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Piezoelectric Paper Fabricated via Nanostructured Barium Titanate Functionalization of Wood Cellulose Fibers

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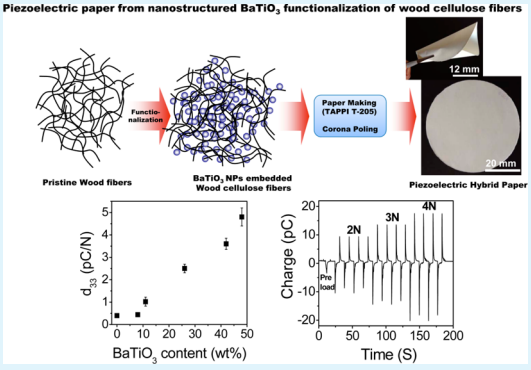
Supporting Information

ABSTRACT: We have successfully developed hybrid piezoelectric paper through fiber functionalization that involves anchoring nanostructured $BaTiO_3$ into a stable matrix with wood cellulose fibers prior to the process of making paper sheets. This is realized by alternating immersion of wood fibers in a solution of poly(diallyldimethylammonium chloride) PDDA (+), followed by poly(sodium 4-styrenesulfonate) PSS (−), and once again in PDDA (+), resulting in the creation of a positively charged surface on the wood fibers. The treated wood fibers are then immersed in a $BaTiO_3$ suspension, resulting in the attachment of $BaTiO_3$ nanoparticles to the wood fibers due to a strong electrostatic interaction. Zeta potential measurements, X-ray diffraction, and microscopic and spectroscopic analysis imply successful functionalization of wood fibers with $BaTiO_3$ nanoparticles without altering the hydrogen bonding and crystal structure of the wood fibers. The paper has the largest piezoelectric coefficient, d_{33} = 4.8 ± 0.4 pC N^{-1}, at the highest nanoparticle loading of 48 wt % $BaTiO_3$. This newly developed piezoelectric hybrid paper is promising as a low-cost substrate to build sensing devices.



KEYWORDS: *wood cellulose fiber, barium titanate, hybrid paper, functionalization, piezoelectric coefficient, piezoelectric paper*

1. INTRODUCTION

Paper is one of mankind's greatest inventions and is produced by pressing moist wood cellulose fibers together. Since its creation, paper has been subjected to a lot of innovation to meet changing requirements. Paper is made from renewable resources (cellulose fibers obtained from various natural sources, such as wood chips, stems, or other plant parts), and the pulp and paper industry is well-established worldwide. Functionalized specialty paper has the potential to extend the traditional applications of paper and serve as a low-cost substrate in the development of new sensing devices. One important motivation for this is the hope that environmentally safe and low-cost materials could allow for more widespread use of sensing technology and enable unique applications that are not possible with other materials. For example, these could include disposable devices, for applications in the biomedical field, environmental control, and for personal monitoring devices. In this context, researchers have recently developed a wide range of sensing devices using paper as a substrate that find applications in the areas of electronics,[1,2] microfluidics,[3−5] energy storage,[6−8] and strain sensing.[9,10]

In addition to the well-known and widely used piezoelectric materials, such as quartz, tourmaline, and pervoskite materials ($BaTiO_3$, PZT), wood cellulose is also known to exhibit piezoelectricity.[11] Fukada[12] and Bazhenov[13] were the first to deliver a comprehensive description of mostly direct macroscopic piezoelectric phenomena in wood. The most important results of their experiments were that wood exhibits both direct (for sensing) and converse (for actuation) piezoelectricity, and they found that the piezoelectric effect is strongest when wood is loaded at an angle of 45° to the direction of the wood fibers, and that a reversal of the load direction results in a change of the polarity of the electric field. However, it is challenging to use this property in implementing practical as wood cellulose possesses very small piezoelectric coefficients. It is reported that regenerated cellulose possesses large piezoelectric constants that match the piezoelectric properties of commercial piezoelectric polymer polyvinylenedene fluoride (PVDF). In order to achieve these results, wood must undergo a multistep process, such as dissolution of wood fibers in organic solvents, centrifugation, curing and washing with solvents, stretching, and electric poling.[14] Unfortunately, the resulting material suffers from inconsistency in the piezoelectric properties from batch to batch. These variations could add significant cost to any commercial-scale production. In addition, the regeneration process involves the use of toxic chemicals.

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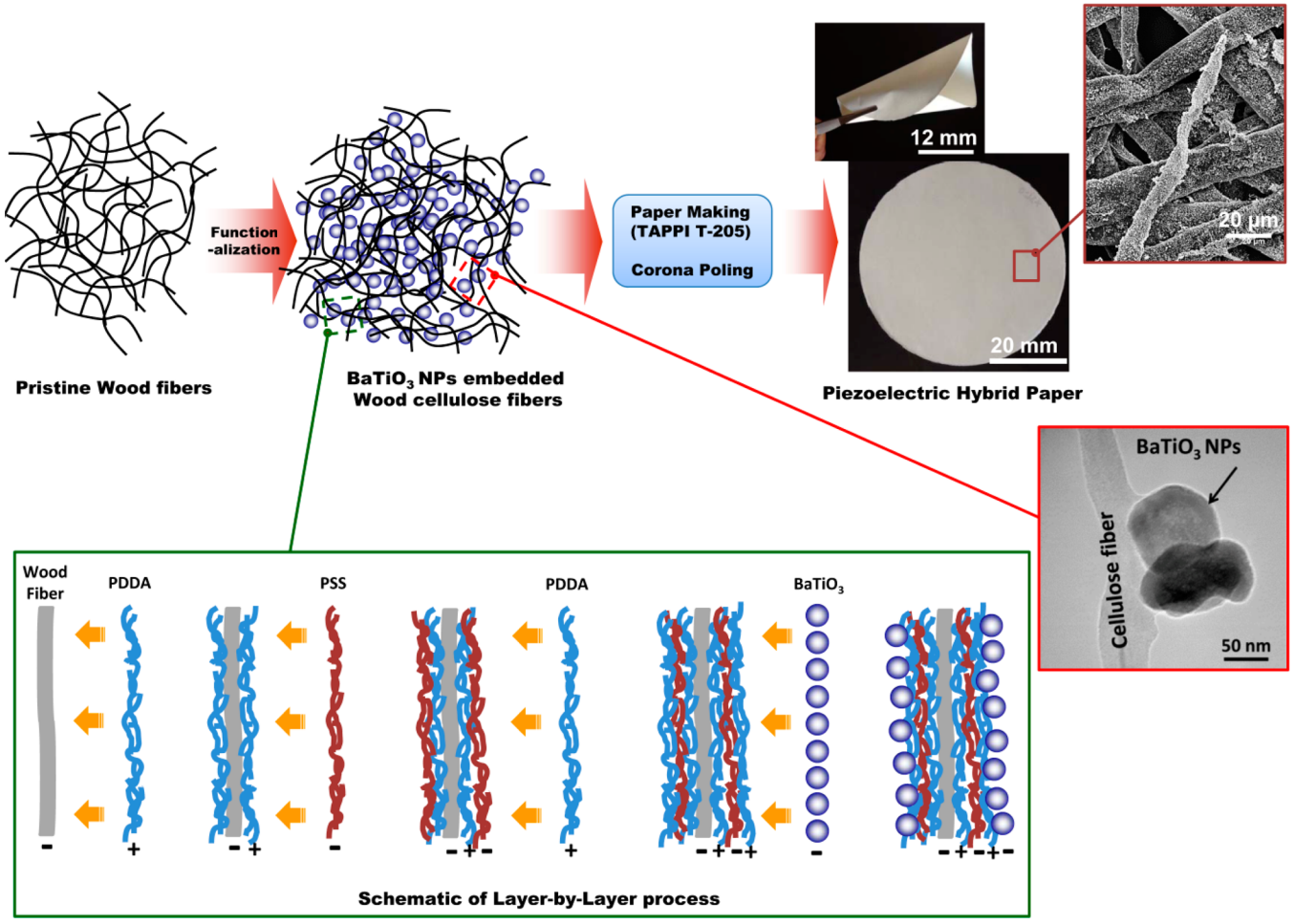

Figure 1. Schematic representation of the piezoelectric hybrid paper fabrication process.

2. BACKGROUND

Mainly driven by the potential inexpensive applications and environmental benefits, significant research efforts have been recently devoted to developing flexible piezoelectric material using paper as a substrate. It was shown that synthesis of nanostructured zinc oxide (ZnO) on a paper substrate is a successful method for realizing flexible piezoelectric paper. Most of the work reported to date relies on wet chemistry, which involves hydrothermal synthesis of ZnO nanostructures on paper substrates at low temperature. Gullapalli et al. have developed a technique for growing piezoelectric ZnO nanostructures on printing paper substrates by adopting a wet-chemistry route and demonstrated its application for strain sensing and energy harvesting.[15,16] A piezoelectric nanogenerator based on paper was reported by Kim et al., wherein well-aligned ZnO nanorods were grown on the paper substrate via a wet-chemistry approach; interestingly, they showed excellent energy harvesting performance even under thermally harsh conditions.[17] Qui et al.[18] recently grew ZnO nanorods on flexible packing paper and demonstrated its capability as a nanogenerator. They employed room-temperature radio frequency (RF) magnetron sputtering to deposit a seed layer prior to the hydrothermal synthesis of ZnO nanorods. More recently Soomro et al. reported a piezoelectric power generator from ZnO−paper.[19] They synthesized ZnO nanorods on a cleanroom paper substrate, using a thin seed layer deposited by spin-coating. In all these instances, ZnO nanostructures were hydrothermally grown only on the paper fibers exposed on the surface of the sheet, and in these cases, paper acts primarily as an inactive substrate to support the growth of active nanostructures. In addition, this technique presents challenges to the scalable mass production of such paper. While growing ZnO nanostructures on paper substrates via an aqueous chemical route, some paper can soften in the heated growth solution, hence making it necessary to use a rigid and insoluble paper substrate for this purpose. The anisotropic properties of the paper substrate due to overlapping and alignment of fibers leads to anisotropic growth of nanostructures on the surface not necessarily aligned with the out-of-plane direction, while other methods employed sophisticated equipment (such as RF sputter) to deposit the seed layer. The fabrication process for synthesizing ZnO on paper can be expensive and time-consuming as it requires several hours to grow the nanostructures. To address these issues, more recently, Ko and Yu proposed a technique to grow ZnO nanorods directly on the cellulose fibers.[20] Their approach involves (i) preparation of wood cellulose fibers from paper, (ii) coating a seed layer onto the fibers, (iii) thermal drying, and finally (iv) synthesizing ZnO nanorods on the fibers. Although, the proposed method ensures the growth of ZnO nanorods on each and every wood cellulose fiber, after immersion into the seed solution, drying in a dark room for 24 h and oven-drying for 5 h (150 °C) is required to ensure appropriate adhesion between the seed material and the wood fibers. This step

significantly increases the fabrication time and also results in the formation of agglomerated pulp clusters, which are difficult to disintegrate by mechanical agitation. Hence, when a paper handsheet is formed, fiber lumps can be seen throughout the paper (see Figure S1, Supporting Information), which significantly hinders the paper quality while the process is expensive, time-consuming, and cannot be easily integrated into the existing paper-making process to produce piezoelectric paper.

In this report, we propose a simple, cost-effective, and scalable manufacturing method to directly attach nanostructured barium titanate ($BaTiO_3$) to each and every wood fiber during the paper-making process. The basic idea of the new manufacturing process involves embedding $BaTiO_3$ into a stable matrix of wood fibers; this can be achieved through fiber functionalization. The fiber functionalization process is realized using a layer-by-layer (LbL) approach, and this results in the creation of a positively charged wood fiber surface. Immersion of thus treated fibers into a $BaTiO_3$ suspension results in electrostatic binding of the $BaTiO_3$ nanoparticles directly onto each fiber.

3. EXPERIMENTAL SECTION

Reagents and Materials. Bleached softwood kraft pulp in the form of sheets was received from Canfor Pulp Limited Partnership, Prince George Mills, BC, Canada. Washing these sheets with distilled water led to sheet disintegration to obtain the wood fibers. Poly(diallyldimethylammonium chloride) (PDDA, 20 wt % in water, MW 100 000−200 000) and poly(sodium 4-styrenesulfonate) (PSS, MW 70 000) were purchased from Sigma-Aldrich. Sodium chloride (ACS certified) and tetragonal $BaTiO_3$ nanoparticles with a particle size of 300 nm (99.9% purity) were purchased from Fisher Scientific and US Research Nanomaterials Inc., respectively. All the chemicals were used as received.

Piezoelectric Paper Fabrication. Piezoelectric paper was prepared by fiber functionalization using an electrostatic self-assembly or LbL processing. First, $BaTiO_3$ suspensions with a range of concentrations (0.125, 0.25, 0.5, 0.75, and 1 wt %) were submitted to sonication. Then, aqueous solutions of positively charged polyelectrolyte PDDA (1 wt % in 0.5 M NaCl) and negatively charged polyelectrolyte PSS (1 wt % in 0.5 M NaCl) were prepared. An approximately 2−3 g (dry weight) of wood fibers in the wet state were alternatively immersed in the solutions of 100 mL of PDDA (+) and 100 mL of PSS (−) and once again in 100 mL of PDDA (+), resulting in the creation of a positively charged surface on the wood fibers. To ensure removal of excess and poorly adsorbed polyelectrolytes, following each immersion step (20 min), the wood fibers were rinsed with deionized water. The treated wood fibers were then immersed in a $BaTiO_3$ suspension, leading to an electrostatic binding of the negatively charged $BaTiO_3$ to the fibers. Finally, paper handsheets were made according to the TAPPI method T-205.[21] In brief, a Handsheet Maker fitted with a polyester mesh screen was used to make handsheets with a diameter of 16 cm and a thickness of 70−100 μm. A 0.4 L $BaTiO_3$-attached wood fiber suspension with 0.3% consistency was poured into the feed cylinder of the handsheet maker containing deionized water and was further diluted by adding water until the engraved line on the cylinder, resulting in a total volume of the suspension in the feed cylinder of 7.25 L, and its final consistency was neither measured nor estimated. After mechanical agitation, the cylinder was drained. The handsheet was couched with blotters, lifted off the screen and pressed (345 kPa for 5 min), and dried at 25 °C and 50% relative humidity. The hybrid paper handsheets were finally subjected to corona poling to render them piezoelectric. Corona poling was performed at 120 °C for 4 h with a needle voltage of 17 kV and a grid voltage of 5 kV; further details on the corona poling setup and the procedure can be found in ref 22. A schematic of the piezoelectric hybrid paper fabrication process is shown in Figure 1. It is important to note at this point that there have been numerous reports published on cellulose fiber functionalization;[15−20,23] however, all of these processes are comparatively expensive and time-consuming and cannot be easily integrated into standard paper-making processes to produce piezoelectric paper. Our proposed piezoelectric paper manufacturing method is simple and can be easily integrated into standard paper-making processes, and it is also cost-effective as it does not employ any sophisticated equipment. In addition, the chemistry used here is environmentally friendly.

Characterization of Piezoelectric Paper. Fourier transform infrared (FT-IR) spectra were recorded in the range of wavenumbers from 600 to 3800 cm^{-1} with a resolution of 4 cm^{-1} using a PerkinElmer Frontier FTIR-ATR. The X-ray diffraction (XRD) patterns were recorded with an X-ray diffractometer (Bruker D8 Advance) using a Cu Kα target at 40 kV and 50 mA, at a scanning rate of 0.015°/min. The diffraction angle ranged from 10 to 70°. Attachment of $BaTiO_3$ nanoparticles to the wood fibers was observed using an FEI Technai G2 transmission electron microscope (TEM). The morphology of pristine and $BaTiO_3$-attached pulp was examined by a scanning electron microscope (SEM Hitachi S570 with electron backscatter diffraction detector). Prior to imaging, the samples were coated with gold (~70 nm thick). Zeta potential measurements were performed on the wood fibers and on the $BaTiO_3$ nanoparticles under different conditions using a Zeta Sizer Nano Series (Malvern) instrument. The amount of $BaTiO_3$ nanoparticle loading of the paper handsheets was estimated by a thermogravimetric analysis (TGA) using a PerkinElmer STA 6000 Simultaneous Thermal Analyzer, with a heating rate of 20 °C/min, in the range of 30−650 °C with air purging at 20 mL/min.

The tensile properties of the piezoelectric hybrid paper were characterized using a standard tensile test and in accordance with the TAPPI Method T 494 using an L&W Tensile Strength Tester; tests were performed at 25 °C and 50% relative humidity and at a pulling rate of 25 mm/min. In each case, 10 samples were tested. The piezoelectric coefficient of the functionalized paper

$$d_{33} = \frac{\text{Induced Charge}}{\text{Applied Load}}$$

was measured by applying a compressive load of 2, 3, and 4 N to a 6 × 20 mm^2 sample and recording the corresponding charge on the electrodes using a computer-interfaced charge meter (Kistler Charge meter 5015 from Inter Technology Inc.). Five measurements were performed for each sample.

4. RESULTS AND DISCUSSION

In our approach, we chose fiber functionalization over a hydrothermal synthesis technique to prepare piezoelectric paper that involves anchoring nanostructured $BaTiO_3$ onto the wood fibers prior to forming the paper sheet. As shown in the FTIR spectrum (Figure 2), wood cellulose fibers contain carboxyl (1646 cm^{-1}) and hydroxyl (3328 cm^{-1}) groups,[24] in

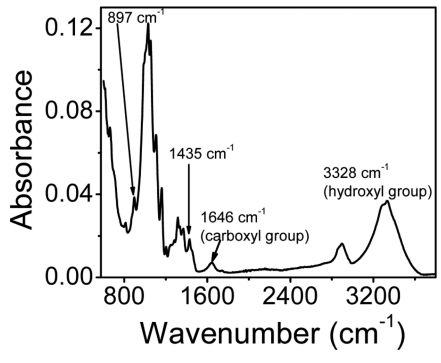

Figure 2. FT-IR spectrum of pristine wood fibers.

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addition to many other characteristic peaks, such as CH_2 scissoring (1435 cm^{-1}), C−O−C asymmetric stretching (897 cm^{-1}), and C−O stretching at C_6 (983 cm^{-1}).[25,26] Among them, carboxyl and hydroxyl groups are highly ionizable and are normally negatively charged in aqueous media. $BaTiO_3$ nanoparticles are also negatively charged when in contact with aqueous media. Zeta potential measurements on the pristine wood fibers and $BaTiO_3$ support this, with zeta potentials of −21.1 ± 3.99 and −23.5 ± 4.13 mV, respectively. This shows the necessity of the intermediate layer; hence, the attachment of $BaTiO_3$ nanoparticles onto wood fibers was enabled through a positive polyelectrolyte interlayer, which results from the alternating deposition of PDDA (+) and PSS (−) and PDDA (+) monolayers. This process generates a positively charged wood fiber surface and ensures charge and morphological homogeneity. Activating the surface modified wood fibers in a $BaTiO_3$ suspension leads to attachment of $BaTiO_3$ nanoparticles to the wood fibers through the strong electrostatic interaction between them. This is supported through the Zeta potential of functionalized fibers before (+45.2 ± 5.19 mV), and after (−21.8 ± 6.08 mV) immersing in the $BaTiO_3$ suspension. Note that no substantial change in $BaTiO_3$ loading on wood fibers was witnessed when a suspension of $BaTiO_3$-attached wood fibers has been subjected to strong mechanical agitation (as revealed by TGA; data not shown). This is due to the strong bonding between the fibers and the nanoparticles through the electrostatic attraction that is comparable to using common adhesives.[27] This demonstrates that the positive polyelectrolyte interlayer is sufficient to maintain a strong association between the fibers and the nanoparticles during the paper-making processes. Please note that this approach can also be employed to functionalize other nanostructured piezoelectric materials (PZT, for example) onto wood cellulose fiber to achieve better piezoelectric properties of the hybrid paper. We also examined the different states (pristine, positively charged, and $BaTiO_3$-functionalized) of the wood fibers by FTIR, to study any changes in their structure, and the data are provided in the Supporting Information. As noticed in Figure S3 (Supporting Information), no significant change in peak position or intensity of the peaks was observed; this suggests that neither the polyelectrolyte nanocoating nor the presence of such nanoparticles on the wood fibers has altered the hierarchal network structure or hydrogen bonding of the fibers. On the other hand, no characteristic FTIR peaks related to the chemical structure of PDDA and PSS (e.g., C−N, C−S, and SO_3) could not be identified. This is due to the fact that FTIR in not sufficiently sensitive to detect an extremely small amount of materials deposited on the wood fibers; in addition, the characteristic absorption peaks of the wood fibers and the polyelectrolytes overlap slightly so that it is difficult to discern a small peak originating from a small amount of polyelectrolyte. Because of these circumstances, UV absorption spectroscopy would be more useful to characterize the polyelectrolytes nanocoating onto wood fibers; further details can be found in the published report by Wang and Hauser.[28]

The wide-angle XRD pattern of the hybrid paper is shown in Figure 3, and it exhibits reflection peaks at 2θ of 15.6° and 22.8°corresponding to the (110) and (200) planes of the cellulose I structure.[29] The remaining peaks located at 22.12, 31.52, 38.76, 55.97, and 65.8° correspond to $BaTiO_3$,[30] while the two Bragg peaks located at 44.8° and 45.4° represent the (002) and (200) planes of the tetragonal phase of $BaTiO_3$.[31] We also performed the XRD measurements on wood fibers,

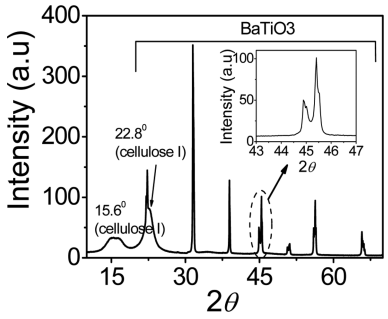

Figure 3. X-ray diffraction pattern of piezoelectric hybrid paper (42 wt % $BaTiO_3$).

before and after coating with polyelectrolyte (data provided in the Supporting Information; refer to Figure S4). These measurements revealed no significant change in intensity, position, and full width at half-maximum (FWHM) of the peaks corresponding to cellulose. This implies that the crystal structure of the wood fibers remains intact following the functionalization process, and these observations are in agreement with the FTIR results. The morphologies of the $BaTiO_3$-functionalized wood fibers at the micro- and nanoscales are provided in Figure 4. They suggest successful attachment of

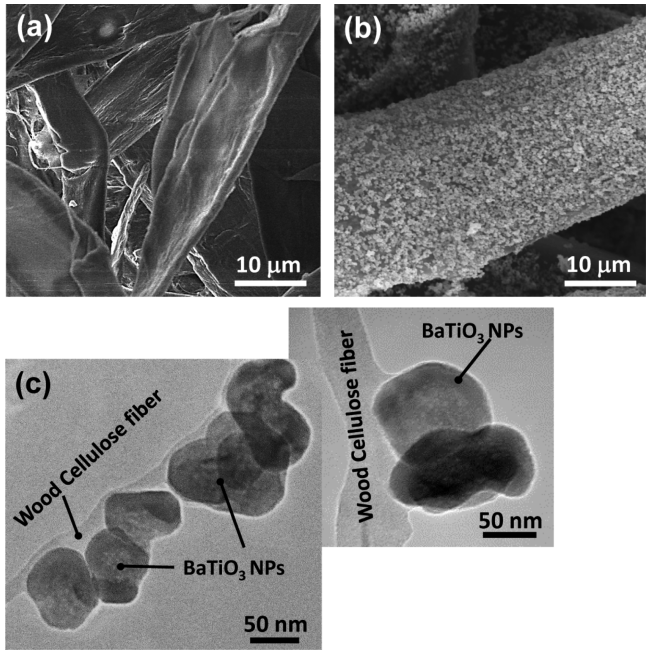

Figure 4. Microphotograph of (a) pristine wood fibers, and (b, c) micro- and nanoscale images of $BaTiO_3$-attached wood fibers (48 wt %).

$BaTiO_3$ nanoparticles onto wood fibers. The nanoparticles are likely to attach to the fiber surface, leading to a compact coating. The attachment of nanoparticles onto wood fibers occurs through the strong electrostatic binding between negatively charged $BaTiO_3$ nanoparticles and the positively charged polyelectrolyte chains previously deposited to the wood fibers. Hence, electrostatic bonding produces a dense coating of $BaTiO_3$ nanoparticles on the wood fibers, as evidenced by the SEM micrograph shown in Figure 4b. Our attempt to attach the $BaTiO_3$ nanoparticles onto the wood fibers without polyelectrolyte nanocoating failed because of the

repulsive forces between the fibers and the nanoparticles. In addition, our attempt to attach the $BaTiO_3$ nanoparticles onto the wood fibers with the assistance of one nanocoating (only PDDA coating) has led to poor attachment of $BaTiO_3$ nanoparticles to the wood fibers. Further details about this study will be discussed in the following section.

TGA was employed to estimate the amount of nanoparticle loading of the hybrid paper. Figure 5 shows the thermogravimetry curves of pristine paper and hybrid paper prepared by activating in 0.75 wt % suspension. Pristine paper undergoes decomposition in two steps (at approximately 378 and 546 °C), and a similar trend was observed for the hybrid paper. The mass residue left after heating to 650 °C indicates the amount of $BaTiO_3$ loading. Pristine paper undergoes complete decomposition at 650 °C, and no mass residue is observed, whereas hybrid paper showed a mass residue even after heating at 650 °C. For example, the residual mass of the hybrid paper prepared by activating the wood fibers in a 0.125 wt % $BaTiO_3$ suspension is approximately 8% (data provided in the Supporting Information; refer to Figure S5), and hence, the $BaTiO_3$ loading of this paper was 8 wt %. This low loading with $BaTiO_3$ nanoparticles is due to the limited availability of nanoparticles in the suspension. The amount of $BaTiO_3$ nanoparticles loaded onto the fibers can be increased by increasing the suspension concentration; by doing so, the largest loading achieved was approximately 48 wt % by activating wood fibers in a 1 wt % suspension, whereas only 35 wt % loading was achieved, when coated with only one layer of PDDA and in a 1 wt % suspension of particles (refer to Figure S6 in the Supporting Information). This implies that a single coating of positively charged polyelectrolyte (PDDA) could create an unstable and/or heterogeneous positively charged surface on wood fibers, leading to a reduction in nanoparticle coverage. However, coating wood fiber with two PDDA layers with the assistance of the negatively charged polyelectrolyte (PSS) as an interlayer creates a stable and homogeneous positively charged surface on the wood fibers and promotes a significant increase in nanoparticle loading.

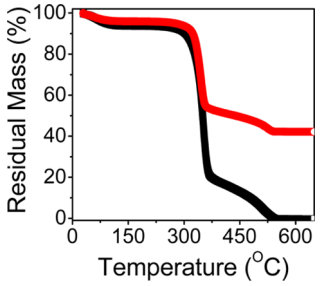

Figure 5. Thermogravimetry curves of pristine paper (black) and piezoelectric hybrid paper prepared by activating in 0.75 wt % $BaTiO_3$ suspension (red).

In our approach, we used wood cellulose fibers as a stable matrix to incorporate and support the piezoelectric nanoparticles; hence, it is also necessary to assess the strength of the resulting paper and ensure that the mechanical properties are not significantly compromised by the functionalization. Figure 6 compares the fracture strength and maximum strain of the hybrid paper as a function of $BaTiO_3$ loading. It was found that incorporating 8 wt % of $BaTiO_3$ nanoparticles into the paper resulted in a reduction of the breaking strength and maximum strain by approximately 15%, in comparison to a pristine paper sheet. These properties tend to decrease further with an increase in nanoparticle loading, and the highest reduction (73%) in breaking strength and maximum strain of paper sheets was observed at 48 wt % nanoparticle loading. We did not expect an improvement in the strength of paper due to nanoparticle loading as we have not employed any surfactant or binders. The reason for the reduction in strength of the hybrid paper is the reduced adhesion between the functionalized wood fibers. As shown in Figure S7 (Supporting Information), with an increased loading of nanoparticles, the surface of the wood fibers is covered with a denser nanoparticle coating. This $BaTiO_3$ coating could potentially interfere with fiber−fiber bonding, leading to a reduction in paper strength. However, this can be addressed by adding commercially available paper-strength-enhancing additives, such as starch and carboxymethyl cellulose (CMC). These strength-enhancing additives will provide the required mechanical strength to the piezoelectric paper by improving fiber−fiber bonding while allowing a high loading with $BaTiO_3$.

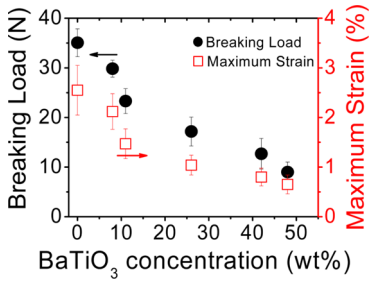

Figure 6. Strength properties of piezoelectric hybrid paper as a function of $BaTiO_3$ concentration.

The piezoelectric behavior of the hybrid paper was examined by subjecting it to electromechanical tests. For that, a compressive load of 2, 3, and 4 N was applied to a 6 × 20 mm^2 sample and the corresponding charge induced by the paper was measured using a charge meter. Each force step was repeated four times. The time constant of 0.1 s was set on the charge meter so that the signal decays before the application of the next pulse. A positive voltage (corresponding to negative charge) was measured by the charge meter due to compression of the paper, while a negative voltage of the same magnitude was measured upon releasing the compressive load, indicating reversal of the polarization. A typical measured response of the hybrid paper to an applied load is shown in Figure S8 (Supporting Information). The piezoelectric charge produced by the hybrid paper when loaded to 3 N is 13.5 pC, and it increases to 23.8 pC for 5 N. The piezoelectric charge measured from the hybrid paper with 48 wt % of $BaTiO_3$ is shown in Figure 7; the data reveals that the piezoelectric response of the hybrid paper significantly increases with $BaTiO_3$ loading (see Figure S9, Supporting Information). We also measured the response of the hybrid paper subjected to 2 and 7 N loadings, each repeated eight times. The paper showed a repeatable piezoelectric response over time (see Figure S10, Supporting Information). Figure 8 shows the effective piezoelectric coefficient, d_{33}, of the hybrid paper as a function of $BaTiO_3$ loading. The measured d_{33} of pure paper (0 wt % $BaTiO_3$) is estimated to be 0.4 ± 0.08 pC N^{-1}. The wood itself possesses piezoelectricity, and cellulose crystallites are mainly responsible for that.[11−13] However, when the $BaTiO_3$ content in the hybrid paper is increased to 11 wt %, d_{33} increases to 1.02 ± 0.2 pC N^{-1}. According to Figure 8, d_{33} tends to increase with

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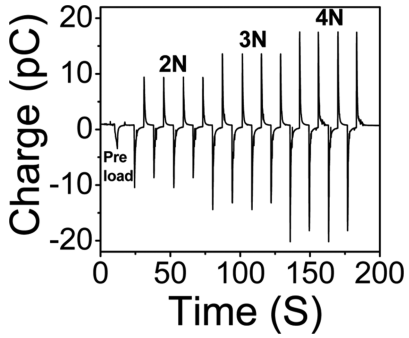

Figure 7. Piezoelectric response of piezoelectric hybrid paper (48 wt % $BaTiO_3$) under mechanical loading.

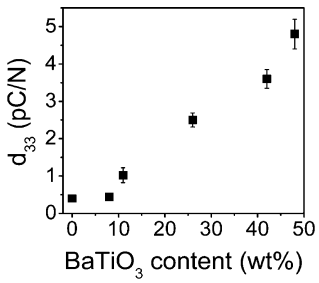

Figure 8. Piezoelectric charge constant d_{33} of piezoelectric hybrid paper as a function of $BaTiO_3$ concentration.

a $BaTiO_3$ loading up to 4.8 ± 0.4 pC N^{-1} at 48 wt % $BaTiO_3$, the highest loading studied in these experiments. Compared to the large piezoelectric coefficient of bulk $BaTiO_3$ (d_{33} = 75–190 pC N^{-1}),[32] our hybrid paper exhibits a significantly lower piezoelectric response. This is not entirely unexpected, and many of the nanostructured piezoelectric material based devices reported in the literature so far have a lower effective piezoelectric coefficient when compared to their bulk and theoretical predictions,[33,34] as shown in Table 1. The small d_{33} values for hybrid paper could be partially due to the different conformation of $BaTiO_3$ crystals on the wood cellulose fibers, and these crystals may be stressed in numerous different modes under an applied load. However, it is most likely that the cellulose fiber network is able to absorb a large proportion of the applied stress, reducing the effective strain in the nanoparticles and contributing to the lower than bulk piezoelectric response.

Table 1. Compared Piezoelectric Constant of Nanostructured and Bulk Piezoelectric Materials

material[a]	piezoelectric coefficient d_{33} (pC N^{-1})	remarks[a]	reference
ZnO nanowire array	0.25	substrate-free, self-supporting ZnO nanowire arrays embedded in PDMS	34
ZnO nanowire array	5–11.5	ZnO nanowire arrays grown on Cu substrate and embedded in PMMA	35
bulk ZnO	12.4		32, 35
$BaTiO_3$ paper	4.8 ± 0.4	nanostructured $BaTiO_3$ embedded in a stable matrix of wood fibers	present work
bulk $BaTiO_3$	75–190		32
PA11/$BaTiO_3$	5	composite prepared by combination of mixing and hot-pressing process	31

[a]PA11: Polyamide 11; PDMS: poly(dimethylsiloxane); PMMA: poly(methyl methacrylate).

5. SUMMARY AND CONCLUSIONS

A simple and new manufacturing method has been proposed to fabricate a piezoelectric paper substrate for various applications. The proposed fabrication approach utilizes wood cellulose fibers and nanostructured $BaTiO_3$ as base materials, and the process involves embedding $BaTiO_3$ nanoparticles into a stable matrix of wood fibers through fiber functionalization. Our proposed manufacturing method can be easily integrated into the existing paper-making process, and it is also cost-effective as it does not employ any sophisticated equipment. In addition, the chemistry used here is environmentally friendly.

Zeta potential measurements on functionalized wood fibers before and after activation in the nanoparticle suspension, microscopic observations, and X-ray diffraction studies of the hybrid paper suggest the successful attachment of $BaTiO_3$ onto the wood fiber through strong electrostatic bonding between the positively charged wood fibers and the negatively charged $BaTiO_3$ nanoparticles. The measurements also suggest that the crystal structure and the hydrogen bonding of the wood fibers remain intact even after nanocoating polyelectrolytes and nanoparticles.

The strength of the piezoelectric hybrid paper decreases with increasing nanoparticle loading, likely due to reduced fiber–fiber bonding. The piezoelectric response of the hybrid paper significantly increases with $BaTiO_3$ content in the paper. The piezoelectric hybrid paper with 48 wt % $BaTiO_3$ exhibits a piezoelectric constant (d_{33}) of 4.8 ± 0.4 pC N^{-1}.

Our experimental results indicate that functionalizing nanostructured $BaTiO_3$ onto wood cellulose fibers may be a promising approach for fabricating piezoelectric paper and to develop inexpensive and eco-friendly devices for sensing applications, thereby enhancing the functionality and value of the paper. Also, the demonstrated new functional paper may overcome the limitations of existing piezoelectric paper in terms of affordability, processability, and versatility.

■ ASSOCIATED CONTENT

Supporting Information

Photograph of ZnO–paper prepared by adopting the method reported in the literature, zeta potential measurement, FTIR and X-ray diffraction results on the different states of the wood fibers, thermogravimetric analysis, SEM images, and piezoelectric response of piezoelectric paper as a function of $BaTiO_3$ content. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

All the authors contributed equally. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Fortunato, E.; Correia, N.; Barquinha, P.; Pereira, L.; Gonçalves, G.; Martins, R. High-Performance Flexible Hybrid Field-Effect Transistor Based on Cellulose Fiber Paper. *IEEE Electron Device Lett.* **2008**, *29*, 988−990.
(2) Mazzeo, A. D.; Kalb, W. B.; Chan, L.; Killian, M. G.; Bloch, J. F.; Mazzeo, B. A.; Whitesides, G. M. Paper-Based Capacitive Touch Pads. *Adv. Mater.* **2012**, *24*, 2850−2856.
(3) Li, X.; Tian, J.; Nguyen, T.; Shen, W. Paper-Based Microfluidic Devices by Plasma Treatment. *Anal. Chem.* **2008**, *80*, 9131−9134.
(4) Li, X.; Ballerini, D. R.; Shen, W. A Perspective on Paper-Based Microfluidics: Current Status and Future Trends. *Biomicrofluidics* **2012**, *6*, 011301.
(5) Sousa, M. P.; Mano, J. F. Superhydrophobic Paper in the Development of Disposable Labware and Lab-on-Paper Devices. *ACS Appl. Mater. Interfaces* **2013**, *5*, 3731−3737.
(6) Hu, L.; Wu, H.; Cui, Y. Printed Energy Storage Devices by Integration of Electrodes and Seperators into Single Sheets of Paper. *Appl. Phys. Lett.* **2010**, *96*, 183502.
(7) Deng, L.; Young, R. J.; Kinloch, I. A.; Abdelkader, A. M.; Holmes, S. M.; Del Rio, D. A. H.; Eichhorn, S. J. Supercapacitance from Cellulose and Carbon Nanotube Nanocomposite Fibers. *ACS Appl. Mater. Interfaces* **2013**, *5*, 9983−9990.
(8) Yuan, L.; Yao, B.; Hu, B.; Huo, K.; Chen, W.; Zhou, J. Polypyrrole-Coated Paper for Flexible Solid-State Energy Storage. *Energy Environ. Sci.* **2013**, *6*, 470−476.
(9) Liu, X.; Mwangi, M.; Li, X. J.; O'Brien, M.; Whitesides, G. M. Paper-Based Piezoresistive MEMS Sensor. *Lab Chip* **2011**, *11*, 2189−2196.
(10) Meiss, T.; Wertschutzky, R.; Stoeber, B. Rapid Prototyping of Resistive MEMS Sensing Devices on Paper Substrates. In *IEEE MEMS 2014 Conference*, Jan 26−30, San Fransisco, CA, 2014; IEEE: New York, 2014.
(11) Fukada, E. Piezoelectricity of Wood. *J. Phys. Soc. Jpn.* **1955**, *10*, 149−154.
(12) Fukada, E. Piezoelectricity as a Fundamental Property of Wood. *Wood Sci. Technol.* **1968**, *2*, 299−307.
(13) Bazhenov, V. A. *Piezoelectric Properties of Wood*, 1st ed; Consultants Bureau: New York, 1961.
(14) Yun, S.; Kim, J. H.; Li, Y.; Kim, J. Alignment of Cellulose Chains of Regenerated Cellulose by Corona Poling and Its Piezoelectricity. *J. Appl. Phys.* **2008**, *103*, 083301.
(15) Gullapalli, H.; Vemuru, V. S. M.; Kumar, A.; Mendez, A. B.; Vajtai, R.; Terrones, M.; Nagarajaiah, S.; Ajayan, P. M. Flexible Piezoelectric ZnO-Paper Nanocomposite Strain Sensor. *Small* **2010**, *6*, 1641−1646.
(16) Kumar, A.; Gullapalli, H.; Balakrishnan, K.; Mendez, A. B.; Vajtai, R.; Terrones, M.; Ajayan, P. M. Flexible ZnO-Cellulose Nanocomposite for Multisource Energy Conversion. *Small* **2011**, *7*, 2173−2178.
(17) Kim, K. H.; Lee, K. Y.; Seo, J. S.; Kumar, B.; Kim, S. W. Paper-Based Piezoelectric Nanogenerator with High Thermal Stability. *Small* **2011**, *7*, 2577−2580.
(18) Qui, Y.; Zhang, H.; Hu, L.; Yang, D.; Wang, L.; Wang, B.; Ji, J.; Liu, G.; Liu, X.; Lin, J.; Li, F.; Han, S. Flexible Piezoelectric Nanogenerators Based on ZnO Nanorods Grown on Common Paper Substrates. *Nanoscale* **2012**, *4*, 6568−6573.
(19) Soomro, M. Y.; Hussain, I.; Bano, N.; Nur, O.; Willander, M. Piezoelectric Power Generation from Zinc Oxide Nanowires Grown on Paper Substrate. *Phys. Status Solidi RRL* **2012**, *2*, 80−82.
(20) Ko, Y. H.; Yu, J. S. Preparation of ZnO Nanorods on Cellulose Fiber Paper and Their Charge-Generating Application for Waste Paper Recycling. *Phys. Status Solidi RRL* **2013**, *7*, 985−988.
(21) Agarwal, M.; Lvov, Y.; Varahramyan, K. Conductive Wood Microfibers for Smart Paper Through Layer-by-Layer Nanocoating. *Nanotechnology* **2006**, *17*, 5319−5325.
(22) Mahadeva, S. K.; Berring, J.; Walus, K.; Stoeber, B. Effect of Poling Time and Grid Voltage on Phase Transistion and Piezoelectricity of Poly(vinylidene fluoride) Thin Films Using Corona Poling. *J. Phys. D: Appl. Phys.* **2013**, *46*, 285305.
(23) Niu, T.; Xu, J.; Xiao, W.; Huang, J. Cellulose-Based Catalytic Membranes Fabricated by Deposition of Gold Nanoparticles on Natural Cellulose Nanofibres. *RSC Adv.* **2014**, *4*, 4901−4904.
(24) Kolpak, F. J.; Blackwell, J. Determination of the Structure of Cellulose II. *Macromolecules* **1976**, *9*, 273−278.
(25) Mahadeva, S. K.; Kang, K. S.; Kim, J.; Ha, S. H.; Koo, Y. M. The Effect of Residual Ionic Liquid for Cellulose based Electro-Active Paper Actuator. *Soft Mater.* **2010**, *8*, 254−262.
(26) Gwon, J. G.; Lee, S. Y.; Doh, G. H.; Kim, J. H. Characterization of Chemically Modified Wood Fibers Using FTIR Spectroscopy for Biocomposites. *J. Appl. Polym. Sci.* **2010**, *116*, 3212−3219.
(27) Yu, Z. Nanoscale Surface Modification of Wood Veneers for Adhesion. M.S. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 2008.
(28) Wang, Q.; Hauser, P. J. New Characterization of Layer-by-Layer Self-Assembly Deposition of Polyelectrolytes on Cotton Fabric. *Cellulose* **2009**, *16*, 1123−1131.
(29) Mahadeva, S. K.; Kim, J. Hybrid Nanocomposite Based on Cellulose and Tin Oxide: Growth, Structure, Tensile and Electrical Characteristics. *Sci. Technol. Adv. Mater.* **2011**, *12*, 055006.
(30) Zhu, X. H.; Zhu, J. M.; Zhou, S. H.; Zhi, G. L.; Ming, N. B.; Hesse, D. Microstructural Characterization of $BaTiO_3$ Ceramic Nanoparticles Synthesized by the Hydrothermal Technique. *Solid State Phenom.* **2005**, *106*, 41−46.
(31) Capsal, J. F.; Dantras, E.; Lydia, L. D.; Jany, D.; Colette, L. Nanotexture Influence of $BaTiO_3$ Particles on Piezoelectric Behavior of PA11/$BaTiO_3$ Nanocomposite. *J. Non-Cryst. Solids* **2010**, *356*, 629−634.
(32) Avrahami, Y. $BaTiO_3$ Based Materials for Piezoelectric and Electro-Optics Applications. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 2003.
(33) Gao, Z.; Zhou, J.; Gu, Y.; Fei, P.; Hao, Y.; Bao, G.; Wang, Z. L. Effects of Piezoelectric Potential on the Transport Characteristics of Metal-ZnO Nanowire-Metal Field Effect Transistor. *J. Appl. Phys.* **2009**, *105*, 113707.
(34) Wang, L.; Tsan, D.; Stoeber, B.; Walus, K. Substrate-Free Fabrication of Self-Supporting ZnO Nanowire Arrays. *Adv. Mater.* **2012**, *24*, 3999−4004.
(35) Tsan, D. Zinc Oxide Nanowires for Dynamic Strain Sensing. M.A.Sc. Thesis, The University of British Columbia, Vancouver, Canada, 2013.