

Towards high performance green piezoelectric generators based on electrochemically poled nanocellulose

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Article

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Abstract

Internet-of-everything (IoE) is defined as networked connections of things, people, data and processes. IoE nodes, preferably shaped as printed flexible systems, serves as the frontier outpost of the Internet and comprises devices to record and regulate states and functions. To power distributed IoE nodes in an ecofriendly manner, technology to scavenge energy from ambience and self-powered devices are developed. For this, piezoelectricity is regarded as a key-property, however current technology typically based on polyvinylidene difluoride (PVDF) co-polymers, are expensive and produced via toxic protocols.

We report piezoelectric characteristics of electrochemically poled cellulose nanofiber (CNFs) thin films processed from water dispersions. Poling these films at humid conditions cause breaking and reorientation of CNF segments, which results in enhanced crystal alignment rendering the resulting material piezoelectric. Generators based on poled CNF show similar piezoelectric voltage and coefficient, here measured to $d_{33} = 46$ pm/V, as for devices including PVDF copolymer layers of similar thickness. Our findings promise for low cost and printable ecofriendly piezoelectric-powered IoE nodes.

Introduction

Internet-of-Everything (IoE) [1] is currently one of the strongest tech-trends with many great applications already in operation and a vast array of opportunities forecasted. To settle this technology as an ecofriendly technology, we need to make sure that all included materials are derived from sustainable origins and that they are processed and recycled under protocols with a minimal impact on the environment [2]. To power and to integrate self-powered devices into IoE nodes, various properties and functions are being explored to enable heavily distributed and remote autarchic nodes within future Fog Computing systems [3]. In this respect, piezoelectric materials have been widely applied in energy harvesting and signal transducing applications.

Piezoelectric materials couple mechanical stress, such as displacement, pressure, vibration and flows to electrical polarization [4, 5]. This property has been used for powering portable electronic devices and wireless sensors [6, 7] as well as in actuators and acoustic devices [8]. The strength of the mechano-to-electric coupling described as the piezoelectric coefficient is defined as the ratio between the generated charge and the applied mechanical force [9]. In recent decades, piezoelectric polymers have become the focus because of the possibility to use atmospheric synthetic routes as well as the ability to make flexible thin films by solution processing, such as printing technologies, despite their typically lower piezoelectric coefficient compared to inorganics [10]. The best-performing piezoelectric polymers are fluoropolymers based on polyvinylidene difluoride (PVDF) and its copolymer P(VDF-TrFE) (polyvinylidene fluoride trifluoroethylene). Recently, a high piezoelectric coefficient (d_{33}) of 52 p CN^{-1} was reported for P(VDF-TrFE) composited with Mxene nanosheets [11]. With the awareness of the human footprint on the environment, IoE applications imply massive number of small devices released in society and nature. Here, the fluorine chemistry and the release of HF toxic fume upon thermal degradation of the PVDF material are issues for chemical synthesis and recyclability [12]. Hence, a new generation of green

piezoelectric materials, comprising features such as low cost, water solution processibility, and an overall environmental friendliness is in urgent need. Bio-material based piezoelectric devices have been reported to generate large output voltage [13–15], however, the highest piezoelectric coefficient (d_{33}) found in biomaterials reaches 38 pC N^{-1} at nanoscale characterized by piezoresponse force microscopy (PFM) [16]. Although this high value was not correlated to piezoelectric devices of practically large area, it showed the potential of biomaterials for piezoelectricity.

As the most abundant and green material on earth, cellulose-based materials have triggered a tremendous research attention over the last decades. The piezoelectricity in wood was discovered already in 1950 [17], followed by explanation that the origin of shear piezoelectricity is correlated to the reorientation of dipole moment from hydroxyl groups in the crystalline cellulose [18]. The intra- and inter molecular hydrogen bonds along the side of the cellulose chain introduce a non-centrosymmetric crystal structure in cellulose [19, 20]. The piezoelectric coefficients of those bulk wood-based materials are very low ($d_{14} = 0.1 \text{ pC/N}$), which hinders their practical applications [21]. More recent, the topic went through a phase of renaissance thanks to the exploration of nanocelluloses that opened up new possibilities to make cellulose material systems with unique properties. Cellulose nanocrystals (CNCs) of diameter between 5–20 nm and a length of about 100–500 nm are the smallest crystalline features extracted from wood via mechanical and chemical treatments. Cellulose nanofibers (CNFs) can be several micrometers long with amorphous and crystalline domains (mentioned as CNC) arranged in quasi-periodical fashion.

For a single cellulose crystal, apart from the shear piezoelectric constants, longitudinal and transverse piezoelectric constants are also present [22–24] because of the permanent dipole moment along their axis [25]. The longitudinal piezoelectric coefficient d_{33} enables the most promising applications because maximum deformation occurs when the charge generation and the applied mechanical strain are in the same direction. Orienting randomly arranged CNCs to aligned structures in a particular direction could increase the piezoelectric constant. However, most of the reported methods only succeeded to align CNFs and CNCs parallel to the substrate [23–27]; thus not leading to any enhancement of d_{33} . The difficulty to orient the nanocellulose homogeneously across large area and the extreme fragility of the CNCs films prevent cellulose to be implemented in efficient and high-performing piezoelectric devices [24]. The practical piezoelectric devices composed of nanocellulose only exhibit a low piezoelectric constant (5 pC N^{-1}), that is 4–5 times smaller than ones based on PVDFs [22]. Till now there is no research showing that pure cellulose can exhibit competitive piezoelectric performance compared to PVDF derivatives in practical devices.

In this work, we report that electrochemical poling greatly enhances the piezoelectric property of CNF thin films, which can be implemented in macroscopic devices (area of about 1 cm^2) to exhibit competitive performance with P(VDF-TrFE)-based piezoelectric devices of similar thickness. Different from reported electric methods to improve piezoelectricity, such as the electric poling process used to polarize ferroelectric materials, and electric field/current or corona poling used to align CNF fibers [23, 28, 29], the proposed electrochemical poling mechanism involves absorbed water from air, breaking and reorientation

of the CNF under electrochemical reactions. Atomic force microscopy (AFM) revealed changes of CNF thin film morphology after electrochemical poling. The mechanism is supported by impedance spectroscopy and grazing-incidence small-angle X-ray scattering (GISAXS). We also confirmed the improved d_{33} piezoelectric coefficient of CNF thin films and measured values reaching up to 46 pm V^{-1} using PFM, which is comparable to P(VDF-TrFE) (45 pm V^{-1}). Our work demonstrates the possibility of nanofibrils of cellulose to compete with PVDF copolymers processed from solution and pave the way for ecofriendly novel all-printed energy technology and sensors for IoE application in general; and may also find its way into some niche-application for large area energy harvesting systems.

Results

Piezoelectric voltage of CNF thin films

The CNF thin films were prepared by drop-casting on doped silicon wafers a fixed amount of the cellulose-water dispersion (0.5 wt% solid content of CNF) (Fig. 1a). The conductive silicon wafer and the top Au electrode were connected to form a close circuit for both electric poling and piezoelectric characterizations (Fig. 1b). The photograph of the device is shown in the inset of Fig. 1c. Silicon wafer was chosen as the substrate to ensure a relatively uniform CNF thin film without peeling off (details in experiment section). The CNF film was poled with gradually increasing voltage from 5 V to 110 V. After each voltage step, its piezoelectric response was recorded while applying a periodically force of 24 N (within the mechanical resistance of the silicon wafer). Figure 1c presents the piezoelectric performance for a Si/CNF/Au device at ambient humidity (RH = 40%). Those traces correspond to the open circuit piezoelectric output voltage upon a periodic applied force at frequency of 3 Hz. There is no obvious periodic piezoelectric response hidden in the voltage noise ($< 10 \text{ mV}$) for the device before poling. On the contrary, after poling below 30 V, a periodic output voltage following the 3Hz input force is observed with an amplitude of around 30 mV. For higher poling voltage, the piezoelectric voltage reaches a maximum of 100 mV (at 70 V). Further poling above 70 V leads to a degradation of the performance. The piezoelectric effect is remnant since even 30 minutes after poling, the piezoelectric voltage remains (Fig. 1c). We noticed however, an asymmetry between positive and negative voltage that is associated to the measurement frequency limit as found in other piezoelectric materials [5, 10]. The same device was characterized again after two weeks and the piezoelectric response maintained similar (Supplementary Fig. 1). These results demonstrate that the piezoelectric performance of the CNF thin films can be greatly improved by electric poling at room humidity and the induced poling effect remains.

The piezoelectric response of CNF films are found to depend on the humidity of the atmosphere during poling process. In Fig. 1d, CNF thin films poled at four different relative humidity levels (dashed columns) are compared with that of non-poled ones (empty columns) using the same applied force. The poling was performed in a climate chamber with fixed humidity after keeping the CNF films inside the chamber for 2 hours; after this procedure, the piezoelectric output voltage was directly measured in ambient humidity. We selected samples with the average thickness about $1 \mu\text{m}$ ($\pm 0.1 \mu\text{m}$), and then poled them with an

increasing voltage between 5 to 110V. The maximum output voltages obtained are presented in Fig. 1d for different humidity levels (the corresponding poling voltage are presented in Supplementary Table 1). The piezoelectric output voltage is the highest for samples poled in room humidity (40% RH) and smallest for samples poled at high humidity (70% RH). This might be due to the presence of more dissociated ions from carboxylic groups on the surface of the cellulose nanofibrils; while the associated cations (H^+ and Na^+) are mobile at high humidity and could screen the piezoelectric polarization [30]. To maximize the piezoelectric response, we thus dried the CNF films (that was poled at 70% RH) for 30 min in relative humidity level of 10%; and then remeasure the piezoelectric response that rises up from 52 mV to 80 mV.

Electrochemical poling: poling with electrolysis

Electric poling is known to enhance the alignment of the electric dipoles in ferroelectric materials, thus improving their piezoelectric performance [31]. When sweeping the CNF films with increasing voltage between $-110V$ to $110V$ (Supplementary Fig. 3), we did not observe typical ferroelectric poling current found for P(VDF-TrFE) with a typical step function with a hysteresis (Supplementary Fig. 2). Hence, the CNF film does not exhibit any ferroelectric properties. It should be mentioned that all ferroelectric materials are piezoelectric but the reverse does not apply. Materials having non-centrosymmetric structure could possess piezoelectricity without being ferroelectric [32]. The mechanism of the improved piezoelectric output voltage in poled CNF thin films is likely different from that in the ferroelectric PVDFs. As cellulose is known to be hygroscopic with a 10–14% water content in equilibrium with the atmospheric humidity (40–50% RH), and as the applied poling voltage exceeds the electrochemical potential for electrolysis of water (1.2-2V) [33, 34], we assume that water degradation takes place upon poling if sufficient current passes through the CNF layer. In Fig. 2a and 2b, the current passing through the CNF film was recorded when the poling voltage linearly increases at 10% RH and 40% RH. Constant scan rate of $5 V s^{-1}$ was used in all scans and the voltage range was increased at each cycle, from 5 V to 110 V. The non-linear change in current upon applied voltage indicates that it is not capacitive in nature. Moreover, the dramatically increasing current with the humidity level of the poling atmosphere suggests that the absorbed water in CNF films undergoes an electrolysis reaction. The fact that the current is lower after each successive cyclic scan at low humidity (10% RH) indicates that water in the film is consumed step by step. The electrochemical origin of the current related to water electrolysis is also supported by the higher current found for more humid atmosphere.

To understand the rate of the water consumption in the CNF film upon poling, a constant potential of 30 V is applied to the CNF thin films for 30s (Fig. 2c) to trigger the electrochemical reaction and the poling current is recorded every 5s. The normalized current vs. time for the films exposed at various humidity levels display an exponential decay that tend to saturate after 25 s. The saturated current level is 85% of the original value at RH = 70%, and decreases with the humidity (55% of their original values at RH = 40%). The current level serves as a probe for the water content in the film. The high current value for the humid sample is explained by a fast dynamic reabsorption of water in the same time as its consumption. The reabsorption of the water from the humid atmosphere can be tracked by recording the current while

applying a short pulse ($t < 1$ s, $V = 30$ V) every 50 s. As shown in Fig. 2d, the increasing current with the exposure time indicates the regaining of water. After 7.5 min, the current recovers almost to the same level as before poling for samples exposed at 40% and 70% RH, showing the hygroscopic nature of cellulose and the complete regaining of water and equilibrium with the atmosphere. On the contrary, in the dry condition (RH = 10%), the normalized current remains at a similar low level, which we interpret as an equilibrium reached between the absorbed water and the atmosphere. The recapture of water in room humidity after poling at 30 V for 30 s is also confirmed by FTIR spectroscopy by following the intensity rise of the OH vibrational stretching intensity (3340 cm^{-1}) versus time (Fig. 2e and 2f). As expected, the correlated trend of water content in Fig. 2f (obtained from the FTIR) and Fig. 2d (obtained from the poling current) enables us to quantify the rate of the reabsorption process for those CNF thin films and the impact of water in complex electrical measurement sequences. Finally, the reabsorption of the water in the CNF films after poling reaches to a similar level as before poling, but the remaining significant difference in piezoelectric voltage induced by poling (Fig. 1e, after 20 mins and Supplementary Fig. 1) proves that the change in the piezoelectric property is not due to the water loss from the film but to a true structure change in the cellulose layer.

Morphology changes upon electrochemical poling

We investigated the structural changes on the surface of the CNF film induced by electrochemical poling at different humidity levels by Atomic Force Microscopy (AFM). As shown in Fig. 3a and 3b, an Au thin film (50 nm of Au on 5 nm of Cr) coated on a PDMS stamp is positioned on the CNF film with slight pressure, which provides a tight and continuous contact with the CNF film and enables effective electric poling (Fig. 3c). After poling at 110 V for 30 s at fixed humidity levels (10%, 40% or 70% RH), the top electrode was removed and the naked CNF surface was characterized with AFM (Fig. 3d). For the samples poled at low humidity (RH = 10%), the topography and phase images (Fig. 3g and 3h) resemble the non-poled films (Fig. 3e and 3f) with only minor changes. After poling at room humidity (40% RH), the morphology of the fibrils becomes blurred (Fig. 3i) compared to the non-poled films. In the phase image of the poled CNF layer (Fig. 3j), nano-ring like structures with diameter around 10 nm to 15 nm can be observed. The size of the rings is similar to the diameter of the nanofibrils; which indicates that those rings are the cross section of the fibrils pointing upwards. For films poled at high humidity (70% RH), similar changes can be found (Fig. 3k and 3l). The nano-rings structure is more obvious in the phase image than in the topography image, because the phase angle of the probe oscillation in tapping mode is sensitive to the local stiffness of the material [35], thus revealing the formation of nano-domains in polymers otherwise invisible in the topography [36]. The obvious change of the CNF structure after poling at relatively high humidity (> 40%) indicates that the electrochemical poling current leads to the breaking of cellulose nanofibers followed by the reorientation of small segments perpendicular to the surface.

Note that the observed structure changes are irreversible and do not disappear even several months after poling, however, they are not uniform on the whole CNF films. As shown in Supplementary Fig. 4 and Fig. 5, different levels of changes can be found on the same sample after poling at relative humidity of 40% and 70%. This could be due to the variation of the CNF films in thickness (up to hundreds of

nanometers) resulting from a non-uniform electrochemical current during poling. Indeed, if a hard Au coated glass was used as top electrode, we could never see the morphology/phase changes because of rough CNF films resulted in a poor contact with the flat and hard Au electrode. To rule out other possible effects than the proposed electrochemical poling, several control experiments were conducted. After annealing those CNF films at 250°C for a short time (to avoid thermal degradation) followed by natural cool down, we could not observe the morphology change (Supplementary Fig. 6a and 6b). Also, no change in morphology was found by applying the same strength of electric field across a thin air gap as dielectric between the Au top electrode and the CNF film (Supplementary Fig. 6c and 6d). Hence, we believe that the poling effect in the CNF films is not due to any local Joule heating or electric field, the key mechanism is likely related to “electrochemical poling” combining electrochemistry, water softening effect and electric field.

The morphology changes in electrochemical poled CNF thin films can be evidenced by the dielectric characterization via impedance spectroscopy (details are discussed in Supplementary Note 2). The typical dynamic phenomena in CNF thin films before poling, freshly after poling and 15 hours after poling were measured by applying a small AC current from frequency range between 1×10^{-1} - 2×10^5 Hz. The results in Supplementary Fig. 7 show obvious changes in the impedance spectrum after poling. Moreover, the change remains even after 15 hours, which indicates that the electrochemical poling truly leads to an irreversible change of the dielectric properties. The Bode (Supplementary Fig. 8) and Nyquist plot (Supplementary Fig. 9) of the CNF thin films poled in different humidity levels further confirmed the role of absorbed water in the electrochemical poling and its correlation with the induced morphology changes.

Piezoelectric device performance

The open-circuit output voltage (V_{piezo}) of piezoelectric devices depends on the applied force (F), the longitudinal piezoelectric coefficient (d_{33}) and the capacitance (C) of the dielectric material according to:

$$V_{piezo} = \frac{d_{33}F}{C}$$

1

We notice that the capacitance at high frequencies (10^5 - 10^6 Hz, RH = 40%, Supplementary Fig. 8) that is critical for piezoelectric response [37], does not vary after poling at different voltages. Hence, we believe that the piezoelectric voltage measured upon poling is not due to the change in capacitance but mostly an effect of the d_{33} coefficient of the film. Note that the effect of humidity on the capacity value is expected as the introduction of water increases the average dielectric constant of the cellulose layer, however, this effect is vanishingly small (Supplementary Fig. 10). Interestingly, the fabrication method of the cellulose film impacts its morphology with the cellulose nanofibrils orientated parallel to the substrate with the spin-coating method due to the centrifugal force upon drying. In this film, the piezoelectric performance is poor and the poling is not accompanied with the formation of nano-rings. (Supplementary Note 3).

Piezoelectric Force Microscopy (PFM) has been widely used to confirm the reversed piezoelectric effect of a material, as well as to locally measure the piezoelectric coefficient d_{33} (Supplementary Fig. 12a). A DC bias is applied between a conductive AFM tip in contact with the surface of the sample and the substrate, and the deformation of the thin film (in thickness) can be detected by the cantilever. By exploiting PFM technique, we can accurately localize the regions on a CNF thin film that experiences morphology change. The deflection amplitude of the AFM cantilever, correlated to the sample deformation upon applied bias is presented in Fig. 4. For non-poled sample, the image displayed in Fig. 4a reveals only weak deformation when applying different bias between the sample and the tip. On the contrary, for poled layer (Fig. 4b), the film deformation increases significantly with the applied bias. The piezoelectric coefficient d_{33} can be calculated from the average linear fitting of the deflection amplitude of the cantilever (correlated to the deformation of the sample) vs. the applied bias (Fig. 4c and 4d). The measured average d_{33} is 46 pm V^{-1} for poled areas and only 10 pm V^{-1} for non-poled areas. As a benchmark for the PFM method, we characterized poled P(VDF-TrFE) thin films (Supplementary Fig. 12b) and obtained d_{33} of 46 pm V^{-1} which is similar to previously reported values. The analogous behaviors in PFM of poled CNF and P(VDF-TrFE) excludes the contribution from triboelectric effect to the generated output voltage of the CNF devices, and confirms that the piezoelectric property of CNF can compete with P(VDF-TrFE).

We now compare the piezoelectric performance of CNF and P(VDF-TrFE) thin films in practical device. The evolution of the piezoelectric voltage versus the applied force is plotted in Supplementary Fig. 13 for the poled CNF thin film (thickness = $0.86 \text{ }\mu\text{m}$) and the P(VDF-TrFE) thin film (thickness = $0.23 \text{ }\mu\text{m}$ and $0.55 \text{ }\mu\text{m}$). The linear behavior is reminiscent of a typical piezoelectric response. The thick P(VDF-TrFE) film exhibits higher piezoelectric output voltage than the thin one due to the reduced capacitance (open square symbols in Fig. 4e) as expected from Eq. (1) (dashed line). The voltage response of non-poled CNF films is below 0.03 V ($F = 24 \text{ N}$) showing the weak piezoelectric property. After poling, the piezoelectric response of CNF films increased with the thickness between 0.2 to $1 \text{ }\mu\text{m}$ as expected by the decreasing capacitance with thickness (see Eq. 1), which thus supports the piezoelectric nature of the phenomenon. It is important to note that the piezoelectric output voltage of CNF films is similar to the PVDF based devices in the same conditions.

The piezoelectric coefficient d_{33} of electrochemically poled CNF is compared with P(VDF-TrFE) films in Fig. 4f. The area capacitance of the P(VDF-TrFE) thin film (thickness = $0.55 \text{ }\mu\text{m}$) is 13.6 nF cm^{-2} as measured by impedance spectroscopy (impedance value at high frequency for which the phase angle = -90° , see supplementary Fig. 15). According to Eq. (1), the d_{33} of the P(VDF-TrFE) film is 44 pC m^{-1} based on the measured output voltage in Fig. 4e. For P(VDF-TrFE) film, d_{33} obtained by this method is similar to the PFM values extracted from the reverse effect in the literature [38–40]. Note that the units of the direct (C/m) and reversed piezoelectric (m/V) coefficient are equivalent. From our measurement of the converse piezoelectric effect, the poled CNF film has a coefficient $d_{33} = \sim 46 \text{ pC m}^{-1}$, thus close to the d_{33} of our P(VDF-TrFE) film. Now, we encounter a challenge when we tried to estimate d_{33} from the direct measurement of the piezoelectric voltage and the Eq. (1). Indeed, due to the uneven morphology of the

CNF films, it is difficult to obtain the absolute value of the capacitance of those films from the same impedance measurement (detailed discussion can be found in Supplementary Note 4). Hence, we cannot calculate the d_{33} of CNF films in the same way as for P(VDF-TrFE). Instead, previously reported dielectric constant of oriented cellulose ($\epsilon_r = 10$) [41–43] are used to calculate the piezoelectric coefficient (d_{33}) of the CNF devices. As shown in Fig. 4f, most of the CNF samples have d_{33} in the range between 35 to 55 pC m⁻¹, which is close to the value obtained from PFM (indicated by the green solid line). We can also see that the effect of electrochemical poling to the piezoelectric performance of CNF thin films depends on the thickness, the maximum improvement of 13 times takes place when the thickness is around 0.7 μm. Our results demonstrate that the piezoelectric voltage and d_{33} of electrochemically poled CNF thin films could reach similar value of P(VDF-TrFE) of similar thickness.

Discussion

As illustrated in Fig. 5a, before poling, CNF fibers composed of alternating amorphous and crystalline regions (enlarged illustration and chemical structures of CNF fiber can be found in Fig. 5d and 5g) are lying relatively parallel to the electrodes. The adsorbed water molecules in the CNF film are mostly bonded to the amorphous region of the cellulose fibers between the crystalline regions (CNC), or on the surface through hydrogen bonding with hydroxyl groups [44, 45]. At high level of humidity, water molecules can accumulate between the nanofibers [46]. During the electrochemical poling (Fig. 5b), the ionic conductivity leads to electrochemical reactions as well as perhaps other additional phenomena, such as formation of a space charge polarization like what is found in PVDF films poled in humid environments [47]. The grounded Si electrode is expected to induce half-reaction of O₂ reduction in presence of absorbed water. To describe that in more details, we remind that the oxygen reduction reaction on a non-catalytic surface in neutral environment leads to the production of hydrogen peroxide through the following reduction reaction $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ and the acid equilibrium $HO_2^- + H^+ \rightarrow H_2O_2$. Therefore, the neutral environment turns rapidly basic upon this electrochemical reaction. Note that both the basic pH and the H₂O₂ are known to degrade cellulose [48]. The half-reaction taking place at the positively bias gold electrode could be the oxidation of cellulose (Fig. 5h and 5i) as well as the oxidation of water. Interestingly, the oxidation of cellulose has been reported to be electrocatalytic with Au nanoparticles and on Au electrodes in alkali medium triggering the formation of carbonyl groups on the cellulose that enhances its solubility [49, 50]. The breaking of the CNF chains into lower molecular weight fractions make cellulose more soluble [51]. The formation of carboxylic group in the cellulose film can be evidenced from the growing characteristic C = O peak at 1730 cm⁻¹ in Supplementary Fig. S17 obtained after poling at higher voltages. The dissolution of cellulose in the alkali solution is known to promote hydrolysis that cleaves the glycosidic linkage of the polymer chains (Fig. 5i) [52, 53]. Further electrocatalytic oxidation paths lead to the formation of gluconate also carrying C = O bonds [49].

Hence, the poling is accompanied with an electrochemical reaction, and that is why we proposed the name “electrochemical poling”. The electrochemical reaction leads to a consumption of the water, and the creation of an alkali medium; which fragilizes the cellulose nanofibrils (Fig. 5e). Finally, the oxidation

of cellulose at the gold electrode is promoted by the poling current, which degrades the cellulose by breaking the chains of the biopolymer (Fig. 5f). We believe that the amorphous regions of the nanofibrils, softened by the absorbed water molecules [54], that are in contact with Au become the centers of the electrochemical degradation of the cellulose nanofibrils. As a result, those surface nanofibrils are cleaved at the level of the amorphous regions; and nanocrystals of cellulose are detached. Finally, the high electric field tends to orient preferentially the nanocrystals perpendicular to the Au electrode (Fig. 5c and 5f). The observation of such a surface in the AFM phase images with nano-rings corresponding to the diameter of the fibers supports the hypothesis. Furthermore, grazing incidence small angle x-ray scattering (GISAXS) experiments performed on non-poled and 110V-poled CNF thin films also reveal the poling induced structural changes in these films. As shown in Supplementary Fig. 18, the scattering feature changes observed in the q_z and q_x linecuts, in conjunction with the information derived by AFM, support the hypothesis of a re-orientation of lying-down fibers, with respect to the substrate, towards standing-up fibers upon poling. This electrochemical cleavage of the cellulose nanofibrils is not complete in dry condition (10% RH) due to the lack of absorbed water, hence only partially degraded flat fibers were observed (without total cleavage, Fig. 5e), while nicely oriented nanocrystals are formed at the surface at and above 40% RH (upon total cleavage, Fig. 5f). The new morphology of compact nano-rings at the interface between the CNF bulk and the Au surface is expected to create a new region of different ionic conductivity, this is supposedly the new ionic transport contribution found by impedance spectroscopy (reduced diameter of the first semicircle in Nyquist plot in Supplementary Fig. S9). Indeed, the reorientation of fiber-like fillers perpendicular to the electrode surface has been previously reported to reduce the resistance [55].

Conclusion

In this work, we have shown piezoelectric devices made of pure nanocellulose can generate as high piezoelectric output voltage (output voltage of 100 mV with 20 N of applied force) as traditional piezoelectric devices made of fluorinated polymer PVDF-TrFE. Thus, we proposed a new way of poling a biopolymer that can compete is competing with a synthetic fluoropolymer for piezoelectricity.

The reason of the unique piezoelectric performance of thin films of cellulose nanofibrils is identified to be a novel mechanism of poling taking place when a high electric field is applied in a humid environment. The newly proposed “electrochemical poling” is different from electric poling of ferroelectric materials and electric field induced fiber alignment. Combining the electrical changes observed from impedance spectroscopy and morphology change in AFM images, we proposed that the improvement of the piezoelectric performance is due to the breaking and re-orientation of the cellulose fibers under electric poling process that induces non centrosymmetric arrangement of the CNC. Despite the competitive d_{33} of the electrochemically poled CNF that is similar to PVDF, there are two drawbacks that could be further improved. First, the electrochemical poling enhancement is only effective for thin CNF films, which limit the output voltage compared to other thick devices, although the d_{33} of those materials are lower than our reported value here. Second, the rigid silicon substrates also limit the applied force. Piezoelectric sensors

based on thin films of pure cellulose are sensitive, non-toxic, biodegradable solution processible, scalable on large area. Those features bring nanocellulose on the map of green and efficient piezoelectric materials with potential impact in self-powered sensing, actuation, wearable and implantable health monitoring etc. with great advantages for internet of things and in wearable and implantable (bio-) electronic applications.

Methods

CNF films and device preparation

Nanofibrillated cellulose (CNF) was produced at Innventia AB, Sweden. 0.5 wt% CNF dispersion in water was used for the thin film fabrication. The CNF are carboxymethylated and has a degree of substitution of 0.1. CNF dispersion in DI water was used to prepare CNF films on doped Si wafers. 0.5 wt% CNF solution was poured dropwise on a Si wafer (500 μm thick) within a PDMS cavity to define the area of the CNF films. The silicon wafers are rigid substrate and not ideal for piezoelectric device fabrication and characterization. But the wafers are strong enough to withstand the imparting force used in this study. No breakage of silicon wafers and peeling off for the CNF films happened during the measurement. It has been studied that silicon wafers can endure higher force on its surface than its edges, as they can redistribute the stress when applied on the surface [56]. In our experimental setup of piezoelectric characterization, the force is applied on the surface with an effective area smaller than the total area of the silicon wafer used for the device. Thus, by avoiding the applied force to be imparted on the wafer edges we manage to characterize the piezoelectric devices with up to 45 N of applied force without breaking the wafers.

It should also be mentioned here that no surface treatment was done to the silicon wafers before CNF film preparation. As the wafers are hydrophobic thus PDMS cavity was used to prepare the films. The drop casted CNF dispersion was spread through the area of the cavity until the capillary rise of the dispersion to all the PDMS walls hold the film intact. Hence, the average thickness of the CNF film can be tuned by dropping different amount of solution. The films were then dried in an oven at 60°C for 3 h and the PDMS cavity were removed after drying.

For AFM and GISAXS characterizations, the prepared CNF films were directly used as the non-poled samples. To perform the poling, PDMS stamps coated with Cr and Au were used as top electrodes that can be removed after poling. Potentials of 110V was applied between the Au coated PDMS and the doped Si wafer for 30 s at room temperature, the top electrode was removed immediately after poling. For impedance and piezoelectric characterization, the top electrode was fabricated by evaporating Cr (5 nm) and Au (50 nm) directly on the top surface of the CNF films through home-cut plastic shadow mask.

Material characterization

A Keithley analyzer (2400) was used to pole the CNF films with different voltage. The impedance measurement was carried out with impedance spectrometer (Alpha high-resolution dielectric analyzer,

Novocontrol Technologies GmbH, Hundsangen, Germany) with an AC voltage of 10 mV in the frequency range of 0.1 Hz to 1 MHz. A dimension 3100 was used for the AFM characterization. The images were recorded in tapping mode with tips of 60 kHz resonance frequency. AFM ICON was used for PFM characterization, the Model of the conductive tip is SCM-PIT-V2 with spring constant of 3 N m^{-1} and standard deflection sensitivity of 85 nm V^{-1} (which was calibrated for each measurement).

The thickness of the CNF films was measured by using a surface profiler Dektak3ST (Veeco) across scratches on the films. Roughness of the CNF films were measured by using optical profilometer PLu neox (Sensofar).

The piezoelectric response from the devices were tested at room temperature and recorded with National Instrument (NI) systems. The applied force was controlled by tuning the amplitude of the shaker, and the frequency was maintained 3 Hz. The distance between the probe and the sample surface was kept at 1 mm for all the tests. The effective contact area is 1.13 cm^2 . The force was monitored using a force sensor (208C01) placed under the sample. The logging system is NI CDAQ 9174 chassis with NI 9263 voltage output and NI 9239 DAC modules interfaced with a computer using LabVIEW software.

Grazing incidence small-angle x-ray scattering experiments (GISAXS) were performed at the NCD-SWEET beamline of the ALBA Synchrotron, located in Cerdanyola del Vallès, Spain. The wavelength of the X-rays, λ , was 0.9998 \AA (12.4 keV), the sample-to-detector distance was 2.538 m and, the angle of incidence, α_i , was set at 0.15° . The diffracted intensity was recorded using a Pilatus 1M Dectris detector. Data were normalized by the incident photon flux and the acquisition time. The scattering vectors in the directions perpendicular and parallel to the substrate, q_z and q_x respectively, are defined as follows: $q_z = 2\pi/\lambda [\sin(\alpha_f) + \sin(\alpha_i)]$ and $q_y = 2\pi/\lambda [\sin(2\theta_f) \cos(\alpha_f)]$, where $2\theta_f$ and α_f are the exit (scattering) angles at the horizontal and vertical directions.

Piezoelectric generator fabrication and characterization

To induce the piezoelectric property in CNF films we poled the films with different poling voltage applied between the top and bottom electrode. At different humidity, the piezoelectric response of the device was recorded first before poling. The poling for each voltage last for 30 s, and afterwards the piezo response was recorded using the same electrical connection as before poling. The piezoelectric response of the poled device was measured directly after the poling finished, and the data was recorded when the signal was stable (the signal is often high at the beginning of the measurement). For the study in high and low humidity levels, the devices were first kept in fixed humidity for 2 hours and the non-poled characterization was carried out in room humidity immediately afterwards. Then the devices were returned to the same humidity for another 2 hours before the poling was conducted in the same humidity. The piezoelectric characterization of poled device was carried out right after poling in room humidity.

Declarations

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Figures

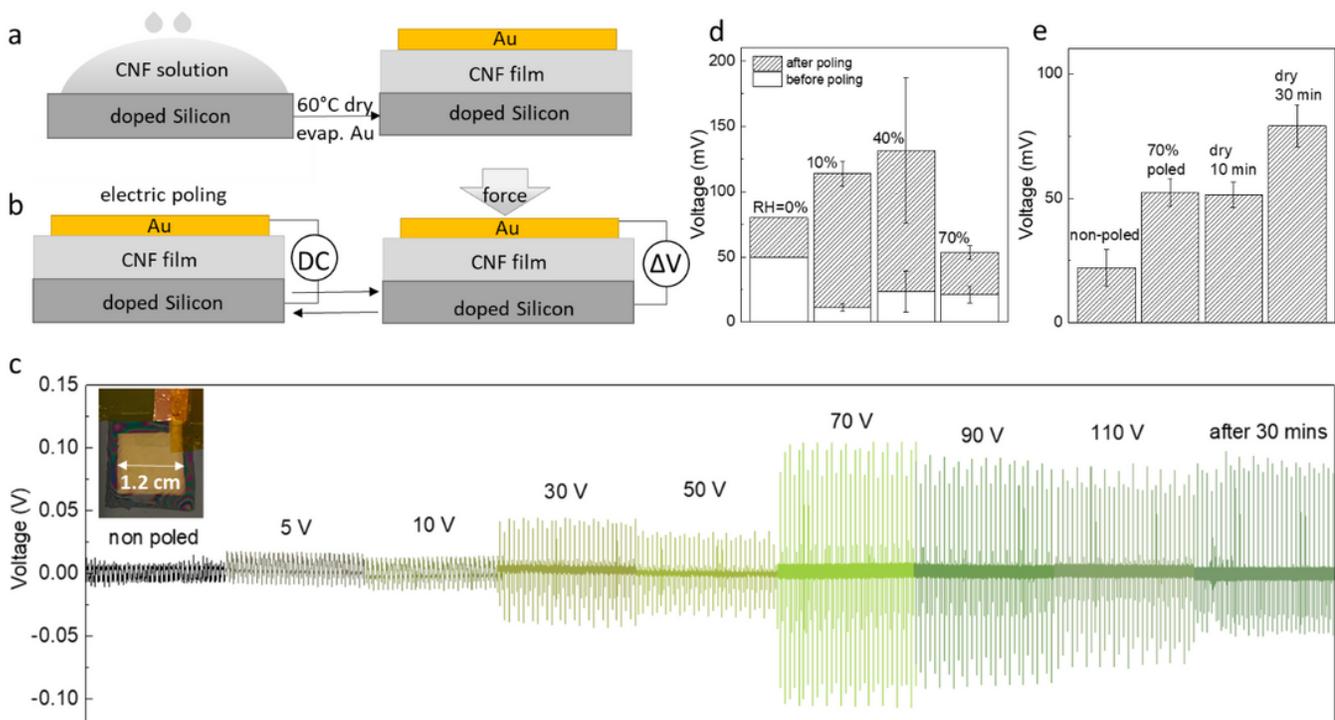


Figure 1

Demonstration of poling induced piezoelectric enhancement in CNF thin films. (a) Schematic illustration of the preparation of CNF thin film-based piezoelectric devices. (b) Poling and piezoelectric measurement of the CNF based devices. (c) Piezoelectric response of CNF film with increasing poling voltage, with an applied force of 24 N at 3 Hz frequency. The effective area of the device is 1.13 cm² where the force is applied. Inset shows the photograph and dimension of a CNF thin film-based piezoelectric device. (d) The piezoelectric output voltage of the CNF films before and after poling at different humidity. The error bars correspond to the standard deviation between 3-5 different samples. (e) The piezoelectric output voltage for CNF samples poled a 70% RH before and after drying in low humidity (10% RH). The error bars correspond to the distribution of the output voltage of the same sample in a measurement period of 20s.

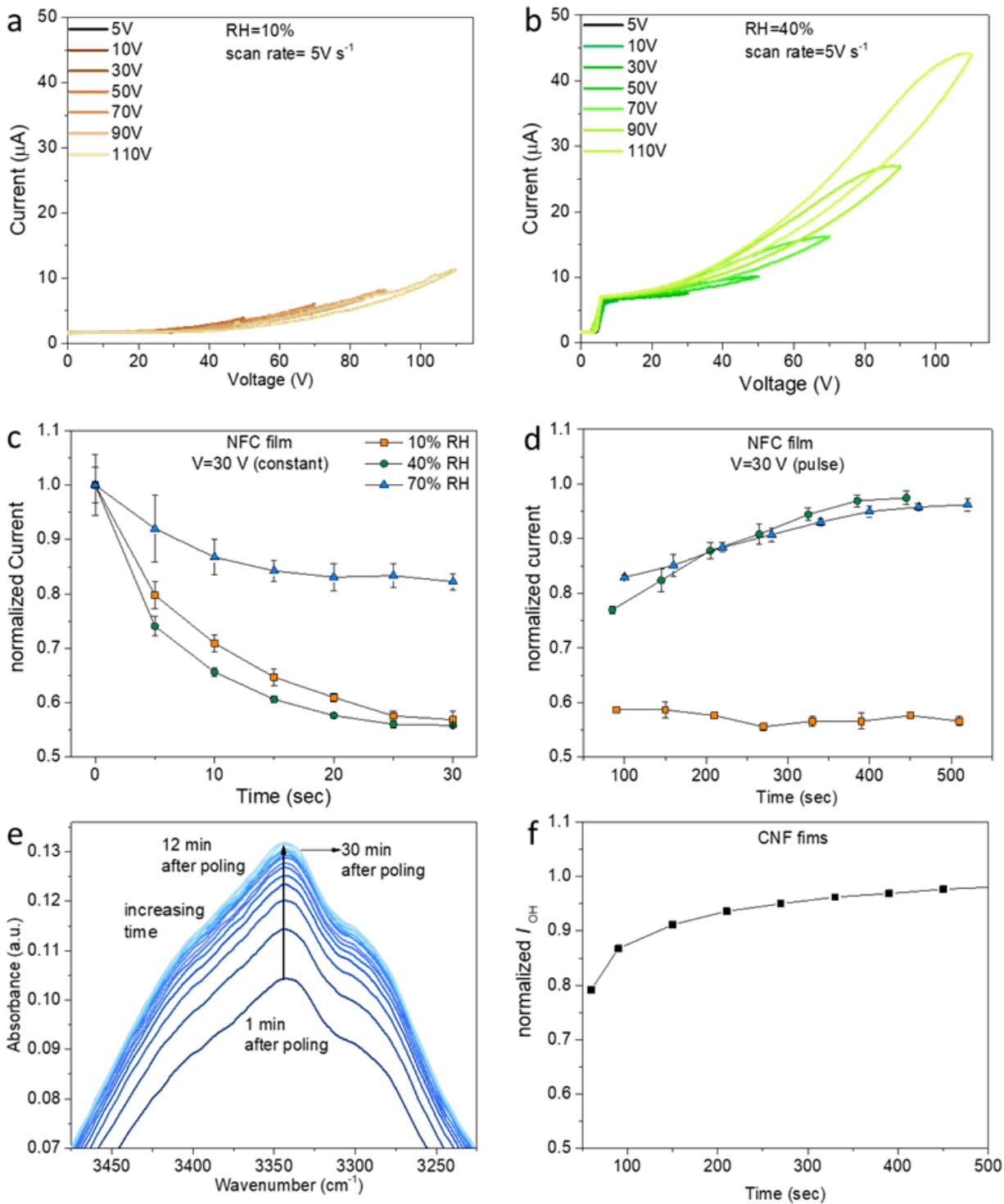


Figure 2

The impact of water in the poling process. The poling current-voltage characteristics (cyclic voltammogram) of CNF devices at (a) 10% RH and (b) 40% RH (scan rate = 5 V s^{-1}). (c) The normalized current change (compare to the current at the beginning of the poling) with time while losing water from CNF film under constant applied voltage of 30V, and (d) while regaining water after removing the constant voltage. The current was recorded by applying a short pulse voltage of 30V. e) The increasing

OH stretching peak of CNF thin film after poling with 30 V for 30s. f) The normalized intensity of the OH stretching peak changing with time. The error bar corresponds to 3 times of measurements of the same sample.

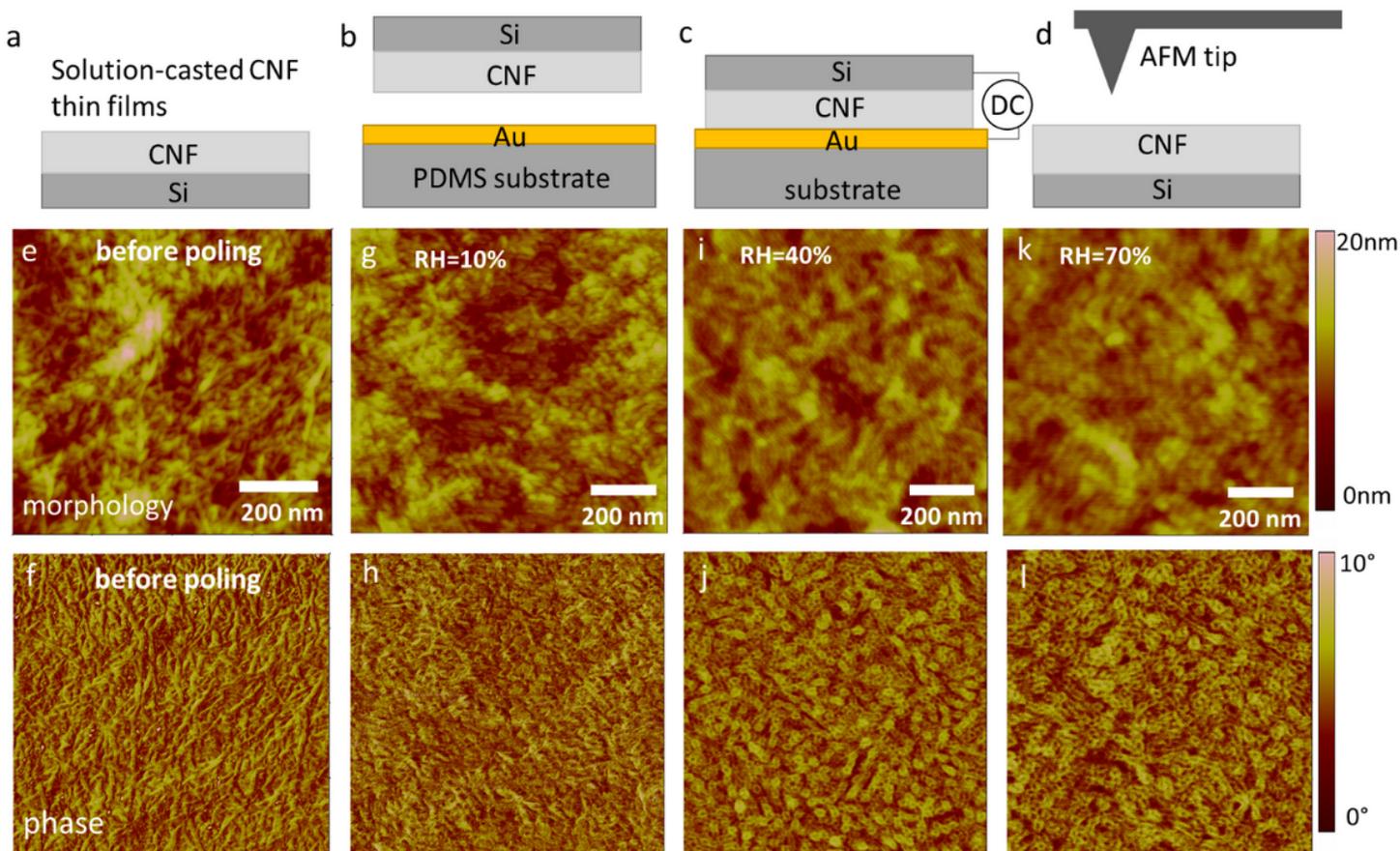


Figure 3

AFM characterization of CNF thin films before and after poled at different humidity. (a) Preparation for CNF film. (b and c) Electrical poling of CNF film (110 V) with detachable soft electrode. (d) Illustration of the AFM characterization of the surface of CNF thin films. Morphology and phase characterization of CNF thin film before poling (e and f), poled at RH=10% (g and h), RH=40% (i and j) and RH=70% (k and l). Note that the samples were kept at those RH levels for 2 hours before poling.

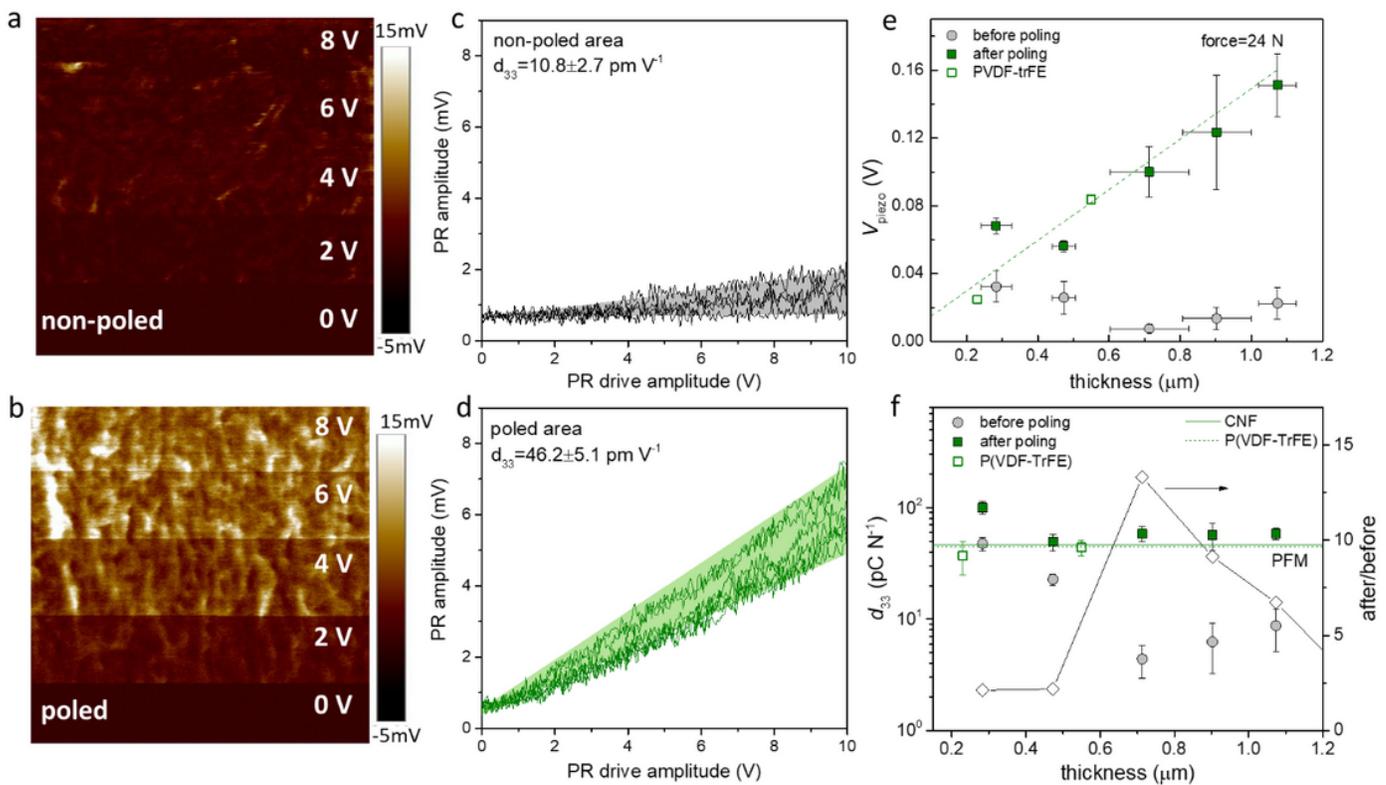


Figure 4

Piezoelectric coefficient (d_{33}) and performance of CNF thin films. The deflection amplitude under different bias for non-effectively poled (a) and poled regions (b) of CNF thin film. The spectroscopy of the deflection amplitude changes with increasing applied bias at non-effectively poled (c) and poled regions (d). 5 spots were measured for non-poled regions and 10 spots were measured for poled areas. (e) Thickness dependent piezoelectric response of CNF and P(VDF-TrFE) thin films before and after poling. The dash line indicates the calculated piezoelectric response of P(VDF-TrFE) with increasing thickness under the same force condition. (f) The piezoelectric coefficient d_{33} and the ratio of the piezoelectric output voltage of CNF films before and after poling. The error bar is the standard deviation from the 3 to 5 samples at each thickness range. The same force of 24N, 3 Hz was used.

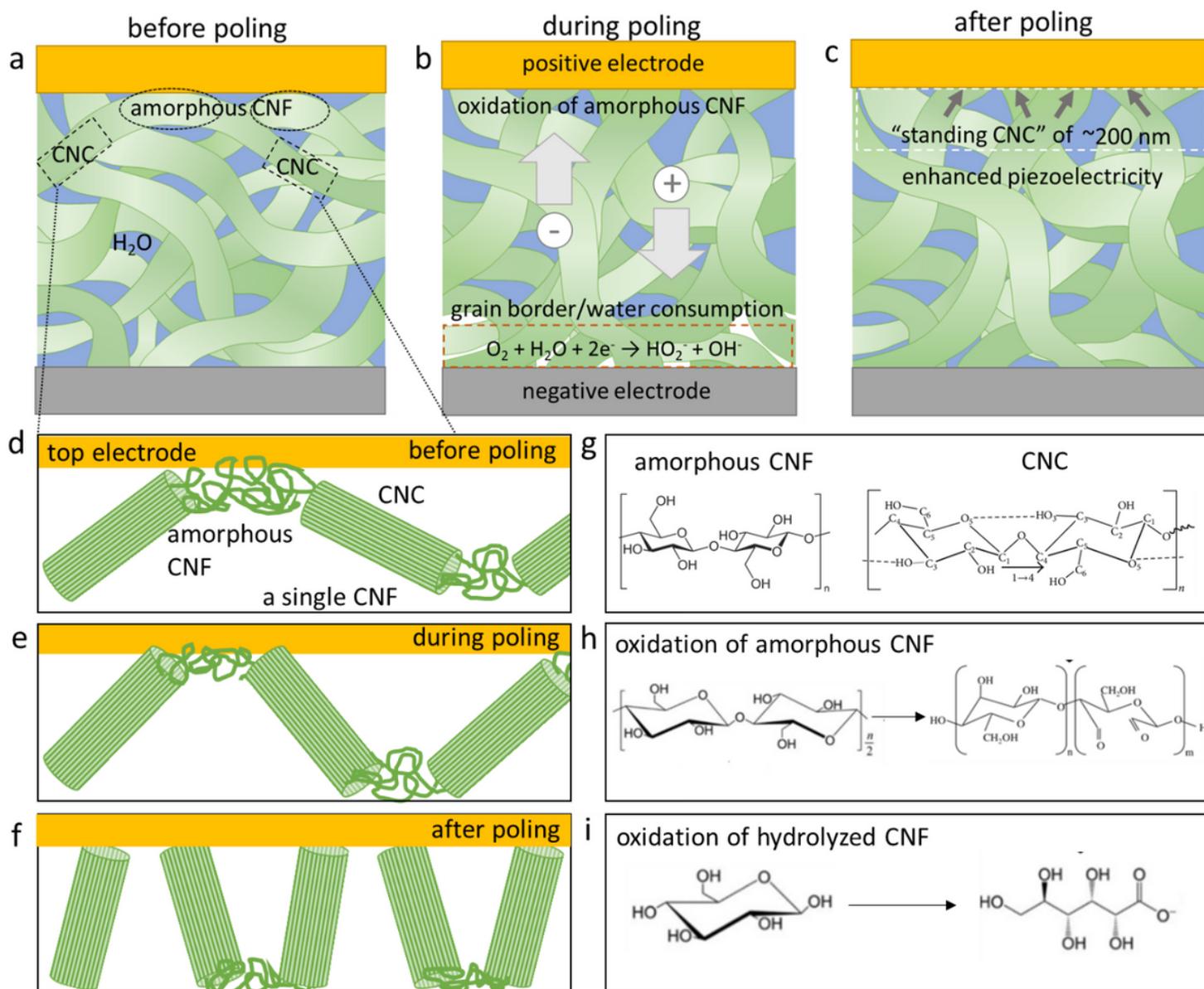


Figure 5

Illustration of the possible changes in CNF thin films during electrochemical poling. The structure of CNF film before (a), during (b) and after (c) electrochemical poling. The structure of a single CNF that is close to the top Au electrode before poling (d), during poling (e) and after poling (f). For CNF films poled at low humidity, the change might stop at (e). The chemical structures of CNF (g) and reactions for oxidation of CNF (h and i).

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