[
CI = \frac{(I_{002} - I_{am})}{I_{002}}
\]

(1)

where the intensity of (002) peak at 22.7 and 22.3 is assigned to cellulose crystalline I and II, respectively. \(I_{am}\) is the intensity of the amorphous component at \(2\theta\) of 18˚ for crystalline I and 16˚ for crystalline II.\[^{22}\] Compared to the \(\alpha\)-cellulose, the CI of CNC nanowhiskers and nanospheres increases from 68.1 % to 89.3 % and 80.5 %, respectively. The increased crystallinity degree of both whisker and spherical CNC is attributed to the reduction of amorphous components as a result of acid-induced polymer degradation. Due to the change in configuration, the freeze-dried nanowhiskers and nanospheres have different appearance and their aqueous suspensions also show different stability (See details in Supplementary Fig. 3 and 4). The high-aspect ratio whiskers are well dispersed after standing for 48 h (Supplementary Fig. 3 a, c), however large spheres (>100 nm) prefer to aggregate and only small spheres (<100 nm) stay in a homogenous phase (Supplementary Fig. 3b, d).

2.2 ME Properties of CNC/Metglas® laminate Composites

To fabricate the CNC-based ME composites, the nanowhiskers and nanospheres are drop casted as films with additional Ca\(^{2+}\) to stabilize the network, and then air-dried under room temperature (RT, 20 °C) or alternatively vacuum-dried under 80 °C in order to remove residual water (see methods section). Due to the fast evaporation of water, severe cracking is observed in the nanospheres films developed under 80 °C and therefore were not considered for further experimental work. The CNC films are coated with surface electrodes and combined with magnetostrictive Metglas®, as shown in Figure 1c. The performance of ME laminates based on three selected CNC films (nanowhiskers under RT and 80 °C, and nanospheres under RT) is evaluated using a dynamic method in which an alternating magnetic field (\(H_{ac}\)) from
Helmholtz coils is superimposed on a constant magnetic field ($H_{dc}$) generated by a pair of electromagnets (Fig. 1d and methods section). The $H_{ac}$ and $H_{dc}$ caused oscillation on the Metglas® film and the conducted strain was transferred to the CNC film to induce ME voltage output.$^{[23]}$ Based on this method, the ME voltage coefficient is evaluated using the following equation:$^{[24]}$

$$\alpha_{ME} = \frac{V_{ME}}{T \times H_{ac}}$$

(2)

where $V_{ME}$ is the actual voltage output collected from surface electrodes, $T$ is the thickness of piezoelectric film and $H_{ac}$ is the strength of the alternating magnetic field. Firstly, the $H_{ac}$ and $H_{dc}$ strength are fixed and the ME output voltage is measured as the function of $H_{ac}$ frequency change. The frequency-dependent ME effect and $H_{dc}$ dependent curves of $\alpha_{ME}$ are displayed in Figure 2a,b. The resonance enhancement phenomenon is observed in all the samples, that is, when the resonance frequency of the magnetostrictive film encounters the $H_{ac}$ frequency, the mechanical strain is dramatically amplified thus giving a significant increase in the ME output voltage. The resonance frequency ($f_r$) of magnetostrictive film, which depends on several factors, including its density ($\rho$), Young’s modulus ($E$) and the length ($L$) along the magnetic field, is calculated using the following equation:

$$f_r = \frac{1}{2L} \times \sqrt{\frac{E}{\rho}}$$

(3)

For Metglas®, $E=100$–$110$ GPa and $\rho=7.18\times10^3$ kg m$^{-3}$. In our case $L=32$ mm, thus the calculated theoretical $f_r$ of $58.31$–$61.16$ kHz is very close to the experimental data shown in Figure 2a. To more accurately determine the ME output voltage, the frequency dependent curves in figure 2a are fitted to a modified Maxwell equation:

$$V(\omega) = A \left| \frac{\omega^2 - 2i\delta_r \omega + \omega_r^2}{\omega^2 - 2i\delta_a \omega + \omega_a^2} \right|^2 + a\omega + b$$

(4)

where $A$ is the amplitude constant. $\omega_r=2\pi f_r$ is the resonance frequency and $\omega_a=2\pi f_a$ is the anti-resonance frequency. $\delta_r$ and $\delta_a$ are the damping constants for the resonance and anti-resonance, respectively. $a$ is the constant corresponding to a linear background noise and $b$ is
the factor fitting the imaginary section to experimental data. The fitting results (dashed line in Fig. 2a) show good agreement with the experimental data points and the same equation (4) is used to also fit the frequency-dependent curves measured under different $H_{dc}$ strength. The fitting parameters are provided in Supplementary tables 1-3 and the peak values of the resonance enhanced $\alpha_{ME}$ corresponding to different $H_{dc}$ strength are given in Figure 2b. The highest output voltage of 2.98 mV is obtained for the nanospheres, with a calculated $\alpha_{ME}$ of 2.33 V cm$^{-1}$ Oe$^{-1}$, followed by the nanowhisker sample vacuum dried under 80 °C and then the air-dried nanosphere sample. These $\alpha_{ME}$ are higher than those previously recorded for the regenerated cellulose$^{[15]}$ and a comparison of all values are provided in Supplementary Table 4.

2.3 Fano-Resonance Enhanced ME Effect

Moreover, a Fano-resonance appears in all the frequency-dependent profiles, consisting of a resonance peak and accompanied by an anti-resonance peak where the ME output voltage sharply drops down to zero (Fig. 3). This anti-resonance effect is clearly different to typical symmetrical Lorentzian resonance profiles seen to date in artificial polymeric ME laminates$^{[25]}$ and also only recently observed in regenerated cellulose-based ME composites,$^{[15]}$ making it seemingly unique to the properties of cellulose. The CNC nanowhisker air-dried sample under RT shows a symmetric Lorentzian resonance profile at $H_{dc}$=8.2 Oe. However, at $H_{dc}$<8.2 Oe a Fano-resonance with anti-resonance peak that appears at a frequency higher than the enhanced-resonance frequency is present though this anti-resonance oppositely occurs at a lower frequency value when $H_{dc}$>8.2 Oe (Fig. 3a-c). The Fano-resonance-dependence on the $H_{dc}$ is very similar to that previously observed for regenerated cellulose-based ME composites$^{[15]}$ though differs to the behaviour of the other two CNC films. For instance, the CNC nanospheres and vacuum-dried nanowhiskers only show a Fano-resonance with anti-resonance at frequencies greater than the enhanced resonance peak and remarkably no symmetrical Lorentzian profile is observed at any applied...
$H_{dc}$ (Fig. 3d-f). As shown in regenerated cellulose-based ME composites, we suggest that water content has an effect on the frequency-dependent curves, including the Fano-resonance profiles. Thermogravimetric analysis (TGA) indicates the air-dried nanowhiskers contain the highest amount of water followed by vacuum-dried nanowhiskers, with the least water content in air-dried nanospheres (Supplementary Fig. 5). Due to the high crystallinity degree and limited porosity within single nanowhiskers, we presume that their inter-spacing facilitates free water content in the films, giving rise to ME resonance profiles similar to those of regenerated cellulose which is shown to contain the most free water when air-dried. Further removal of free water from the nanowhisker film by vacuum heating leads to a phenomena whereby no symmetrical ME resonance profile, and only a Fano-resonance persists, at all $H_{dc}$ and is unique to CNC. Interestingly, however, the CNC nanospheres are also air-dried yet show a similar ME response to the heated nanowhiskers samples (Fig. 3h-j). This may be due to nanospheres that can more easily be compacted, e.g. where smaller particles fill in the interstices, producing a film structure that inherently limits the available space for free water, as supported by TGA results (Supplementary Fig. 5). The effect of water content is also seen on the damping constants related to the quality factor of the enhanced ME resonance. The CNC nanowhisker air-dried sample, containing most free water, shows the broadest peak or lowest quality factor, with damping constant of $\delta_r=-0.0418$ under $H_{dc}=4.0$. In contrast, the CNC nanospheres and heated nanowhisker samples with lower water content show narrower resonance peaks, with significantly lower damping constants of $\delta_r=-0.0190$ and $\delta_r=-0.0242$, respectively (Supplementary tables 1-3). Therefore, the presence of free water in these CNC and cellulose in general effects the ME resonance profile, presumably through changes in the mechanical properties and/or ion migration during electrical polarization.

To address the above, the mechanical properties of the different CNC films were measured using tensile testing and their ME output voltage shown to be dependent on the Young’s modulus. The highest $\alpha_{ME}$ of 2.33 V cm$^{-1}$ Oe$^{-1}$ (Fig. 2b) for the CNC nanospheres correlates
to the highest Young’s modulus of 2.30 GPa (Fig. 2c). $\alpha_{ME}$ of 1.40 and 0.75 V cm$^{-1}$ Oe$^{-1}$ (Fig. 2b) for CNC nanowhisker vacuum-dried (80 °C) and nanowhisker air-dried samples correlate with their respective Young’s moduli of 0.96 and 0.08 GPa (Fig. 2c), confirming the greatest output voltages and $\alpha_{ME}$ are achieved from higher modulus CNC films. The mechanical difference of the CNC films was accociated to their water content. For example the air-dried nanowhiskers contain much more residual water than the vacuum dried nanowhiskers and the nanospheres (Supplementary Fig. 5), and as the result its Young’s modulus is the lowest of all three samples. In contrast the compacted nanospheres limited the water content to the lowest level (Supplementary Fig. 5) thus gave rise to higher Young’s modulus than the two nanowhiskers samples (Fig. 2c). In addition to mechanical properties, the local piezo-response of the three CNC films is investigated by switching spectroscopy piezoresponse force microscopy (SS-PFM) (Fig. 2d and Supplementary Fig. 6). During a fully reversible dipolarization of 180˚, the CNC nanospheres air-dried (Fig. 2d, red) and nanowhiskers vacuum-dried samples under 80 °C (Fig. 2d, blue) show a typical butterfly loop in amplitude displacement curves and their respective piezoelectric coefficient values estimated to be 9.52±0.25 and 10.20±0.57 pm V$^{-1}$. Considering they have similar piezoelectric coefficients despite the CNC nanospheres giving a ≈ 50% increase in ME output voltage, it is reasonable to deduce that their mechanical properties in Figure 2c play a dominate role in the magnitude of the ME response. The CNC nanowhisker air-dried samples under room temperature (Fig. 2d, green) show a differently shaped hysteresis loop, particularly a narrower coercive field and 180˚ phase reversal at lower applied voltages. For the same type of ferroelectric material, a thinner film will have lower coercivity.[26] However, the thicknesses of the different CNC films are quite similar (Supplementary table 4) thus the narrower coercive field and non-classical butterfly loop in the CNC nanowhisker air-dried film is attributed to its higher water content (Supplementary Fig. 6, TGA results), including the movement of free Ca$^{2+}$ (introduced in film casting process) that could influence the electrical dipolarization. Further
drying of the CNC nanowhiskers at higher temperatures (45 °C) to eliminate residual free water content causes the hysteresis loops to convert to a typical butterfly shape in amplitude displacement curves, with wider coercive field present in the phase loops (Supplementary Fig. 7). Clearly, a higher water content in CNC films has a causative effect on the ME resonance profiles, such as the $\alpha_{\text{ME}}$ and damping constants, occurring through changes in the mechanical and piezoelectric properties. The removal of free water, or alternatively CNC nanostructures that limit water content, increase the mechanical strength and optimize the piezoelectric response to provide an overall higher ME response.

2.4 Anisotropic ME Effect

Having established the CNC-based ME composites, a key objective is to investigate the ability to observe an anisotropic ME effect by introducing piezoelectric nanomaterials. To achieve this, a home-built ‘spinner’ is used to align the CNC nanowhiskers (Fig. 4a and experimental section) and preferred over other techniques such as doctor blade\cite{27}, as the ‘spinner’ can provide a constant shear that is expected to achieve better alignment. AFM height and phase images confirm the alignment of the nanowhiskers, with large whiskers arranged perpendicular to the shear orientation and tiny whiskers displaying branch-like structures on the surface (Fig. 4b). In contrast, a random array of nanowhiskers is observed when no shear is applied for drop casted films (Fig. 4c). The nanowhisker films are vacuum dried under 80 °C, using Ca$^{2+}$ as framework stabilizer, and then combined with magnetostrictive Metglas® via epoxy to enable the strain coupling. The Metglas® films with the same dimension are attached onto the CNC film at different angles to the aligned orientation of the nanowhiskers. Specifically, the long-edge of the Metglas® film is aligned parallel (0°), perpendicular (90°) or intermediate at a 45° angle to the aligned orientation of the nanowhiskers (Fig. 4d). Using the dynamic testing method as above (Fig. 1d), stimulating magnetic fields $H_{\text{ac}}$ and $H_{\text{dc}}$ are applied longitudinally along all the ME laminates. The frequency and $H_{\text{dc}}$ dependent curves are shown in Figure 4e and f, respectively. For all three
ME laminates, an ME resonance enhancement with Fano-resonance profile is observed (Fig. 4e) and the $\alpha_{\text{ME}}$ values increases dramatically from 0-4.0 Oe and then decreases gradually according to the increasing $H_{\text{dc}}$ (Fig. 4f). The good performance under low $H_{\text{dc}}$ (up to ~4.0 Oe) is attributed to the high magnetic permeability and low field saturation of the magnetostrictive Metglas® film and all fitting parameters based on equation (3) are provided in Supplementary tables 5-7. Significantly, the highest output voltage of 2.23 mV, with calculated $\alpha_{\text{ME}}$ of 1.92 V cm$^{-1}$ Oe$^{-1}$ is obtained when the magnetostriction is induced perpendicular (90˚) to the CNC nanowhisker aligned orientation and the lowest is from that applied parallel (0˚) (Fig. 4e, f and Supplementary Table 4), confirming an anisotropic effect in the ME response. Furthermore, intermediate values of $\alpha_{\text{ME}}$ are obtained at an applied angle of 45˚. These findings are in agreement with converse piezoelectric effects of natural wood sheets that show the greatest mechanical strain when the direction of wood grains are at 90˚ to the applied electrical field\textsuperscript{[21]}. Rotation of the wood grains to 45˚ gives an intermediate strain, while the lowest strain is observed at an angle of 0˚. Therefore, by successfully reconstructing the orientated cellulose fibril structures found in natural plants via the spinning-induced alignment of CNC nanowhiskers, an anisotropic effect originating from the piezoelectric phase in ME composites is attained. To confirm whether the mechanical strength of the aligned whisker CNC films also plays a role, tensile tests were conducted by stretching samples at the three different angles to the aligned CNC orientation and show that the Young’s modulus is highly dependent on the applied angle of the tensile test (Fig. 4g). However, on this occasion for the aligned CNC, the lowest modulus sample at a tensile testing angle of 90˚ shows the highest ME output voltage, which is opposite to the non-aligned CNC. Interestingly, a linear dependence is not observed as the highest and intermediate modulus samples, with respective testing angles of 45˚ and 0˚, interchange with respect to the ME output voltage. Thus, despite the interplay between effects of piezoelectric anisotropy and mechanical properties, the results suggest that the strain coupling direction, \emph{i.e.}
magnetostriction relative to the piezoelectric orientation, is important for producing the highest ME output voltage in aligned CNC. To confirm the above anisotropic effect, we also fabricated control samples by attaching Metglas® films at angle intervals of 0˚, 45˚ and 90˚ onto drop casted CNC films with randomly aligned nanowhiskers, as seen in Supplementary Figure 8a. At all angles, the peak voltage ($V_{\text{peak}}$) outputs are very similar with a value of ~1.75 mV under $H_{\text{dc}}=4.0$ Oe (Supplementary Fig. 8b), confirming a non-anisotropic effect for these randomly-aligned samples.

3. Conclusions

In conclusion, an anisotropic ME effect provides new opportunities for the development of polymer-based ME composite with vector sensing ability, which as yet cannot be achieved using bulk, homogeneous, piezoelectric polymer films. Although the incorporation of nanomaterials into polymer-based ME composites has enabled the demonstration of anisotropic ME sensors\cite{28}, the use of nanomaterials is restricted to inorganic magnetostrictive components, such as magnetic nanowires (iron, nickel and Galfenol)\cite{29} or nanosheets, such as δ-FeO(OH) or CoFeOOH \cite{28,30}, within 0-3 particulate composites that inevitably show very small output voltages at the micro-volt level. A significant advance in this work is that the introduction of a piezoelectric nanomaterial into polymer-based ME composites enables an anisotropic ME effect that produces an output voltage an order of magnitude higher (the maximum $\alpha_{\text{ME}}=2.33$ V cm$^{-1}$ Oe$^{-1}$) than those from previous anisotropic ME devices (the maximum $\alpha_{\text{ME}}=0.51$ mV cm$^{-1}$ Oe$^{-1}$).\cite{28} The ME composites also take advantage of cellulose as a renewable and cheap material, as well as biocompatible and biodegradable properties, and demonstrates the general concept of using piezoelectric biomaterials in ME composites. In using cellulose, it is therefore possible to have facile synthesis of a diverse array of CNC that by virtue of their nanoscale dimensions bring new function and capabilities to polymer-based ME composites.
4. Experimental Section

**CNC Preparation:** CNC was prepared via acid hydrolysis using 65 w.t.% H$_2$SO$_4$. To prepare CNC whiskers, 4g α-cellulose (sigma-aldrich C8002) was blended with 30 mL H$_2$SO$_4$. A pre-swell treatment is involved to develop spherical CNC. 4g of α-cellulose was first immersed in 10 mL distilled (DI) water overnight, and then the acid concentration is adjusted by adding 80 w.t.% H$_2$SO$_4$ into the cellulose slurry under ice bath condition, until the target concentration is reached. The hydrolysis reaction took place under 55 °C with constant stirring at 1,400 rpm for 40 min. To cease the reaction, 250 mL iced DI water is added, and then the resultant suspension was washed by centrifugation at ~10,000 rpm several rounds until the upper layer became turbid. The obtained two types of CNC were gel-like materials.

**CNC crystalline characterization:** X-ray diffraction (XRD) was performed on the raw material and the freeze-dried CNC powder using a GBC MMA XRD (λ = 1.54Å) in a range of 10-45°. The voltage, current and scanning speed were set as −40 kV, 25mA and 1° min$^{-1}$, respectively. The Fourier transform infrared spectroscopy (FT-IR) spectrum was performed on a Shimadzu AIM8000 FT-IR spectrometer. The raw materials and the freeze-dried CNC powder were measured using a KBr-pellet method in the range of 700-4000 cm$^{-1}$.

**CNC film casting:** For non-aligned films, the gel-like CNC was poured into a casting well with 0.8 mm in depth and then immersed in 0.5 M CaCl$_2$ solution for 5 min, following with rinse by DI water and dried as films under room temperature (20 °C) or 80 °C. To develop aligned whisker CNC film, the whisker CNC was added into a small vial which has PET film covered the wall as casting substrate. The vial was then sealed and loaded in our home made spinner, running 0.5 h at ~1,000 rpm. After the CNC whiskers were well aligned, then PET film was transferred to CaCl$_2$ solution, following the aforementioned method to prepare film.

**Tensile test:** Tensile strengths and Young’s Moduli were tested by using a Shimadzu EZ-TEST system with a 50 N testing cell. The samples were tailored into strips with 5mm in with and at least 20 mm in length. The thickness of each film was measured by using micrometer.
ME Laminate Composite Fabrication: The CNC films were sputtering coated with 30 nm gold layers on both sides as interface electrodes (the sputtering is conducted as 1 min on-0.5 min off cycles to avoid degradation) and then were tailored into a 40 mm×8 mm rectangular by using scalpel. To fabricate the ME laminate composites a 32 mm × 7 mm Metglas® 2605 SA1 plate was glued on the central part of cellulose films using commercial Devcon epoxy. Then copper wires were assembled with the laminate on each of the surface electrode by using silver paint.

Bulk ME Effect Measurement: An alternatingly generated Helmholtz coil was used to apply ac fields from 20.1-92.1 KHz and an electromagnet was use to conduct dc field with various strength. Both the ac and dc fields were provided along the length direction of the ME laminate composites. The induced output voltage was recorded by using a model SR8 10 DSP lock-in amplifier.

Thermogravimetric analysis (TGA): TA Instrument SDT Q600 thermal analysis system was employed for thermogravimetric analysis. The measurements were run under an atmosphere with 9:1 oxygen/nitrogen flows from 35~425 ℃ at a ramping rate of 10 ℃ min⁻¹.

Atomic Force Microscope (AFM) Measurement: An asylum MFP-3D system was use for surface morphology study and the tip was budget sensors Tap300-G with resonant frequency of 300 kHz and spring constant of 40 N m⁻¹. The images were obtained in tapping mode with scanning rate of 1.0 Hz.

Local Piezoelectricity Measurements: The local piezoelectric response of CNC was analysed by using an asylum MFP-3D system and the conductive tip was Olympus OMCL-AC240TM (Pt/Ti coating) with resonant frequency of 70 kHz and spring constant of ~2.0 N m⁻¹. The morphology, amplitude and phase images were obtained in dual ac response tracking (DART) mode[31] with contact resonant frequency around 260 kHz. Piezoelectric response was measured as the first-harmonic of bias-induced tip deflection: 

\[ d = d_0 + A \cos(\omega t + \varphi), \]

where \( d_0 \) is the equilibrium position of the tip; \( A \) is the amplitude and \( \omega \) is the frequency of
applied bias; $\varphi$ is the phase yielded information on the polarization direction below the tip. To study the polarization switching dynamic, the switching spectroscopy technique was used to obtain the local piezoelectric hysteresis loop. For each laminate sample, spectroscopy measurements were acquired across a $3 \times 3 \, \mu\text{m}^2$ area by applying bias on at least 5 points. The voltage during the SS-PFM measurement was applied in the range of $\pm 29 \, \text{V}$, with the frequency of 0.5 Hz, and this loading is expected to switch the polarization component back and forth. We modified the system by connecting an external amplifier because the upper limit of output signal is $\pm 10\, \text{V}$, which is too weak to induce a saturated switching dynamic. The driving amplitude has been settled on 200 mV for all aforementioned measurements.

**Supporting Information**

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

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Figure 1. (a,b) AFM height images of two types of CNC: nanowiskers and nanospheres, the scanning size is 1×1 µm. (c) Schematic view of CNC based ME laminate structure. The CNC films were first sputter coated with 30 nm thick gold electrodes on both sides and then glued with Metglas® 2605 SA1, of which the thickness is 25 µm. To ensure even distribution, the Epoxy was pre-heated to 60 °C to improve the liquidity. (d) Schematic view of the bulk system for ME voltage measurement. The output voltage was collected from the interface gold electrodes and monitored as root mean square (RMS) values using a lock-in amplifier.
Figure 2. (a) ME output voltage as a function of $H_{ac}$ frequency under $H_{dc}=4.0$ Oe and $H_{ac}=0.4$ Oe. The experimental data (dots) are fitted to equation 4 and the results are shown as dashed lines. (b) Resonance enhanced ME voltage coefficient as a function of $H_{dc}$, and the $H_{ac}$ strength is fixed as 0.4 Oe. (c) Tensile curves of CNC films displayed as stress against strain (d) The hysteresis loops representing the bias induce amplitude displacement as well as the phase changes corresponding to the hysteresis loops.
Figure 3. (a-c) ME output voltage of aired nanowhiskers samples as a function of $H_{ac}$ frequency under (a) $H_{dc}=2.2$ Oe, (b) $H_{dc}=8.2$ Oe and (c) $H_{dc}=17.4$ Oe. (d-f) ME output voltage of nanowhiskers samples dried at 45 °C as a function of $H_{ac}$ frequency under (d) $H_{dc}=2.2$ Oe, (e) $H_{dc}=8.5$ Oe and (f) $H_{dc}=17.7$ Oe. (g-i) ME output voltage of aired nanospheres samples as a function of $H_{ac}$ frequency under (g) $H_{dc}=2.1$ Oe, (h) $H_{dc}=8.2$ Oe and (i) $H_{dc}=17.3$ Oe. The experimental data (dots) are fitted to a modified Lorentzian equation (4) (shown as solid lines).
Figure 4. (a) Schematic view of CNC whisker alignment. An adhesion removable polyester (PET) film (water contact angle=100.1˚) is used as casting substrate. (b) AFM height (insect section, displayed as in ±25 nm) and phase images of aligned CNC whisker film. The solid and dash arrows indicate the alignment and rolling or shear directions, respectively. (c) AFM height (insect section, displayed as in ±15 nm) and phase images of drop casted non-aligned CNC whisker film. The scanning size of all AFM images is 3×3 µm. (d) The schematic illustration of magnetostrictive and piezoelectric combination. The actual laminate is fabricated by tailoring the aligned whisker CNC film into desired size through different directions, sputter coating surface electrodes, and then glued with Metglas®. (e) ME output voltage as a function of $H_{dc}$ frequency under $H_{dc}$=4.0 Oe and $H_{ac}$=0.4 Oe. The experimental data (dots) are fitted to equation 3, the results are shown as dash lines and the fitting parameters are provided in supplementary tables 5-7. (f) Resonance enhanced ME output voltage as a function of $H_{dc}$, and the $H_{ac}$ strength is fixed as 0.4 Oe. (g) tensile curves obtained from aligned whisker CNC film at testing angles of 0˚, 45˚ and 90˚. The results are displayed as stress against strain.