Supporting Information

Piezoelectric Nanocellulose Thin Film with Large-Scale Vertical Crystal Alignment

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S1. Calculation of interfacial energy of CNCs-PTFE

Interfacial energy between CNCs and PTFE could be calculated by following equation:

$$\varepsilon_{CNC-PTFE} = \gamma_{CNC} + \gamma_{PTFE} - W_{CNC-PTFE} \quad (1)$$

where the $\varepsilon_{CNC\text{-}PTFE}$ represents the interfacial energy between CNCs and PTFE in air or vacuum, γ_{CNC} and γ_{PTFE} represent the surface energy of CNCs and PTFE respectively and $W_{CNC\text{-}PTFE}$ represents the interaction energy between CNCs and PTFE. Consider the existence of water-ethanol solvent, equation (1) changed to equation (2):

$$\varepsilon'_{CNC-PTFE} = \varepsilon_{CNC-PTFE} - \varepsilon_{CNC-Solvent} - \varepsilon_{PTFE-Solvent} = W_{CNC-PTFE} + W_{Solvent-Solvent} - W_{CNC-Solvent} + W_{PTFE-Solvent} \quad (2)$$

where the $\varepsilon'_{CNC\text{-}PTFE}$ represents the interfacial energy between CNCs and PTFE in water-ethanol solvent, $\varepsilon_{1\text{-}2}$ and $W_{1\text{-}2}$ represent the interfacial energy and interaction energy between two subscripts respectively. $W_{1\text{-}2}$ could be further calculated by equation (3):

$$W_{1-2} = 2(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p}) \quad (3)$$

where the γ^d and γ^p represent the dispersion part and polar part of surface energy respectively.[7] The related parameters of water, ethanol, water-ethanol binary solvent, CNCs and PTFE were listed in Table S2.

S2. Calculation of orientation parameter (OP).

The OP could be calculated by equation (4):

$$OP = (180° - \Delta\Phi)/180° \quad (4)$$

where $\Delta\Phi$ is the full width at half maximum (FWHM) intensity. The value of OP ranges from 0 to 1, where 0 represent totally random orientation and 1 represents the perfected uniaxial orientation.

S3. Calculation of piezoelectric coefficient.

d = (PFM amplitude [V] – PFM amplitude offset [V]) ÷ lock in amp. gain [V/V] ÷ ratio A-B (AC) gain to A-B (DC) gain [V/V] × A-B sensitivity [um/V] ÷ 5 ÷ ac bias

amplitude [V] (5)

where PFM amplitude represents the PFM amplitude signal of sample, PFM amplitude offset represents the PFM amplitude signal before approaching, lock in amp. gain = 100, ratio A-B (AC) gain to A-B (DC) gain = 1, A-B sensitivity = 0.0093 um/V and ac bias amplitude = 2.000 V in this work.

Table S1. Dielectric constants of water, ethanol, water-ethanol binary solvent and PTFE at 293.15K.

Substance	Dielectric constant
Water[1]	80.4
Ethanol[1]	25.0
Water-Ethanol (χ_e= 80%)[1]	33.9
PTFE[2]	2.1

Table S2. Surface energy of water, ethanol, water-ethanol binary solvent, CNCs and PTFE at 293.15K.

Substance	γ	γ^d	γ^p
Water[3, 4]	72.8	20	52.8
Ethanol[3, 4]	22.1	18.8	2.6
Water-Ethanol (χ_e = 80%) [3, 4]	24.3	18.9	5.4
CNCs[5]	62.1	40.9	21.2
PTFE[6]	20	18.4	1.6

Table S3. Piezoelectric coefficient of e-CNC film.

Area number	Piezoelectric coefficient (pm/V)
1	17.9
2	15.8
3	20.7
4	23.5
5	18.7
Average	19.3 ± 2.9

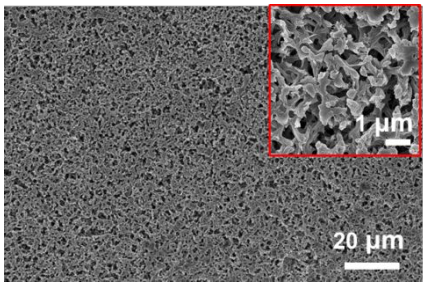

Figure S1. SEM image of filter paper. The average pore size is 450 nm.

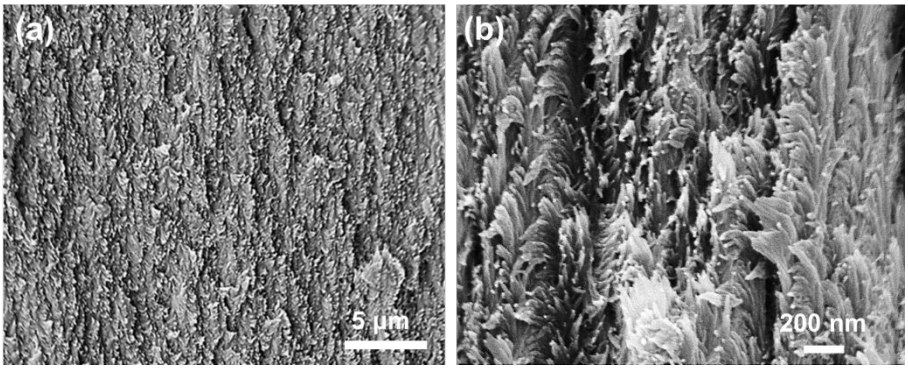

Figure S2. (a) Low- and (b) high-magnification SEM images of CNC film fabricated from CNC aqueous solution (χ_e = 0%) by confinement cell assembly.

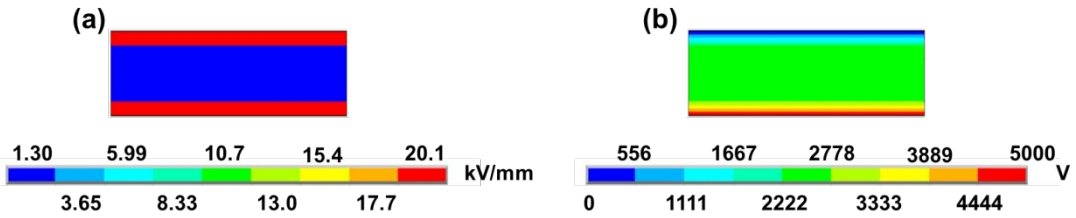

Figure S3. FEA simulation of the distributions of (a) electric field and (b) potentials.

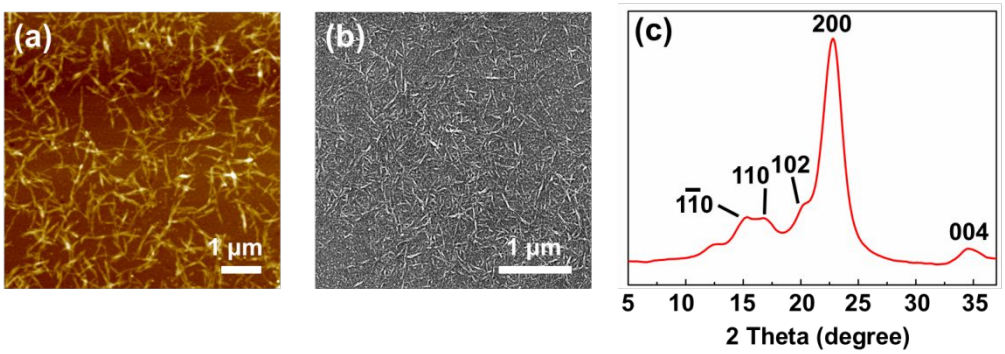

Figure S4. (a) AFM image, (b) SEM image and (c) XRD of CNC sample.

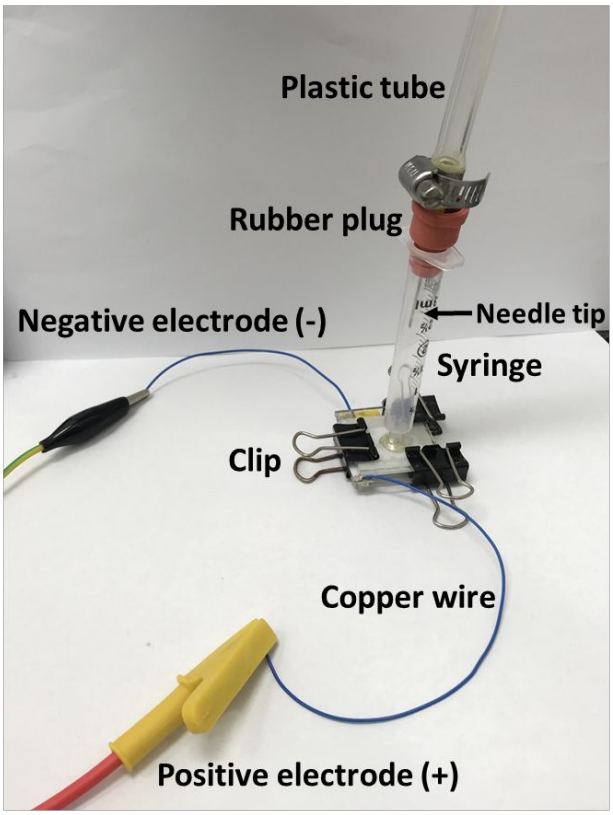

Figure S5. Experimental setup used for CNCs alignment.

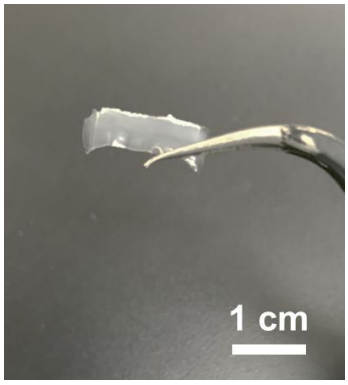

Figure S6. Photos of vertically aligned CNC film.

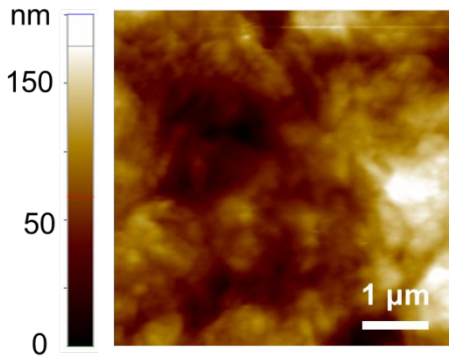

Figure S7. AFM topography image of vertically aligned CNC film.

Reference

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