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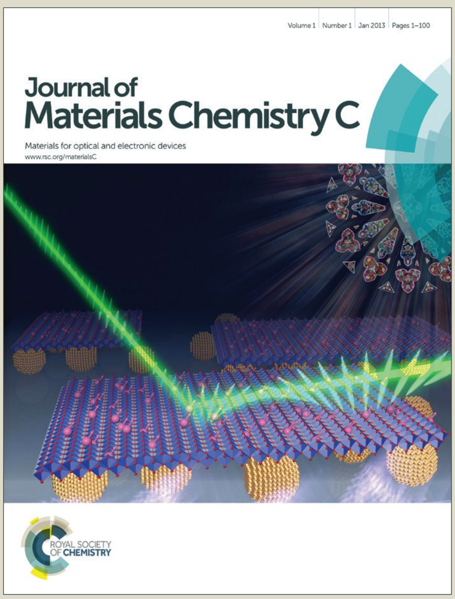

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PAPER

Flexible and robust hybrid paper with large piezoelectric coefficient

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This report describes the fabrication of hybrid paper made from wood fibers to which barium titanate ($BaTiO_3$) nanoparticles were anchored. This hybrid paper is mechanically as strong as commercial printing paper (breaking strength =1.55N/mm^2), it is flexible and possesses a large piezoelectric coefficient (d_{33}= 37- 45.7±4.2 pC/N). Using this paper, we demonstrate an accelerometer, with a sensitivity of 82.45 pC/g. Accelerometer is formed by laminating piezoelectric paper with electrodes made from conductive ink and a seismic mass is bonded to this assembly. According to our model, the dynamic range, 1-70 Hz, of the sensor can be increased by reducing the seismic mass at the expense of a lower sensitivity.

1. Introduction

The development of low-cost and environmental friendly functional material is critically important for developing inexpensive sensing systems that improve safety, health, and the quality of life[1,2]. Wood cellulose is a promising material for sensing applications because it is biodegradable, naturally available, low-density, and easy to process. The molecular structure of cellulose includes hydroxyl groups, making cellulose extremely sensitive to changes in its local environment, but also making it compatible with chemical modifications that enable the fabrication of selective sensors[3-5]. To enhance the functionality of paper, many attempts have been made in recent years to integrate nanostructured materials with wood fibers; for example Anderson integrated single-walled carbon nanotubes (SWCNTs) into wood fibers prior to paper making to produce electronically conductive composite paper[6], while titanium dioxide (TiO_2) was functionalized onto wood fibers through controlled hydrolysis[7] to obtain highly opaque paper. Likewise, polyelectrolytes and conjugated polymers functionalized onto wood fibers via polymerization-induced adsorption[8], and a layer-by-layer approach[9] for producing conductive wood microfibers for smart paper applications. More recently, multiple research groups have developed several paper-based sensing devices with broad applications in the MEMS area including strain sensing[10, 11], energy storage[12], biosensing and microfluidics[13], and detection of volatile organic compounds (VOC)[14] with the goal of fabrication, and low cost. Here paper also has the benefit of being disposable and biodegradable. In recent years, many researchers have attempted to develop robust piezoelectric paper with large piezoelectric coefficient through (i) a hydrothermal synthesis route[15-20], and (ii) wood fiber functionalization[21,22] approach and demonstrated applications of piezoelectric paper to strain sensing[16], electronic devices[15], energy harvesting[17-19], and a touch pad[19]. Hydrothermal synthesis involves immersion of a paper substrate in a reaction bath for a specific duration, leading to the growth of zinc oxide (ZnO) nanostructures, while wood fiber functionalization involves anchoring barium titanate ($BaTiO_3$) nanoparticles into a stable matrix of wood fibers during the paper making process. These techniques presents challenges to the scalable mass production of such paper [15-20], and suffers from poor mechanical and piezoelectric properties [21,22]. Paper with significant piezoelectric properties and high mechanical strength has never been realized to best of our knowledge.

Herein we describe fabrication process for hybrid paper that has a large piezoelectric coefficient and tensile properties similar to commercial printing paper. The process reported here is simple, relatively low-cost, and can be readily integrated into the existing paper making process. The hybrid paper developed in this work is sustainable and green material, can be potentially used as an inexpensive substrate for building inexpensive sensors. We also demonstrated the application of this hybrid paper as a sensor capable of detecting low acceleration levels.

2. Experimental Section

Fabrication of Hybrid Paper: We utilized wood fiber functionalization to prepare a robust and flexible hybrid paper with a significantly large piezoelectric coefficient. The first step in the fabrication process involves the treatment of wood fibers by immersing them alternatively in a aqueous solution of poly(diallyldimethylammonium chloride) (PDDA, 1 % wt/v in 0.5 M NaCl) and poly(sodium 4-styrenesulfonate) (PSS, 1 % wt/v in 0.5 M NaCl), and once again in PDDA, resulting in the creation of a positively charged surface on the wood fibers. The second step

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involves the activation of the treated wood fibers in a $BaTiO_3$ suspension (1 wt%), leading to the electrostatic binding of the negatively charged $BaTiO_3$ to the fibers. $BaTiO_3$ nanoparticles were purchased from US Research Nanomaterials Inc., with a particle size of 300 nm (99.9% purity) having a tetragonal crystal structure, in-depth microscopic and crystallographic analysis of the BaTiO3 structure has been reported in our previous paper[22]and the origin of its piezoelectricity has been studied in detail and is well documented in the literature[23-25]. The next step involves the activation of the wood fibers with the anchored $BaTiO_3$ nanoparticles in a suspension of commercially available paper-strength-enhancing additive (sodium carboxymethylcellulose: CMC, AF0705 from AkzoNobel Pulp and Performance Canada Inc) with a range of concentrations (0, 2, 3, 4, 5, and 6 wt%) over 10 hours. This step ensures a uniform coating of the $BaTiO_3$ nanoparticles attached wood fibers with CMC (Figure 1f) and results in improved fiber-fiber bonding. Paper hand sheets (ϕ=16 cm) are made according to the TAPPI method T-205[22]. Finally hybrid paper is subjected to corona poling to render it piezoelectric. Corona poling was performed at 120℃ for 4 h using a custom made corona poling station that consists of a poling dome placed above the hybrid paper in contact with the ground electrode. Typically, a poling dome includes one or several needles suspended in it, referred as corona needles. The air within the dome becomes ionized when the high voltage (V_N= 17 kV) is applied to the corona needles, this results in an ion flux directed at the sample. The ions create a charged layer on the surface of the sample, generating the poling field across the sample to the ground plate located beneath[26-29]. Above the hybrid paper, a conducting grid is affixed and held at a constant voltage (V_g= 5 kV) to ensure uniform distribution of charged ions and to control the potential at the sample surface. The dipoles of the $BaTiO_3$ crystal structure are aligned through the poling process, generating a net piezoelectric effect. The net polarization of the $BaTiO_3$ particles results from the alignment of the individual dipoles of the crystals within the nanoparticles causing them to collectively exhibit piezoelectric behavior with an orientation defined by the poling process.

Characterization of Hybrid Paper: The morphology of the hybrid paper is examined by scanning electron microscopy (SEM Hitachi S570 with electron backscatter diffraction detector). Prior to imaging the samples were coated with gold (~70 nm thick). Attachment of $BaTiO_3$ nanoparticles to the wood fiber is observed using a FEI Technai G2 transmission electron microscope (TEM). The tensile properties of the hybrid paper were evaluated by measuring the stress and strain. For that purpose, the piezoelectric paper was cut into strips with dimensions of 50 mm × 5 mm. These strips were then subjected to tensile testing using a BOSE ElectroForce® 3100 uniaxial tensiometer. The two ends of a test strip were fixed between the upper and lower grips of the instrument, with a gauge length of 20 mm. The test was performed at room temperature and a relative humidity of approximately 40% with a displacement rate of 0.01 mm/s. The piezoelectric coefficient (d_{33}) of this hybrid paper was measured by measuring the charge induced on the electrodes under ambient conditions due to the application of a load to the sample. The induced charge generated during the compression loading is used to determine the piezoelectric charge constant,

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

For each sample, five charge constants were measured and the average value was calculated.

Also, we estimated the electrical conductivity of the hybrid paper by measuring its resistance across its thickness using a source meter (Keithley 2635A) at ambient room conditions. An electrode (1x1) cm^2 was formed on both sides of the hybrid paper using silver conductive grease (Circuit Works® from ITW Chemtronics, Georgia, USA). The voltage V was scanned between -0.5 V and +0.5 V and the resulting *dc* current I was measured. Fig. S1 (Supplementary Information) shows the Current-Voltage (I-V) curve of the piezoelectric paper; its electrical conductivity is 9.19×10^{-7} S/cm.

Sensor Fabrication: We have developed a novel process for fabricating paper-based accelerometers. Fig. S2 (Supplementary Information) shows the fabrication process of the piezoelectric paper based sensor: the paper (625 mm^2) is cut with scissors, the electrodes are applied by dispensing conductive ink (400 mm^2) using CircuitWriter™ precision conductive ink dispenser from Caig Labs Inc., copper foil conductors are attached, and the paper is laminated using an office laminator (GBC Heatseal® H220), followed by bonding a seismic mass (0.1, 0.2 and 0.3 kg over 755 mm^2) to one side of the laminate.

3. Results and Discussions

The fabrication of hybrid paper is accomplished through anchoring $BaTiO_3$ nanoparticles onto wood fibers as detailed in the experimental section. Fig. 1(a) shows the photograph of the as prepared hybrid paper. The hybrid paper is flexible, white in colour, macroscopically flat and smooth on one side and possesses about 48 wt% of $BaTiO_3$ nanoparticles.

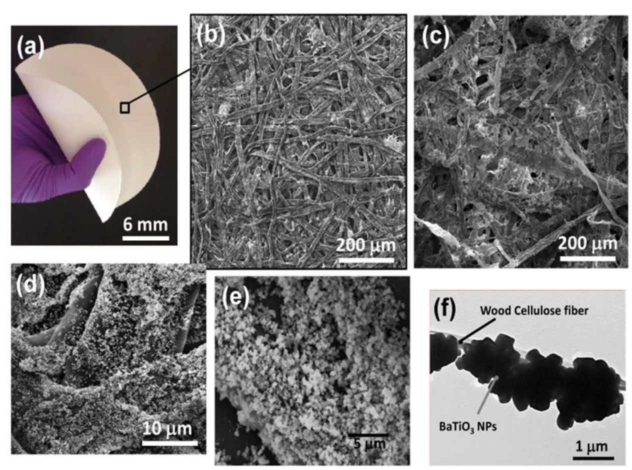

Fig. 1 (a) Photograph of hybrid paper showing its flexibility, (b) surface SEM image of hybrid paper, (c-e) mid-thickness SEM images of hybrid paper at different magnification, and (f) TEM image of $BaTiO_3$ nanoparticles anchored to a wood fiber after activation in a suspension of CMC.

The surface and mid-thickness morphologies of this hybrid paper at micro- and nanoscales are provided in Fig. 1(b- f). These images indicate a dense coating of $BaTiO_3$ nanoparticles over the wood fibers through strong electrostatic bonding.

Microscopic images of $BaTiO_3$ nanoparticles anchored to a wood fiber before and after activation in a sodium carboxymethylcellulose (CMC) suspension is presented in Fig. S3 (Supporting Information); CMC activated $BaTiO_3$ nanoparticles anchored to wood fibers appear larger than their unfunctionalized counterparts due to coverage with CMC (Fig. 1f); CMC is a paper dry strength enhancing additive that improves fiber-fiber bonding leading to hybrid paper with high tensile strength and flexibility. The tensile strength of hybrid paper is determined by subjecting it to tensile load using a tensiometer, and the stress-strain curve as a function of CMC concentration is provided in Fig. S4 (Supporting Information).

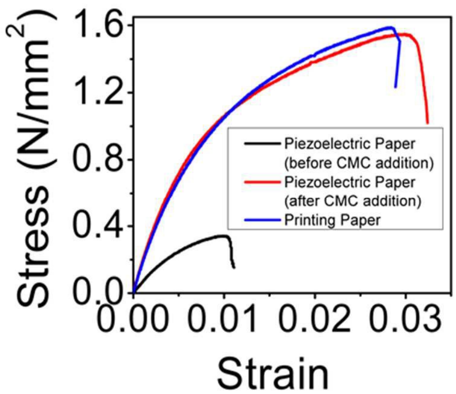

Fig. 2 Compared stress-strain curves of hybrid paper and commercial printing paper.

The tensile properties such as yield strength, breaking strength, and breaking strain of hybrid paper are shown to improve significantly with increased CMC concentration. For example, the breaking strength of pristine hybrid paper (0 wt% CMC) is estimated at 0.34 N/mm^2, and is improved to 0.54 N/mm^2 upon activation in a 2 wt% CMC suspension, and increases with CMC concentration and reaches a maximum of 1.55 N/mm^2 at 6 wt% CMC. These results are in agreement with published literature; Ma *et al.*[30] reported a significant improvement in the mechanical properties of starch films due to CMC addition, while Ankerfors *et al.*[31] report a significant improvement in the mechanical properties of paper with the addition of CMC. Improvement in the tensile properties of hybrid paper due to CMC addition may be attributed to the interfacial interaction between matrix and filler[32] that arises due to chemical similarities between wood fibers (cellulose) and CMC. Interestingly, CMC improved the paper strength without reducing flexibility; such a combined effect cannot be achieved with other paper strength additives such as clay, and synthetic resin at relatively large concentration[33]. We restricted the CMC concentration to a maximum of 6 wt%, as the handsheet formed on the polyester mesh screen of a handsheet maker transforms to a gel-type material at CMC concentrations of 7 wt% and above; that material is difficult to couch with blotters and lift off the screen.

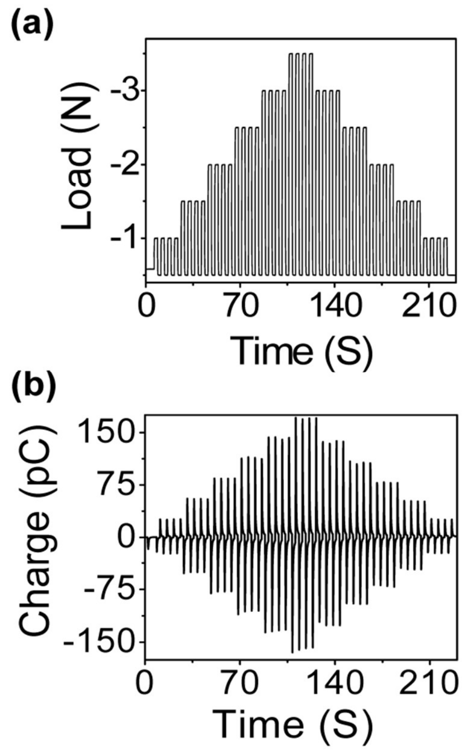

Fig. 3 (a) Pattern of typical compressive load applied to hybrid paper to measure it piezoelectric property, (b) piezoelectric response of hybrid paper.

At 6 wt% CMC, the tensile properties of hybrid paper are comparable with those of commercially available office print paper (A1™ MultiUse-PAPER from Huge Paper, Aurora, ON, Canada with 75 gsm) as shown in Fig. 2.

We also determined the piezoelectric coefficient (d_{33}) of the hybrid paper by subjecting it to varying compressive load from 0.5 N to 3 N to 0.5 N in steps of 0.5 N as shown in Fig. 3 (a). The load was applied onto a (7×25) mm^2 sample and the corresponding piezoelectric charge induced by the paper was measured using a charge meter (Kistler Charge meter 5015A). Each step is repeated four times. During this process, the charge amplifier supplies charge to the electrodes of the paper sample in response to the polarization of the piezoelectric material caused by external force. Upon removal of that force the piezoelectric polarization disappears and the charges present on the electrodes are removed via the charge amplifier at the set time constant. In our experiments we set the time constant to 0.1 s. Since the time constant is smaller compared to the duration of the force applied we see peaks of identical height in positive and negative direction. The typical piezoelectric response of the hybrid paper (5 wt% CMC) is presented in Fig. 3(b). The paper produced a piezoelectric charge of 55 pC when loaded at 1 N and the amplitude of piezoelectric charge increased with the applied load and reached 113 pC at 2 N and 170 pC at 3 N. The hybrid paper exhibited a repeatable piezoelectric response over time. We used this data to estimate the piezoelectric coefficient, d_{33}, of the hybrid paper and Fig. 4(a) shows d_{33} of hybrid paper as a function of CMC concentration (2, 3, 4, 5, and 6 wt%);

the CMC concentration had no significant influence on the d_{33} of the hybrid paper, that is estimated to be in the range of 37 - 45.7 ± 4.2 pC/N, which is approximately 8-times larger compared to that of pristine hybrid paper (0 wt% CMC)[22]. The large piezoelectric coefficient of CMC added hybrid paper is most likely due to a reduced absorption of the applied stress by the wood fiber network and a more effective transfer of strain to the nanoparticles in the hybrid paper as a result of the improved fiber-fiber bonding.

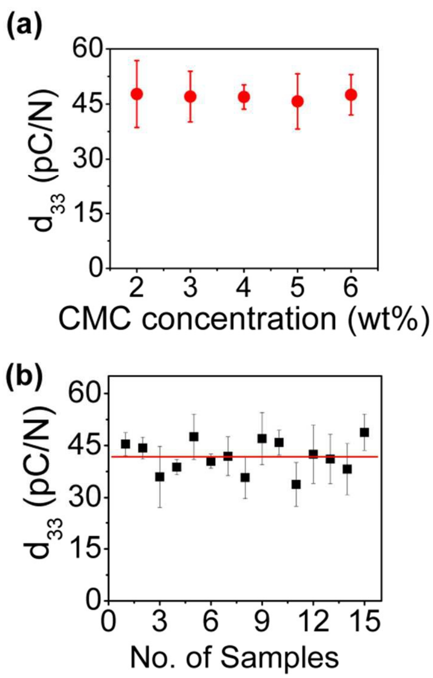

Fig. 4 (a) Piezoelectric charge constant d_{33} of hybrid paper as a function of CMC concentration, (b) Piezoelectric charge constant d_{33}, repeatability and reliability of the hybrid paper fabrication process.

Also, this piezoelectric coefficient is the largest d_{33} value reported for paper to date and is comparable to the piezoelectric coefficient of commercially available piezoelectric polymers such as polyvinylidene fluoride (PVDF) with $d_{33} = 30$ pC/N[34]. We also examined the repeatability and reliability of the hybrid paper fabrication process. For that purpose, we prepared 15 hybrid paper samples over a period of 3 weeks and determined the piezoelectric coefficient. The data in Fig. 4(b) shows that the piezoelectric coefficient of all of our hybrid paper samples fall well within the range of 37 - 45.7 ± 4.2 pC/N, suggesting repeatability and reliability of the hybrid paper fabrication process. We conducted a durability test with our hybrid piezoelectric paper to assess the d_{33} stability. For that purpose, we repeatedly subjected it to a compressive load of 3 N for 70 minutes and recorded the piezoelectric response in Fig. 5. Initially, the amplitude of the charge signal decayed continuously up to 500 s and remained stable thereafter. A reason for the initial signal decay is most likely the rearrangement of the fiber network[10]. Our hybrid paper retained its piezoelectric properties and we noticed only 11.6% - 27.5% reduction in its piezoelectric activity after aging for 14 months (Fig. S5, Supporting Information). Note that, our hybrid paper is not only mechanically strong and possesses a large piezoelectric coefficient, but it is also affordable in terms of cost; for example, the material cost for preparing a circular sheet of hybrid paper of a 11 cm diameter is about $7.14 (refer to Supporting Information for details). This corresponds to $752/m^2 25-times less than commercially available piezoelectric PVDF[35]. In addition, the fabrication process for our paper is environmental friendly and does not require any expensive cleanroom equipment.

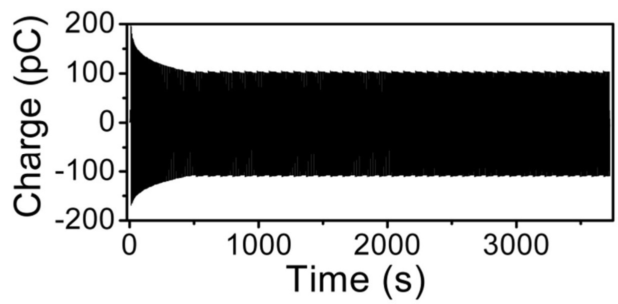

Fig. 5 Piezoelectric response of hybrid paper showing durability as a function of time.

We used this hybrid paper as a substrate to build an accelerometer as a demonstration for the applicability of this material to sensing. The fabrication process involved paper cutting, electrode deposition, laminating, and finally wiring the sensor using copper foil. Manually fabricating eight piezoelectric paper-based sensors typically takes less than one hour, and can be done using simple office equipment (scissor, CircuitWriter™ precision conductive ink dispenser from Caig Labs Inc., and a laminator). Prior to characterizing the sensing capabilities of this assembly,

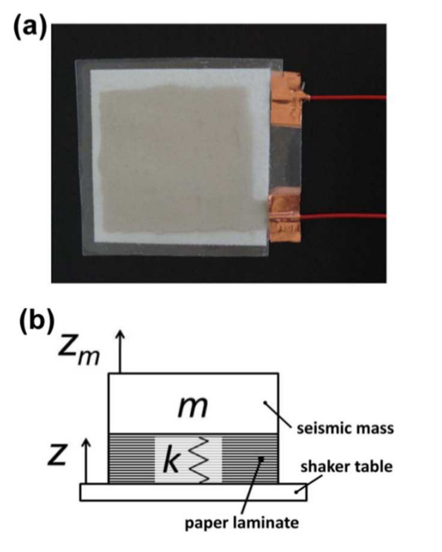

Fig. 6 (a) Photograph of fabricated paper sensor, and (b) configuration of the paper accelerometer.

The compression property of the paper laminate was evaluated by subjecting it to compression load using BOSE ElectroForce® 3100; from its force-displacement curve (Fig. S6, Supporting Information) we estimated the stiffness around 7 kN/m. The sensor structure consisted of hybrid paper sandwiched between two electroded lamination pouches (Fig. 6a). The accelerometer was completed by attaching a seismic mass, *m,* to the top of this assembly. This mass will apply a force to the piezoelectric paper when subjected to an acceleration, *a,* according to the relationship $F=ma$.

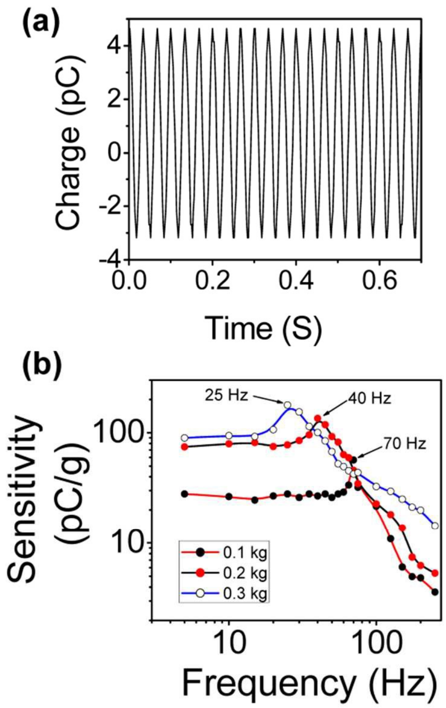

Fig. 7 (a) signal measured from the paper accelerometer at 30 Hz and 0.1 g acceleration amplitude, and (b) response of the paper accelerometer as a function of frequency for different seismic masses.

When connected to the charge-voltage converter (Kistler 5015A) the force is converted into an electric charge, *Q,* through the piezoelectric effect. The lower electrode is fixed to a shaker table, as shown in Fig. 6(b). The paper-based accelerometer is characterized using a custom built shaker table with a reference accelerometer (ADXL203 EB by Analog Devices). Fig. 7(a) shows the paper accelerometer signal as picked up by the charge-voltage converter, note that the output signal recorded from the paper accelerometer matches the signal from the reference accelerometer (Fig. S7 in Supporting Information). The paper sensor response is measured for different acceleration amplitudes; the sensor output amplitude is proportional to accelerations up to 1 g, and the sensor response saturates above a = 1 g. The frequency response of the accelerometer as a function of seismic mass in Fig. 7(b) shows second order behavior with a resonance frequency that to increases as the seismic mass decreases. For example the resonance was at 25 Hz with a sensitivity of 94.3 pC/g for a seismic mass of 0.3 kg and it increased to 70 Hz upon reducing the seismic mass to 0.1 kg, with a sensitivity of 27.9 pC/g. This increase in resonant frequency due to a reduced seismic mass increases the operating range of the paper accelerometer while simultaneously reducing its sensitivity. These results are close to the expected resonance predicted by our model (Supporting Information). For example, for a seismic mass of 0.2 kg, the resonant frequency of the paper accelerometer is around 40 Hz, close to the expected resonance at 30 Hz predicted by our model; the sensitivity of $Q / a = d_{33}/m$ = 82.45 pC/g is close to the estimated sensitivity of 94 pC/g of our model. Below 1 Hz charge (Q) leakage in the piezoelectric paper becomes significant[22] and limits the operating range of this device.

Our study suggests that the piezoelectric paper is promising low cost and environment-friendly substrate for building various physical sensors and energy harvesting.

4. Summary and Conclusions

In summary, robust and flexible hybrid paper with a large piezoelectric coefficient was fabricated by anchoring BaTiO3 nanoparticles to wood fibers. In contrast to the existing piezoelectric paper fabrication methods in which growth of ZnO nanostructures on paper substrate reply on a seed layer, fabrication of the hybrid piezoelectric paper is facilitated through anchoring barium titanate nanoparticles to wood fibers followed by activation in a sodium carboxymethylcellulose suspension. This piezoelectric paper is mechanically strong and has the largest piezoelectric coefficient reported for paper to date (d_{33}=45.7±4.2 pC/N), comparable to commercially available piezoelectric polymers (polyvinylidene fluoride; PVDF d_{33}=30 pC/N). As an initial demonstration, we fabricated a piezoelectric paper sensor, which can be used to detect low-g acceleration and/or mechanical vibration, and can potentially be used as a energy harvesting.

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Flexible and robust hybrid paper with large piezoelectric coefficient

Table of Content

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