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Supplementary Information

# A Composite Generator Film Impregnated with Cellulose Nanocrystals for Enhanced Triboelectric Performance

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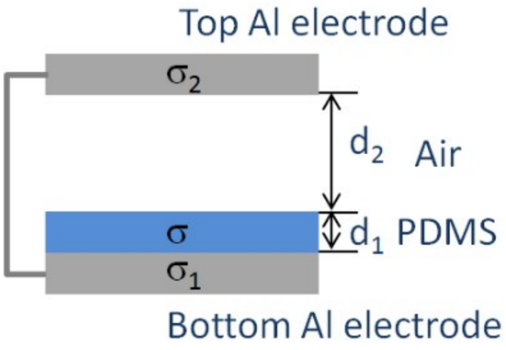
## Fabrication of the Composite-Structured Film (PDMS Film with Oriented Cellulose Nanocrystal Flakes)

To prepare cellulose nanocrystals, commercially available dissolving pulp dry lap made from southern pine was acid hydrolyzed by 64% sulfuric acid at 45°C for approximately 1.5 h under a nitrogen blanket with constant stirring. A 5% aqueous sodium hydroxide solution was used to neutralize the acid, and the sodium sulfate and other salts were then removed by ultrafiltration. In the experiment, a sulfuric-acid-hydrolyzed cellulose nanocrystal (in rod shape) suspension (1.0 wt%) was circulated in a self-designed wet ball milling system to fabricate nanoscale cellulose spheres (particles) with an average diameter of 25 nm. Zirconium oxide ($ZrO_2$) balls with a diameter of 800 μm were employed as grinding media. The milled cellulose suspension was freeze dried and grinded, leading to cellulose nanocrystal flakes (CNCFs) with a diameter of 25 ± 7 μm and a thickness of 1.6 ± 0.5 μm. Various dried CNCFs with concentrations of 1.0, 2.5, and 5.0 wt% were dispersed in 2-propanol, followed by dispersion in diluted 60 wt% PDMS (Sylgard 184, Dow Corning, US) using 2-propanol as the solvent. Ultrasonication enhanced CNCFs dispersion, followed by solvent evaporation on a hot plate at 80 °C. After solvent evaporation was completed, a curling agent was added into the PDMS/CNCFs solution at a weight ratio of 1:10. Spin coating followed to fabricate PDMS/CNCFs composite films and to control the thickness at 200 ± 5 μm. Finally, the films were dried in a vacuum oven at 80 °C for an hour, and then cut into testing samples with an effective area of 1.5 cm × 1.5 cm for both pure and composite PDMS films. All film samples were pretreated by cyclic compression with a 40 N normal force for 5 minutes prior to testing.

## Characterization and Measurement

The morphologies of the cellulose nanocrystal flakes and composite-structured PDMS films were characterized by scanning electron microscopy (SEM). Periodic compression test equipment was custom-made using a programmed solenoid with control functions for compressive force and frequency. A mixed signal oscilloscope (Infiniivision MSO-X 3054A, Agilent Technologies, US) and a sourcemeter (2601B, Keithley Instruments Inc., US) were used to measure the electrical voltage and current. Compression tests were carried out on a rheometer (AR 2000ex, TA Inc., US) at a constant compression rate of 2 μm/s, with a maximum normal force of 50 N, to measure the elastic modulus. Capacitance values in force-response curves were calculated using the equation $C = \varepsilon_0 \varepsilon_{rp} S/d$, where $\varepsilon_0$, $\varepsilon_{\mathrm{rp}}$, $S$, and $d$ were the permittivity of free space ($8.854\mathrm{e}^{-12}$ F/m), dielectric constant of PDMS film, contact area (2.25 $\mathrm{cm}^2$), and the distance (200 μm) between the top and bottom electrodes, respectively. The dielectric constants of pure and composite PDMS films were measured by an Agilent E4980A precision LCR meter with an Agilent 16451B dielectric material test fixture.

### Surface Charge on an Insulator as a Driving Force to Enhance Induced Charges on Metal Electrodes



The TENG was treated as a flat-panel capacitor. The surface charge density on the PDMS was assumed to have a uniform distribution, $\sigma$. The charge density on the top Al electrode was denoted as $\sigma_2$, and that on the bottom Al electrode was denoted as $\sigma_1$. According to the total charge induction and conservation between the PDMS film and the Al electrodes:

$$-Q = Q_1 + Q_2 \tag{S1}$$

They have the same contact area ($S$) with each other, thus,

$$-\sigma = \sigma_1 + \sigma_2 \tag{S2}$$

The electric potential difference between the two Al electrodes can be calculated by the electric field strength based on the Gauss theorem:

$$\begin{aligned} V &= V_{bottom\,Al} - V_{top\,Al} \\ &= E_1 \times d_1 - E_{air} \times d_2 \\ &= (-)\frac{\sigma_1}{\varepsilon_0}\left(\frac{d_1}{\varepsilon_{rp}} + d_2\right) - \frac{\sigma}{\varepsilon_0} \times d_2 \end{aligned} \tag{S3}$$

where $V_{\text{top Al}}$ and $V_{\text{bottom Al}}$ are the voltages of the two Al electrodes, respectively; $E_1$ and $E_{\text{air}}$ are the electric field strength inside the PDMS and the air gap, respectively; $d_1$ and $d_2$ are the thicknesses of the PDMS film and the gap distance between the PDMS and the top Al film, respectively; and $\varepsilon_0$ and $\varepsilon_{\text{rp}}$ are the relative permittivities of the PDMS and air, respectively. As for the equilibrium state, $V = 0$, we can get:

$$\sigma_1 = (-)\frac{\sigma}{1 + \left(\frac{d_1}{d_2}\right)\varepsilon_{rp}} \tag{S4}$$

If $d_2$ is close to 0, meaning that contact between the PDMS and the Al film is near zero, then $\sigma_1 = 0$, and $\sigma_2 = -\sigma$.

If $d_2 >> d_1$, meaning that the PDMS and the Al film are fully separated, then $\sigma_1 = -\sigma$, and $\sigma_2 = 0$.

For composite PDMS films, the CNCFs with positive charges can enhance $\sigma$ by $\Delta\sigma$. Thus, Eq. 4 was revised as follows:

$$\sigma_1 = (-)\frac{\sigma + \Delta\sigma}{1 + \left(\frac{d_1}{d_2}\right)\varepsilon_{rp}} \tag{S5}$$

The enhanced surface charge density of the composite film can induce more charges between the two Al electrodes, thus leading to a higher output performance in comparison with pure PDMS. $\Delta\sigma$ depends on the net electric field built by positively charged CNCFs, work function, and so forth, as indicated in Eq.1 in the main manuscript.

## The Calculation of Energy Conversion Efficiency

The conversion efficiency ($f$) is defined as the ratio between the electrical energy ($W_{\text{output}}$) that is delivered to the load by CTGs and the input energy power ($W_{\text{input}}$). The input power contains the mechanical energy caused by composite film deformation and the power required to move the top Al electrode away and toward the PDMS film during the electrostatic induction process. The power delivered by the CTGs is equal to the Joule heating energy ($Q$) over time on the external load of resistance,

$$W_{output} = \frac{Q}{\Delta t} = \frac{1}{\Delta t}\int_{t_1}^{t_2} \frac{U^2}{R} dt = \frac{1}{\Delta t R}\int_{t_1}^{t_2} U^2 dt \qquad (S6)$$

where $U$ is the voltage and $R$ is the external load resistance.

The input mechanical energy power ($W_{input,\,mech.}$) causes pure and composite PDMS film deformations,

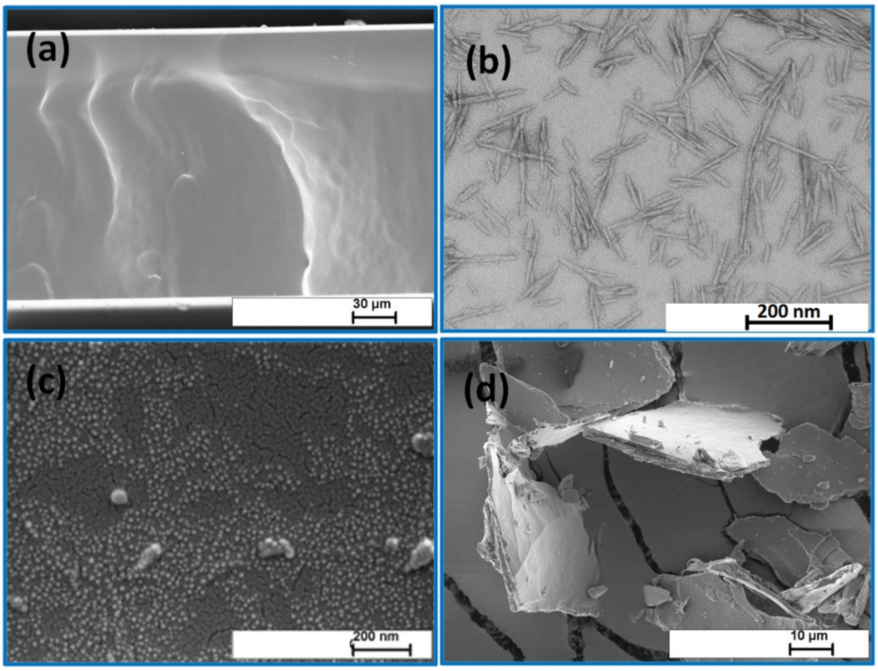
$$W_{input,\,mech.} = \int \sigma d\epsilon \qquad (S7)$$

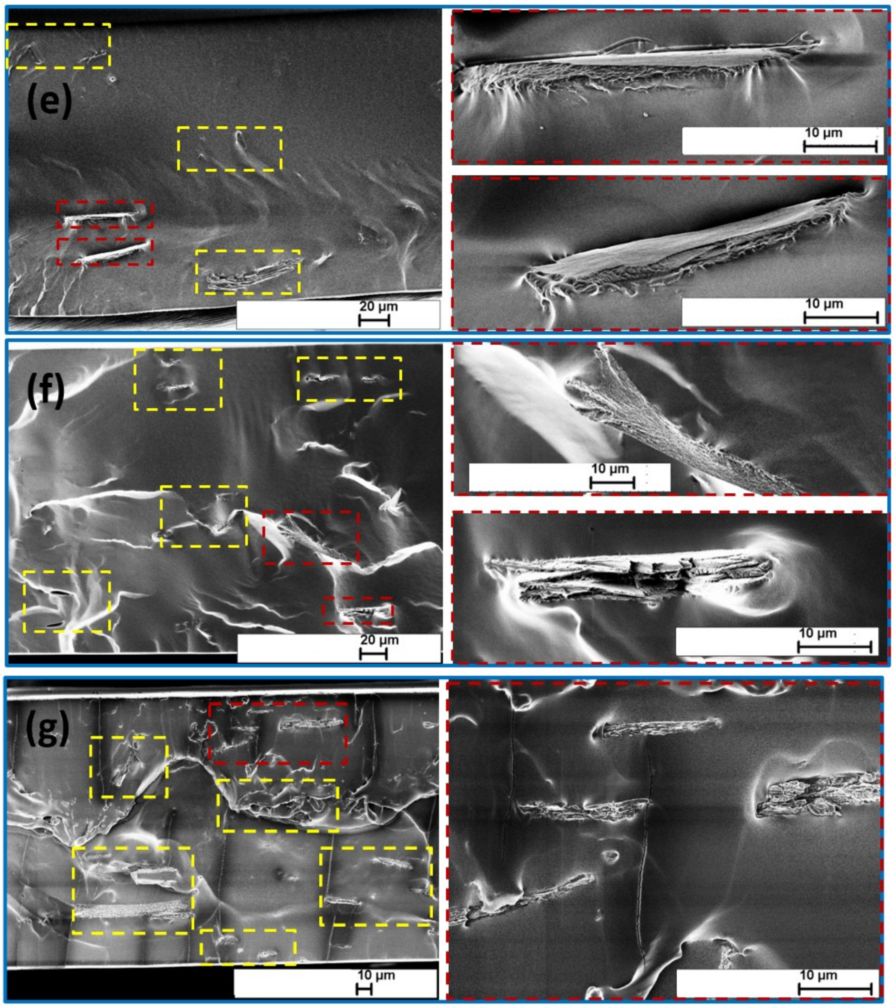
where $\sigma$ is the compressive pressure on the film and $\varepsilon$ is the responding strain, as shown in Figure S4 (b). The power required to move the top Al electrode away and toward the PDMS to overcome Coulomb force attractions is as follow,

$$W_{input,\,elec.} = \frac{1}{\Delta t}\int_{t_1}^{t_2} \frac{kQ_{PDMS}Q_{Al}}{d^2} v dt \qquad (S8)$$

where $k$ is Coulomb's constant ($8.99*10^9$ $\text{Nm}^2\text{C}^{-2}$), $Q_{\text{PDMS}}$ and $Q_{\text{Al}}$ are surface charges on the contacted surfaces, $d$ is the gap, and $v$ is the velocity. Therefore, the energy conversion efficiency can be calculated as:

$$f = \frac{W_{output}}{W_{input,\ total}} = \frac{W_{output}}{W_{input,mech.} + W_{input,elec.}} 100\% \qquad (S9)$$


(a)
30 µm
(b)
200 nm
(c)
200 nm
(d)
10 µm


(e)
20 µm
10 µm
10 µm
(f)
20 µm
10 µm
10 µm
(g)
10 µm
10 µm

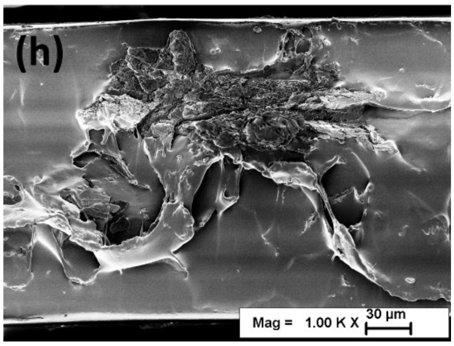


**Figure S1.** SEM images of cellulose nanocrystals with different dimensions and composite-structured films with various CNCFs concentrations. (a) The cross-section of a pure PDMS film. (b) Acid hydrolytic cellulose nanocrystal rods with a diameter of ~20 nm. (c) Cellulose nanocrystal spheres with a diameter of 15~20 nm through wet ball milling. (d) Freeze-dried CNCFs with an average diameter of ~30 μm and a thickness of ~3 μm. Composite PDMS films had CNCFs concentrations of (e) 1.0, (f) 2.5, and (g) 5.0 wt%. The dashed rectangles highlight the oriented CNCFs and the red boxes indicate the higher-magnification CNCFs. (h) Agglomerates of CNCFs were found in PDMS with 5 wt% CNCFs.

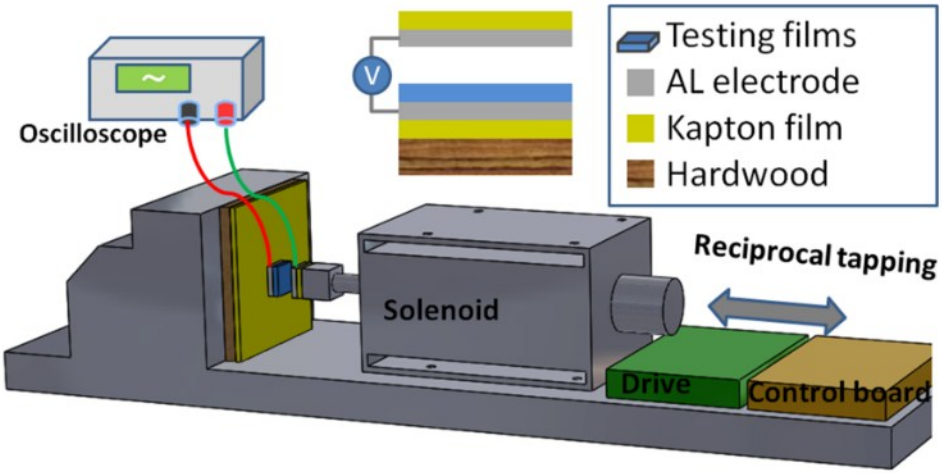


**Figure S2.** Schematic illustration of the layered structure of CTG and the testing device design based on a programmed solenoid with functions for compression pressure and frequency control.

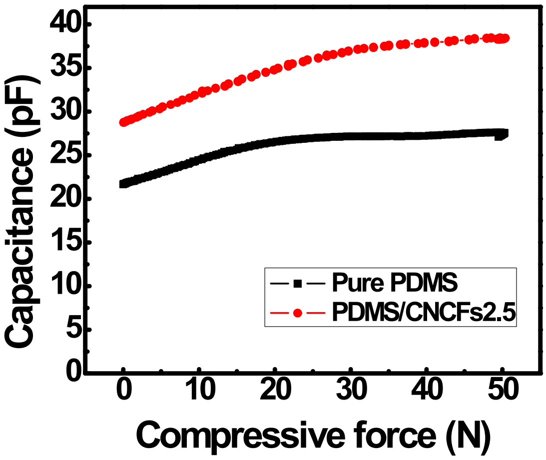


**Figure S3.** Capacitance curves of pure PDMS and composite-structured PDMS with 2.5 wt% CNCFs.

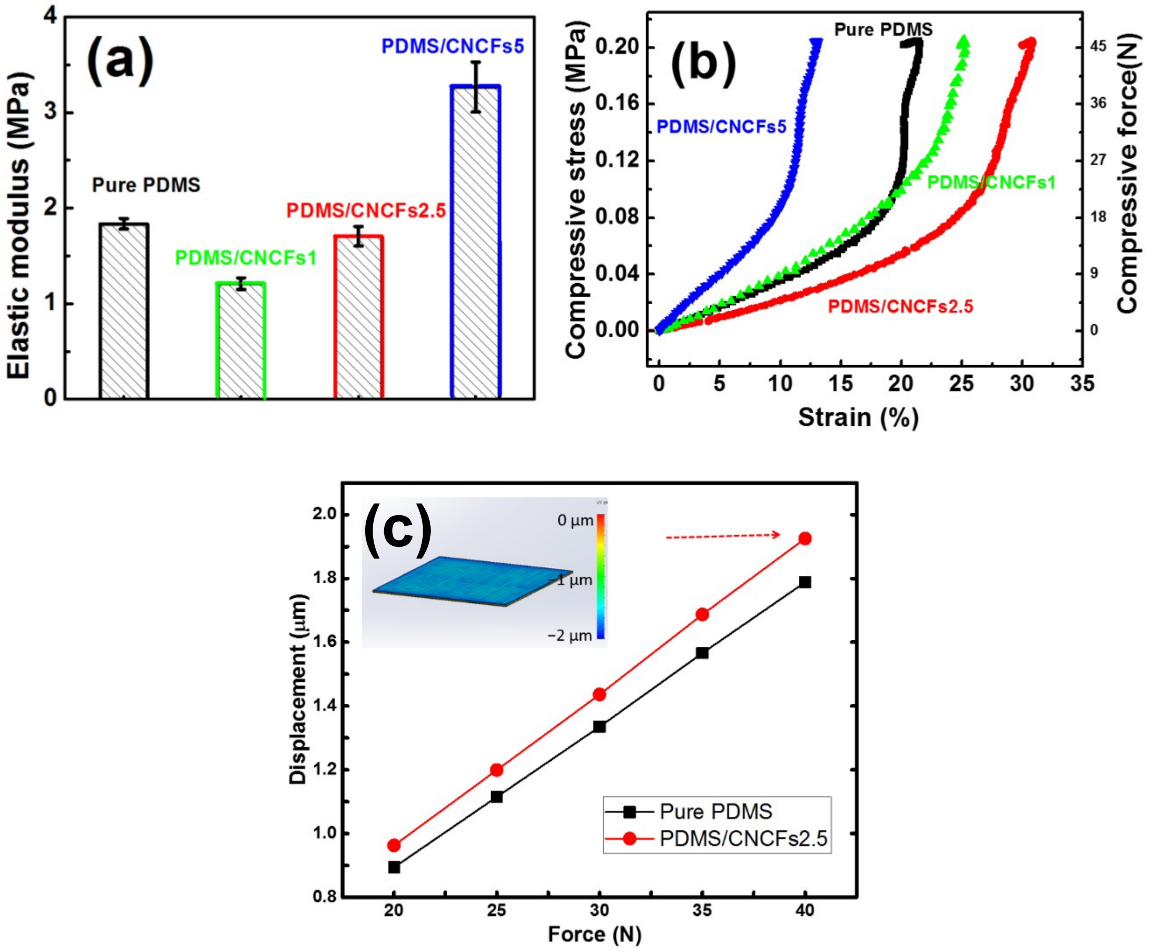


**Figure S4** Compression measurements of pure PDMS films and composite-structured films. (a) Elastic modulus. (b) Compressive force and pressure curves of films with CNCF concentrations of 1.0, 2.5, and 5.0 wt%. SolidWorks software simulation results of displacements of pure and filled PDMS films with various compressive forces from 20 to 40 N. Compared with pure PDMS film, composite films with small amounts of CNCFs (i.e., 1 or 2.5 wt%) exhibited a lower modulus since CNCFs were not compatible with the PDMS matrix resulting in loose contacts. However, the elastic modulus increased with additional CNCFs fillers due to their high modulus of 138 GPa [1].

[1] T. Nishino, K. Takano, K. Nakamae, K. Saitaka, S. Itakura, J. Azuma, K. Okamura, *Journal of Polymer Science Part B-Polymer Physics*, 33 (1995): 611.

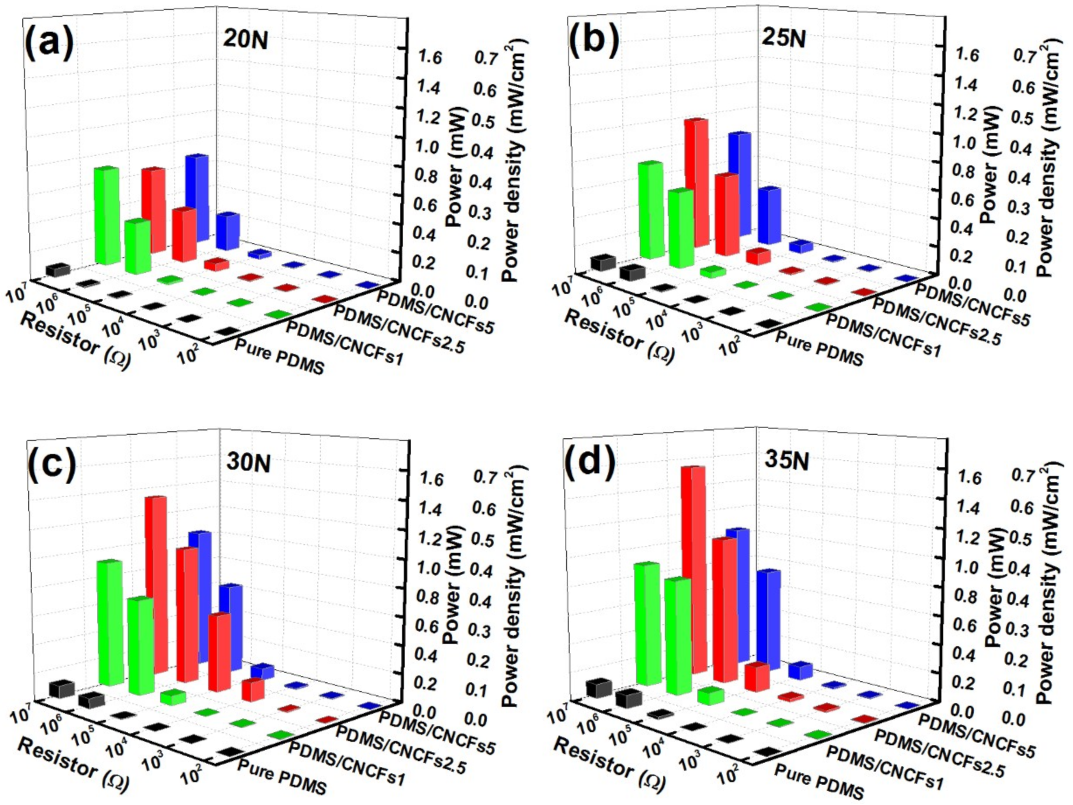


**Figure S5.** The dependence of the instantaneous output power on the external load resistance under a periodic contact force of (a) 20 N, (b) 25 N, (c) 30 N, and (d) 35 N. The maximum power and power density were achieved at a load resistance of 10 MΩ.

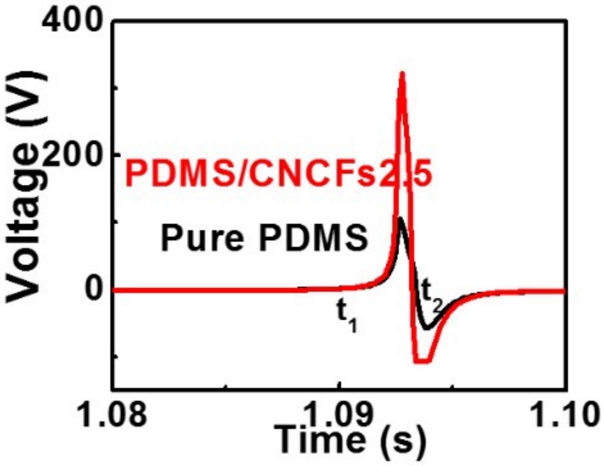


**Figure S6.** A magnified image of a single voltage peak corresponding to one compression cycle.