Discovery of Cellulose as a Smart Material

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ABSTRACT: The past 10 years has witnessed a renewed interest in cellulose research and application, sparked mostly by technological interests in renewable raw materials and more environmentally friendly and sustainable resources. In this paper, we further expand the current knowledge in cellulose applications and technologies by reporting our discovery of cellulose as a smart material that can be used for biomimetic sensor/actuator devices and micro-electromechanical systems. This smart cellulose is termed electroactive paper (EAPap). It can produce a large bending displacement with low actuation voltage and low power consumption. The actuation phenomenon and its characteristics are illustrated in this paper. Because cellulose EAPap is ultra-lightweight, inexpensive, and biodegradable, it is advantageous for many applications such as micro-insect robots, micro-flying objects, micro-electromechanical systems, biosensors, and flexible electrical displays.

1. Introduction

Cellulose is the most abundant natural polymer on earth, consisting of glucose−glucose linkages arranged in linear chains, where every other glucose residue is rotated in the opposite direction.[1] It has been estimated that the yearly biomass production of cellulose is 1.5 trillion tons, making it an inexhaustible source of raw material for environmentally friendly and biocompatible products.[2] Cellulose derivatives are used for coatings, laminates, optical films, pharmaceuticals, foods, and textiles. Numerous new applications of cellulose take advantage of its biocompatibility and chirality for the immobilization of proteins and antibodies and for the separation of enantiomeric molecules as well as the formation of cellulose composites with synthetic polymers and biopolymers. Wood pulp remains the most important source in cellulose processing used for papers and cardboards. The discovery of an electromechanical coupling effect in wood dates back to 1950 when Bazhenov reported a piezoelectric response in wood.[3] In 1955, Fukada experimentally verified the piezoelectric coefficients of wood and demonstrated that oriented cellulose crystallites were responsible for the observed shear piezoelectricity.[4] Piezoelectricity, a linear coupling between electrical and mechanical properties, is displayed by crystal structures that lack a center of symmetry (non-centrosymmetric). Most biopolymers, such as hair, wool, bone, collagen, DNA, protein, and wood,[4,5] are naturally oriented and exhibit shear piezoelectricity due to the internal rotation of polar atomic groups associated with asymmetric carbon atoms. Oak, pine, spruce, birch, alpha cellulose, and wood pulp are all cellulose-based biopolymers that exhibit shear piezoelectric constants comparable to that of quartz crystal.[3] Shear piezoelectricity in woods varies depending on the type of wood, orientation of wood samples, moisture, and temperature. Despite these early studies, however, the potential of cellulose as a smart lightweight material that can be used as a sensor and an actuator has not been fully explored.

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$$(C_6H_{10}O_5)_n + n\mathrm{NaOH} \rightarrow (C_6H_9O_4ONa)_n + n\mathrm{H_2O} : \textit{Sodium cellulose, swelled cellulose}$$

$$(C_6H_9O_4ONa)_n + n\mathrm{CS_2} \rightarrow n\,(\mathrm{SC{-}OC_6H_9O_4})_n : \textit{Sodium cellulose xanthate}$$

$$n\,(\mathrm{SC{-}OC_6H_9O_4})_n + \mathrm{H^+} \rightarrow (C_6H_{10}O_5)_n : \textit{regenerated cellulose}$$

Figure 1. Regenerated cellulose process with xanthate cellulose solution.

As a naturally occurring biopolymer, cellulose is a type of electroactive polymer (EAP).[6−10] EAPs, also termed artificial muscles due to their operational similarity to biological muscles, refer to a class of materials that has received much attention in the past 10 years, owing to the unique set of promising characteristics such as large strains in response to an electric stimulus, low density, ease of processing, and good mechanical properties. To demonstrate the applicability of cellulose as a smart EAP, a bending actuator is processed, fabricated, and tested in our laboratory using cellulose paper. The fabrication process, actuation phenomenon, and the test results are explained.

2. Experimental Section

Preparation of Cellulose EAPap Actuator. Cellulose EAPap is made with a cellulose film. Cellulose film can be made by dissolving cellulose fibers into a solution and cast it. Cellophane is a well-known cellulose film made with cellulose xanthate solution. Commercial cellophane made from Weifang Co., China, was used as a cellulose film for EAPap actuator. Figure 1 shows the chemical reaction for cellulose xanthate process. Cotton pulps are saturated with sodium hydroxide and allowed to steep for enough time for the caustic solution to penetrate the cellulose and convert it into sodium cellulose. After pressing, shredding, and aging process, the solution is treated with gaseous carbon disulfide to form xanthate ester groups. Then the solution is allowed to stand for a period of time to ripen. After the solution is made, it is extruded through a nozzle into two sulfuric acid baths, followed by drying process. Once the solution is coagulated in the acid bath, it is converted back to pure while cellulose. A roller system is conveying the film via these baths, and washing and drying processes are followed by a reel system.

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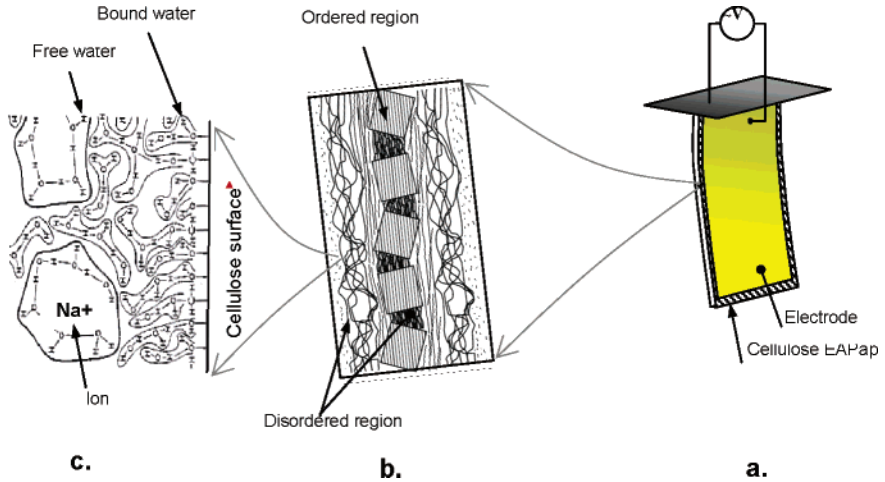


Figure 2. Concept of electroactive paper actuator: (a) cellulose microfibril has ordered crystalline regions and disordered regions; (b) EAPap is made from cellulose paper on which gold electrodes are deposited on both sides; (c) water molecules are bonded with hydroxyls on the cellulose surface (bound water) or clustered in free (free water).

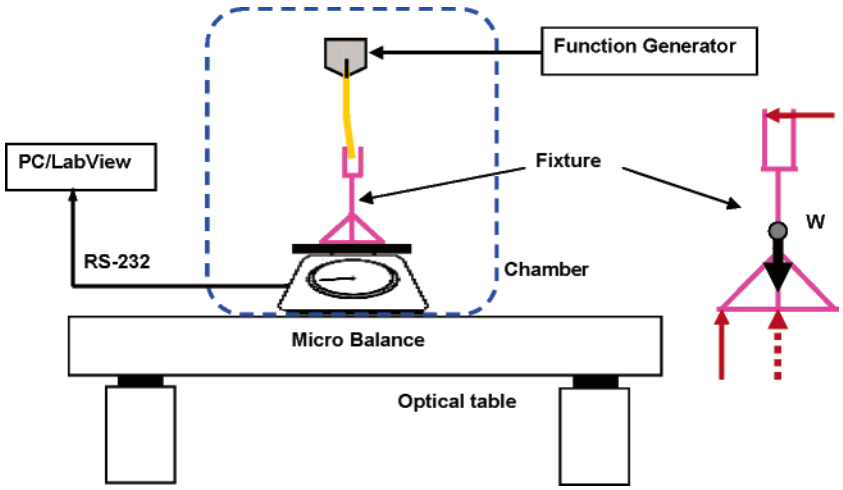


Figure 3. Schematic diagram of the force measurement system.

Figure 2a shows the cellulose electroactive paper (EAPap) as a bending actuator. Gold electrodes are deposited on both sides of the cellophane by means of physical vapor deposition. The thickness of gold electrodes was extremely thin, so that its stiffness was negligible compared to that of the cellophane. The size of sample was 30 mm × 10 mm, and the thickness was 0.03 mm. In nature, cellulose never occurs as a single chain but exists from the moment of its synthesis as a crystalline array of many parallel, oriented chains—microfibrils—which are its fundamental structural units. A microfibril of cellulose has both crystalline and amorphous domains (Figure 2b).

To understand the fundamental behaviors of the material, physical and chemical characterization is necessary. The Young's modulus of the material was measured using the material testing system (Instron 5542). Since cellulose film has different mechanical properties in the machine direction (0°) and transverse direction (90°), samples were cut into three orientations, 0°, 45°, and 90°. Three samples in each orientation were pulled with slow speed, and strain and stress were recorded in the computer of the testing system. To investigate the ion concentration in the cellulose films, a chemical analysis was performed by using inductively coupled plasma mass spectrometer (ICP-MS). The dielectric constant of the cellulose film was measured using the LCR meter (HP 4284A).

Bending Displacement Measurement. To measure the tip displacement of EAPap actuators, a computerized displacement measurement system was made. An EAPap actuator was supported vertically in an environment chamber that can be controlled the humidity and temperature. Function generator (Agilent 33220A) controlled by a computer sent out the excitation voltage to the actuator, and it produced a bending deformation. The tip displacement of the EAPap actuator was measured by the high-precision laser Doppler vibrometer (Ometron VS100) mounted on an optical table, and the signal was converted to the displacement through the Labview software in the computer. Simultaneously, the current probe (Tektronix TCPA300) measured the input current supplied from the function generator.

Force Measurement. The measurement of output force of EAPap actuator is important for the performance evaluation. To simultaneously acquire the tip blocked force, a microbalance was used. Figure 3 shows the schematic diagram of the force measurement system. An EAPap actuator was fixed vertically in the environmental chamber by using tongs and the microbalance (Precisa XT220A, micronewton resolution) was mounted on an optical table. A vertical fixture was placed on the balance, and the tip of the actuator was contacted with the fixture. Since the tip of EAPap actuator was contacted by the top of the fixture, a horizontal pushing force on the fixture was converted to the vertical force due to the moment equilibrium of the fixture structure. The pure vertical force was measured by the balance after nullifying the initial weight of the vertical fixture.

XRD Test and TSC Test. To understand the actuation phenomenon, X-ray diffraction (XRD) and thermally stimulated current (TSC) measurement were performed. XRD was measured with the X-ray diffractometer (D/MAX-2500, Rigaku). XRD patterns with Cu Kα radiation at 40 kV and 30 mA were recorded $2\theta = 5-80°$. TSC was used to characterize cellulose-based EAPap under electric field and temperature conditions. TSC analysis is a more sensitive tool to detect the relaxation phenomena for the material composing

Table 1. Ion Contents in the Cellulose Film (in ppm)

element	amount	element	amount
Na	1693.08	S	2867.59
Al	391.95	Cu	89.47
Cr	97.81	Pb	117.08
Co	1.281	Zn	179.13

of molecular chains with dipolar nature such as cellulose. From this analysis, the relaxation phenomena can be inferred, which is associated with orientation polarization of permanent or induced dipoles and real charge injection. The classical procedure in TSC includes (1) heating the sample to a given temperature (200 °C), (2) applying the electric field at this temperature for a time *t*, (3) cooling the sample down to room temperature with the field on to freeze-in any dipolar alignment, (4) reheating the sample at a slow rate while monitoring the current to quantify any dipolar alignment that took place in step 2 (350 °C), and (5) the sample is reheated one last time while current is monitored once again (350 °C). This last step may differentiate between current discharge due to dipolar alignment and real charge injection (space charge); real charge injection may not fully escape the material in one heating. Before testing the TSC, the sample was kept at 80 °C in the vacuum oven for a day to remove the free water in the cellulose paper sample. The glass transition temperature of the cellulose film was 203 °C.

3. Results and Discussion

Characterization of Cellulose EAPap Material. Before testing the performance of the cellulose EAPap actuator, its physical and chemical properties were tested. When the material was tested, the Young's modulus ranged from 4.3 to 7.1 GPa, depending on the orientation. The Young's modulus in mechanical direction was higher, and the transverse direction was lower; meanwhile, the 45° direction was 5 GPa. The density of the cellulose film was 0.77. The ion concentration in the cellulose film was analyzed using ICP-MS (Table 1). Large amounts of sodium and sulfur were observed. Notice that the amount of sulfur is almost twice that of sodium, which is expected from the xanthate reaction. Also, some other metallic ions such as aluminum and chrome were observed. These ions might be observed from the bathing and washing processes. The relative dielectric constant was measured at 20 Hz, and it was between 40 and 20, depending on the orientation. The mechanical direction exhibited a higher dielectric constant. This dielectric constant value is larger than ordinary papers.

Performance of Cellulose EAPap Actuator. When an electric field was applied across the thickness direction of the paper, it produced a large bending deformation. For a 30 mm long EAPap sample, a maximum tip displacement of 4.2 mm and the maximum force of 12.7 mN were obtained under the applied voltage of 0.23 V/μm, at 7 Hz, 95% relative humidity and in room temperature (Figure 4). The corresponding electric field required to reach displacement saturation is 1−2 orders of magnitude lower than that of other electronic EAPs.[8] The humidity affects the displacement, where a high relative humidity leads to a large displacement. The displacement increases by as much as 2 orders of magnitude when the humidity is increased from 50% to 95%.

According to Prof. Zhang's paper,[9] the elastic energy density can be found as $E = (1/2)Y\epsilon^2 = (1/2)9 \times 10^9(3.8 \times 10^{-4})^2 = 650$ J/m^3 = 0.84 J/kg. Here, the bending strain ϵ was found by $\epsilon = h/2\rho$, where h is the thickness and ρ the radius of curvature. The radius of curvature can be found from the maximum tip displacement, 4.2 mm. According to ref 6 (p 82), the required net energy density for biological muscles is 0.2−40 J/kg. Thus, the specific energy density of EAPap is marginally within the requirement for artificial muscle actuators. The high Young's modulus of cellulose EAPap material, compared with that of other ionic EAP materials, can allow the possibility of enhancing the storable energy density.

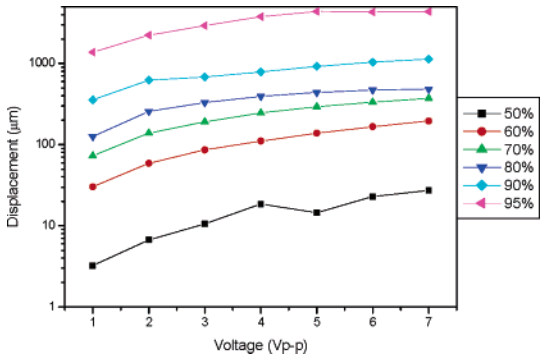
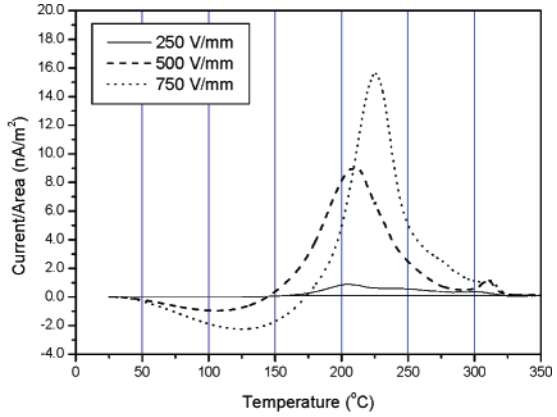


Figure 4. Tip displacement of EAPap bending actuator with different relative humidity (%): room temperature (23 °C) and 4 Hz actuation frequency.

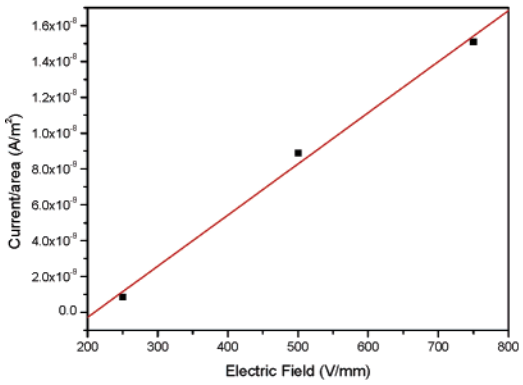
The electrical power consumption was 18 mW, which corresponds to 5 mW/cm^2. This low electrical power consumption is promising for achieving a microwave-driven actuator. Cellulose EAPap can be integrated with a microstrip antenna, so-called rectenna (rectifying antenna). When microwave arrives at the rectenna, it converts the microwave power into dc power, and this power is distributed to the EAPap actuator via power allocation device (PAD) circuit. Since rectenna and PAD are thin film based, they can be integrated onto cellulose EAPap, which comprise a remotely driven EAPap actuator. This means that EAPap actuators can be remotely driven using microwaves, making them attractive candidates for ultra-lightweight multifunctional applications such as micro-insect robots, flapping wings for flying objects, smart wallpaper, MEMS, and so on.

Actuation Phenomenon. To successfully transit cellulose EAPap actuators into these applications, it is crucial to ascertain the actuation mechanism responsible for the performance parameters mentioned above. On the basis of the cellulose structure and our processing of the cellulose-based EAPap, we believe that the actuation is due to a combination of two mechanisms: ion migration and dipolar orientation. In the rest of the paper, we present experimental evidence of both.

Cellulose EAPap material is a sheet of regenerated cellulose. Morphologically, regenerated cellulose has ordered and disordered regions, in which the ordered domains are mostly crystalline. The disordered molecules retain preferential direction parallel to the chains in the microfibrils, and they form surface disorder on the microfibrils. Figure 2b shows the concept of microfibril. The EAPap material has large regions of disordered cellulose chains, where water molecules can be found attached to hydroxyl groups (Figure 2c). During the paper making process, sodium ions were injected in the paper fiber.[11] When an external electric field is applied, these ions can be mobile and migrate to the anode. In addition, the molecular motion of free water in disordered region cannot be restricted by the cellulose molecules, and the water molecules can be interacted with ions in the cellulose. In the presence of electric field, the sodium ions surrounded with free water molecules will move to the anode. Selective ionic and water transport across the polymer under electric field results in volumetric changes, which in turn lead to bending. When a dc electric field was applied, the cellulose EAPap actuator was bent to the positive electrode, which confirmed the above explanation. The ambient humidity effect on the EAPap actuator performance is a further evidence of this, where ion transport is facilitated when humidity intake is higher.



a.



b.

Figure 5. TSC results of cellulose EAPap: (a) the depolarized current with temperature with different poling electric fields; (b**)** the peak current values as a function of the poling electric field. The straight line shows the linear relationship between the electric field and the depolarization current.

Cellulose EAPap material is composed of molecular chains with a dipolar nature. In particular, the crystal structure of cellulose II is monoclinic, which is non-centrosymmetric and exhibits piezoelectric and pyroelectric properties. To investigate the dipole effects in EAPap, TSC analysis[12] was used. Figure 5a shows the depolarized current with temperature with different poling electric fields, and Figure 5b shows the peak current values as a function of the poling electric field. The depolarization current increases linearly as the poling electric field increases. This behavior is usually indicative of dipole orientation.[13] Generally, the polarizability of dielectric materials may be separated into several parts. An electronic contribution arises from a displacement of the electron shell relative to a nucleus and an ionic contribution from the displacement of a charged ion with respect to other ions. In cellulose material that possesses molecular groups having permanent molecular dipole moments such as water or the hydroxyl and carboxyl groups will also make a contribution.[11] At low frequency all of these parts contribute to the polarizability, as will any free ions (space charges) in the material. As the frequency increases, the space charges and permanent dipoles relax out. Space charges are usually the first to relax out, followed by the permanent dipole groups. In the cellulose EAPap, the presence of disordered region gives rise to localized states associated with hydrogen bonding of cellulose chains. Since there are many localized states, the release or excitation of the carriers in these states may dominate the charge transfer process. Thus, the disordered region mainly contributes to the dipolar orientation, by stabilizing dipoles and leading to a permanent polarization, resulting in a piezoelectric behavior.

Further investigating the actuation behavior of EAPap material, XRD was done on an EAPap sample before and after the electrical actuation. Figure 6 shows the XRD results. Table 2 summarizes the X-ray diffraction peaks before and after the actuation. After actuation, the (110) peak at $2\theta = 12.26°$ decreases to 12.08° while the (200) peak at $2\theta = 21.64°$ increases slightly to 22.02°. Quality factors were found on these peaks. A large quality factor indicates sharp peak. It is cleat that the (110) peak sharpened after the actuation while the (200) peak was changed to blunt. This confirms that the first peak was increased, and the second peak was decreased. Notice that the small peak at $2\theta = 16.78°$ only appears after the electrical activation. This means that some structural change have happened during the electrical actuation, which may be associated with the crystallization of amorphous region. In other words, crystallization of amorphous cellulose of EAPap sample

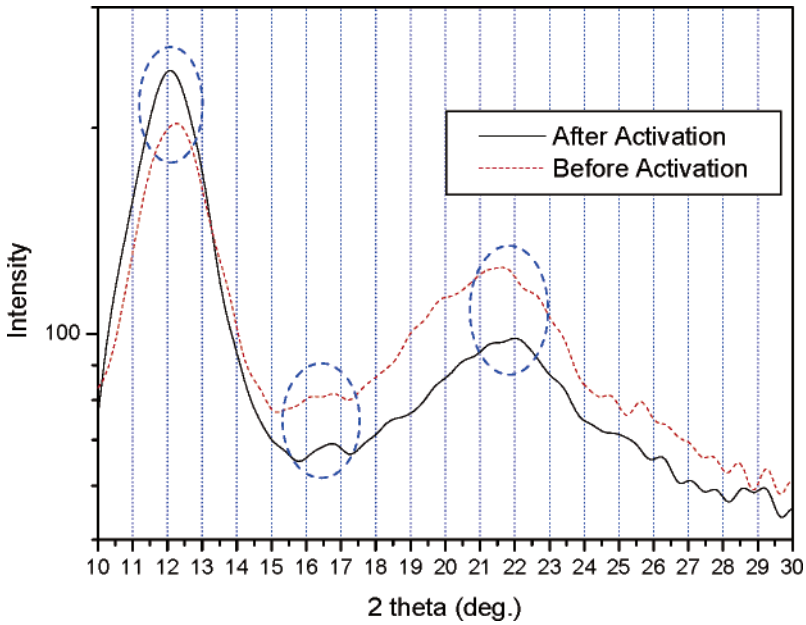
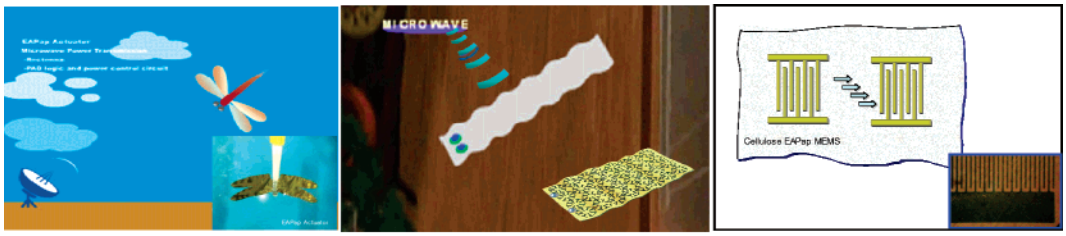


Figure 6. XRD result: the (110) peak at 12.26° was decreased to 12.08°, and the (200) peak at 21.64° was increased slightly to 22.02°, while the small peak at 16.78° was started to appear after the electrical activation.



A. B. C.

Figure 7. Cellulose paper applications: (A) micro-flying object; (B) micro-insect robots; (C) biodegradable MEMS.

Table 2. X-ray Peaks of Cellulose EAPap Material before and after Electrical Actuation (Last Two Columns Show the Peaks for Cellulose I and II for Comparison)

	before		after			
	peak location	*Q* factor	peak location	*Q* factor	cellulose I	cellulose II
(110)	12.26	67.7	12.08	87.9	14.80	12.10
($1\bar{1}0$)	16.78		16.74		16.30	19.8
(200)	21.46	22.6	22.02	12.9	22.60	22.0

is accelerated by molecular rearrangement during the electrical activation, leading to a structure closer to that of cellulose II allomorph. Structural changes of native cellulose crystals have been made by annealing in aqueous alkaline and acid solutions in high temperature.[14] However, there has not been any report that the cellulose polymorphs can be changed in the presence of electric fields. Our observation may be the first report on the structural change of cellulose by applying electric field. PVDF is a phase transformation example: alpha phase is transformed into beta phase in the presence of electric field. Moisture content may cause crystal growth in regenerated cellulose material accompanied by molecular rearrangement due to sorbed water.[15] The electrical activation is believed to enhance the recrystallization. This enhanced crystallization may improve the piezoelectricity of EAPap material.

4. Summary and Conclusions

We reported the discovery of cellulose paper as a smart material by demonstrating a EAPap bending actuator that exhibted a large displacement, low actuation voltage, and low electrical power consumption. We note that the cellulose-based EAPap material has recrystallized in the presence of electric field in such a way that the material exhibits enhanced bending actuation. The recrystallization happens mostly in the disordered region of cellulose. By combining piezoelectricity of cellulose and ionic transport, this oriented EAPap material will enable inexpensive and lightweight biomimetic actuators and MEMS devices. Cellulose-based EAPap material is also promising as biosensors since it is biodegradable, biocompatible, sustainable, and capable of broad chemical modification and has high mechanical stiffness and strength. Control of disordered region, recrystallization, and orientation of cellulose are all issues that need to be addressed in order for cellulose EAPap to fulfill its promise as a smart material.[16,17]

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