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Piezoelectric Effect of Cellulose Nanocrystals Thin Films

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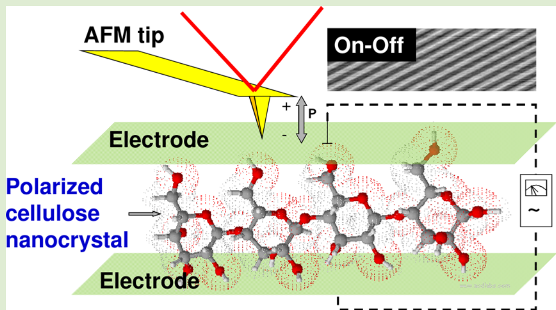
Supporting Information

ABSTRACT: Ultrathin films of aligned cellulose nanocrystals (CNCs) were assembled on mica supports by using electric field-assisted shear. The relationship between polarization gradients and strain mechanics of the obtained films was examined by monitoring their deflection with an atomic force microscope operated in contact mode. The piezoelectric response of the films was ascribed to the collective contribution of the asymmetric crystalline structure of the cellulose crystals. The magnitude of the effective shear piezoelectric constant (d_{25}) of highly ordered CNC films was determined to be 2.1 Å/V, which is comparable to that of a reference film of a piezoelectric metal oxide.



Asymmetric crystalline structures can display inhomogeneous deformation of strain gradients, associated with the piezoelectric response due to an applied electric field. Biopolymer structures with such property include cellulose, which can be used as soft electroactive material. Thus, cellulose nanocrystals (CNCs), nanoparticles of low density, high mechanical strength, thermal stability, chemical resistance, and biocompatibility,[1] can be potentially used in components requiring a piezoelectric response, including sensors and actuators, biomedical devices, and so forth.

Piezoelectricity is related to the change in polarization density and the occurrence of dipole moments within a material. It has been generally considered of significance only in highly crystalline materials. The piezoelectric effect in wood was first reported by Bazhenov in 1950.[2] However, the magnitude of the piezoelectric constant in fibers and wood is small mainly due to the random, heterogeneous distribution and a relatively small amount of crystalline cellulose in the lignocellulose matrix. The experimental verification of both direct and inverse piezoelectric effects and quantification of the constants in the piezoelectric matrix were carried out by Fukada in 1955.[3] Only the shear piezoelectric constants $-d_{14} = d_{25}$ are finite while the other components are zero, according to uniaxially oriented system of cellulose crystallites. Different wood species show considerably different piezoelectric properties. Further, the piezoelectricity of a given species varies depending on factors such as density, percentage of latewood, and so forth.[4] The piezoelectric modulus upon heat treatment of spruce increases initially and then decreases, following changes in crystallinity.[5] Hydration also plays a role since it has been shown that the piezoelectric constant of bamboo in the dry state is larger than that in hydrated form.[6] The piezoelectricity in chemical wood pulps, cotton, and cellulose derivatives such as cellophane, celluloid, and viscose rayon has been reported to depend on the fibril orientation.[7] The piezoelectric constant of regenerated nanocrystalline cellulose (II) was measured to be 35−60 pC/N, which was considered suitable for energy harvesting and power generation.[1]

Ultrathin films of CNCs have been manufactured by several methods.[8−21] Therefore, given the native crystalline nature of CNCs it is reasonable to ask the question if they can collectively yield a large piezoelectric effect. Could this specially be the case in films of highly aligned CNCs? Could such films induce high energy conversion and piezoelectricity? If this was the case, films or materials made with aligned CNCs could be useful to produce and detect sound, to generate voltage, or to manufacture nanosensors, actuators, microbalances, devices for ultrafine optical focusing, and so forth.[22] The deconstruction of fibrillar cellulose by acid hydrolysis yields cellulose nanocrystal rod-like, highly crystalline nanoparticles.

In studies related to the piezoelectric behavior of cellulose fibers, different preparation and modification routes as well as characterization techniques have been considered.[23,24] Corona poled electro-active paper made from cellulose, cyanoethylated cellulose, and LiCl-DMAc modified cotton (0.32 index of crystallinity) were reported to have piezoelectric constants of 0.167,[23] 0.1−0.2,[25] and 0.16[25] Å/V, respectively. Such previous work involved the use of cellulose (in fibers or in composites) combined with chemical additives or electrolytes to allow the piezoelectric response; however, to our knowledge ultrathin films of CNCs has not been considered yet. Therefore, our present work explores the effective piezoelectric coefficient d_{25}

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of CNCs assembled in ultrathin films which were previously manufactured by a combination of shear and electric fields. The degree of alignment of the CNCs within the films (as a function of voltage, frequency, and shear used during their manufacturing) is proposed to allow control of the piezoelectric behavior of the system and produce a large piezoelectric response.

The dielectrophoretic properties of CNCs were investigated and reported in a recent contribution.[26] The dipole density or polarization of CNCs was calculated by summing up the dipole moments per volume of the crystallographic unit cell.[27] The Clausius−Mossotti factor allowed the description of the critical and characteristic frequencies as well as the peak dielectrophoresis of CNCs. We also determined the optimal field strength for isotropic alignment in thin films. Using the same methods of our previous work,[21] we obtained ultrathin films of aligned CNCs. By using shear forces coupled with externally applied electric fields we investigated the effect of alignment on the piezoelectric response of the CNC film.

The polarizability of CNCs under uniform electric fields and shear forces during withdrawal of a deposition plate induced alignment. Mica was used as solid support for the CNCs.[21] Two reference films were obtained, without application of electric field, and used to elucidate the influence of the solid support. Film formation was observed to depend on the withdrawal rate as well as rate of solvent (water) evaporation. Homogeneous CNC deposition was observed when the solid support was modified with a positively charged polymer layer. Thus, preadsorption of low molecular weight polyethyleneimine (PEI) was used to facilitate a linear growth of ultrathin films of CNCs on mica. The buildup of single or multiple layers of CNCs depended on the concentration of the dispersion and other factors. The length of the deposited CNC films on mica with preadsorbed PEI was 5 cm. The typical film thickness and root-mean-square roughness (atomic force microscope, AFM) were of the order of 38 and 2.5−3 nm, respectively.

The piezoelectric response from the CNC film was monitored by measuring the height deflection by using a conductive AFM diamond tip. The 10 Hz signals of low and high voltage resulted in deflection perpendicular to the z-direction of the film, as observed in Figure 1. Three different sections are shown in this figure to represent the cyclic (on−off) response of the film subject to three different alternating voltages (10 Hz): 10 V (upper section), 15 V (middle section), and 0 V (bottom section). According to the shift in height as a result of changes in AC electric fields, the strain response of the film was found to be linear and nonhysteretic. To our knowledge, no detailed work related to piezoelectricity of crystalline cellulose or CNC films is available to date. Thus, this contribution provides the first experimental results showing that CNCs display such piezoelectric effects.

Piezoelectric experiments were performed on four different supported CNC films, with different degrees of particle alignment. For a given voltage 7−10 repetitions were performed and the average used to calculate the piezoelectric constant (Figure 2). A linear correlation between the measured effective displacement and the applied voltage was observed. The values reported in Figure 2 were corrected for the contribution from the solid support (mica sheet on gold-coated glass wafer). Films of partly aligned CNCs (obtained by electric field assisted-shear at 800 V/cm, 45 Hz) yielded a piezoelectric constant of 0.97 Å/V. A similar value, 1.10 Å/V, was obtained with films manufactured under slightly lower electric field strength and higher frequency (400 V/cm and 200 Hz). The respective degree of alignment for these films was 42 and 46%, respectively (Table 1). CNC films with a higher degree of alignment (88% alignment degree obtained under assembly at 800 V/cm and 2 kHz) yielded a higher piezoelectric response,

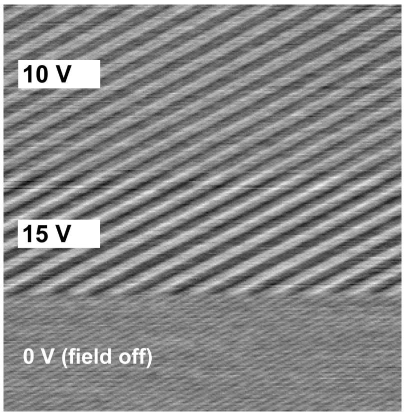

Figure 1. Map showing the extent of CNC film displacement (z direction) as a result of their piezoelectric effect. The extent of displacement is indicated by lighter or darker fields as monitored by an AFM (conductive) diamond tip in contact with the film. A single point was monitored under given intermittent electric fields (10, 15, and 0 V). The deflection measured was used to calculate the piezoelectric constant of the films. The x and z scales in the image are dimensionless but indicate film deflection evolution with time as the voltage is turned on and off (see Figure 3 for the experimental setup).

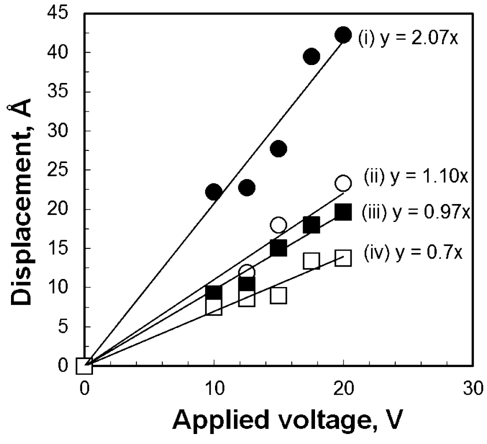

Figure 2. Vertical displacement of CNC films subject to externally applied electric fields. Included are results for films produced under four different conditions during electric field-assisted shear (films i−iv, Table 1). The films with the higher degree of alignment produced a higher piezoelectric response, as indicated by the slopes of the profiles. The displacements and voltages are both peak-to-peak values.

Table 1. Field Strength and Frequency Used during the Manufacture of CNC Films (i−iv) by Using an Electric Field-Assisted Shear Assembly Setup[a]

sample	field strength (V/cm) /frequency (Hz)	degree of alignment of CNCs (%)[26]	piezoelectric coefficient (d_{25})
i	800/2000	88	2.10
ii	400/200	46	1.10
iii	800/45	42	0.97
iv	100/2000	77	0.7

[a]The degrees of alignment of the obtained films as well as measured piezoelectric coefficient d_{25} are reported (see Figure 2).

2.10 Å/V. Thus, the alignment of polarization gradient in CNC films increased the electromechanical actuation and strain. When CNCs were aligned perpendicular to the withdrawn direction (100 V/cm at 2 kHz), a lower piezoelectric coefficient of 0.7 Å/V was measured (Table 1). Despite the expected high particle rotation at the high frequency (2 kHz), the low field strength in this case (100 V/cm) was not sufficient to effectively polarize the nanoparticles.

An explanation for the observed high piezoelectric constant of CNC films comes from the native crystalline cellulose, which comprises chains arranged parallel with a 2-fold screw symmetry along the chains due to the β-1,4 linkage of the D-glucose subunits.[28,29] The piezoelectricity of cellulose is due to the anisotropic triclinic and monoclinic unit[30−32] crystal structure association with unevenly distributed carbon atoms and change of polarization density of charged atomic groups under electric fields. This involves the occurrence of electric dipole moments within the CNC particles. The triclinic unit cell of Sugiyama et al.,[31] first suggested by Sarko and Muggli as a two-chain cell,[32] has a single-chain P1 structure, with adjacent molecules shifted monotonically by one-quarter of the unit cell size in the c direction. In the two-chain monoclinic unit cell, the corner chain is shifted $c/4$ relative to the center chain, such that the overall configuration displays staggering of adjacent chains.

A key observation is the fact that the piezoelectric response of CNC films changes as a function of CNC alignment. However, the identification of the detailed mechanism for the piezoelectric effect is beyond the scope of this study. However, it is associated with the dipolar orientation, the crystallinity and alignment of CNCs in the films. More specifically, the piezoelectricity of CNC particles involves the occurrence of electric dipole moments within the particles; this may be associated with unevenly distributed carbon atoms and change of polarization density of charged atomic groups under electric fields within the anisotropic crystalline structure of cellulose I. Overall, the naturally long-range ordered polymer chains and its polarizability are responsible for the observed high shear piezoelectricity.

The calculation of the ratio of the overall macromolecular charge and crystal skeleton constant indicates that CNCs have high flexoelectrical capacity. We note that the CNCs lie flat on the solid support and the bottom gold-coated glass slide serve as electrode. When the signal generator applies different voltages between the top and bottom electrodes, a strain of 0.02−0.1% is induced in the film, leading to a vertical displacement of the film. Such displacement $D_{i,j,k}$, due to the external electric field can be determined by eq 1:

$$D_{i,j,k} = d_{i,j,k}\sigma_{i,j,k} \tag{1}$$

where d is the piezoelectric coefficient and σ is the tensile stress. The displacement is related to the generated charge by the following relation

$$q = \int\int D_{i,j,k} dA_{i,j,k} \tag{2}$$

where dA is an infinitesimal electrode area normal to the displacement. If we consider that the piezoelectric effect is reversible, the applied voltage (or generated voltage from the strain), V, can be related by the capacitance of the thin CNC film (C_{CNCfilm}):

$$V = q/C_{\mathrm{CNCfilm}} \tag{3}$$

with

$$C_{\mathrm{CNCfilm}} = \frac{\varepsilon_{\mathrm{cell}}\varepsilon_0 l_{\mathrm{CNCfilm}} w_{\mathrm{CNCfilm}}}{t_{\mathrm{CNCfilm}}} \tag{4}$$

Here $\varepsilon_{\mathrm{cell}}$ is the relative permittivity of cellulose (4.032 F/m), ε_0 is the vacuum permittivity (8.85×10^{-12} F/m), and the dimensions of the thin film are $l_{\mathrm{CNCfilm}} = 5 \times 10^{-2}$, $w_{\mathrm{CNCfilm}} = 5 \times 10^{-3}$, and $t_{\mathrm{CNCfilm}} = 38 \times 10^{-9}$ m corresponding to the length, width, and thickness, respectively. The calculated capacitance is thus ∼235 nF. Using the measured displacement of the film it is possible to calculate the known, applied voltage using eq 3 in one direction only:

$$V = \frac{d_{14}\sigma dA}{C_{\mathrm{CNCfilm}}} = \frac{d_{14}Et_{\mathrm{CNCfilm}}}{C_{\mathrm{CNCfilm}}}\int \varepsilon t_{\mathrm{CNCfilm}} \mathrm{d}t \tag{5}$$

where E is the elastic modulus of nanocrystalline cellulose (assumed to be 137 GPa[11]). Equation 5 results in a calculated applied voltage on the thin film of 23.9 mV. Thus, the range of applied voltages (10−20 V) used for generating the piezoelectric displacement seems sufficient enough for 10% measurable strain in the film in the perpendicular direction of the c axis. As the film thickness increases, a lower capacitance and hence a higher generated output voltage or piezoelectric response can be expected. However, further investigation needs to be carried out to elucidate more details about the effect of the CNC thin film thickness. We note that the inherent structure (CNC alignment) of the thin film was not considered in this calculation, and therefore the results are only provided as a guesstimate.

Some of the CNC films tested here yielded a piezoelectric constant which was higher than the d_{33} value measured for a 400 nm ZnO film, 1.3 Å/V. This latter experimental value was in agreement with reported figures and provided verification of our measurement system.[33] Note that the piezoelectricity of ZnO thin films is thickness- and crystal orientation-dependent; hence Ar sputtering of the ZnO thin film can enhance c-axis orientation and the piezoelectric constant.

In conclusion, we report the first experimental results showing that CNCs have a large piezoelectric response. In addition, the design and fabrication of ultrathin films of CNCs induce a high electromechanical actuation and strain which changes as a function of CNC alignment. Such structures can result in high mechano-electrical energy transfer. Thus, the electromechanical properties of ultrathin films of CNC can be considered in potential applications given their flexoelectric behavior, biodegradability, and renewability.

■ MATERIALS AND METHODS

Details about the source and production of cellulose nanocrystals[34] (CNCs) and the manufacturing of aligned CNC films[26] are given in the Supporting Information document. Typical CNC film thicknesses were estimated to be of the order of 38 nm, and therefore they consisted of CNC multilayer structures (approximately 6 layers, considering the measured CNC dimensions).

A high degree of CNC orientation in the films is a key characteristic for the piezoelectric response. Electric fields (10 Hz) of different strengths were applied on the films, which resulted in strain due to the converse piezoelectric effect. Piezoelectric measurements were performed in contact mode by measuring the deflection of the AFM tip in a Quesant Q-Scope AFM (x−y scans were disabled; see Figure 3). Commercially available conducting diamond AFM tips were used to avoid electrostatic interaction between the tip and the sample. These experiments were carried out in an environment with constant relative humidity (50%) and temperature (23 °C). The bottom electrode, underneath the CNCs films fixed on the AFM stage, was

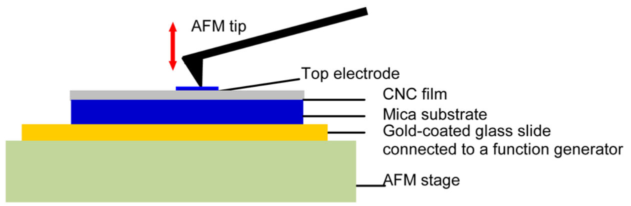

Figure 3. Schematic illustration of the AFM system used to measure the displacement of CNC films in contact with an AFM diamond tip and under given applied voltages (10 Hz frequency).

connected to a signal generator using commercially available BNC cables. For the top electrode, a copper probe was used. Each measurement lasted ca. 30 s. The AFM tip deflection in the *z*-direction (extension or contraction) was recorded using a built in lock-in-amplifier. To avoid the tip–sample electrostatic interaction, the AFM stage was grounded. For the piezoelectric measurement a 10 Hz sin frequency signal was employed using Wavetek M134 signal generator; this frequency was selected on the basis that it is below the tip resonance and most environmental noise (20–200 Hz). The peak-to-peak voltage was varied by 2.5 V units with a maximum value of 20 V. During the experiment at one given voltage, 7–10 displacement measurements were carried out, and the averaged value was used in the calculation. The piezoelectric constant was calculated from the correlation slope of the measured tip displacement at the applied voltage. Reference measurements were performed on (420 nm) ZnO thin films. The ZnO film was obtained from deposition on silica wafer using an argon sputtering technique, and platinum (Pt, 164 nm) is used as the bottom electrode.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details about the source and production of CNCs and the manufacturing of aligned CNC films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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