GRAVIMETRIC PARTICULATE MATTER SENSING WITH PIEZOELECTRIC PAPER

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ABSTRACT

Paper substrates have recently attracted significant interest as porous, flexible and biodegradable platforms for low-cost physical and chemical sensor systems. We have leveraged these properties in this work to develop a gravimetric particulate matter (PM) sensor based on piezoelectric nanocomposite paper substrates. Our sensor prototypes are estimated to have mass sensitivities of 0.34 Hz/µg and 0.37 Hz/µg respectively, with an quality factor of 20. These piezoelectric nanocomposite paper substrates were manufactured using a repeatable, semi-conventional papermaking process with the out-of-plane piezoelectric coefficient d_{33} = 25.4 pC/N.

KEYWORDS

Particulate matter sensor, piezoelectric paper, barium titanate, gravimetric sensing.

INTRODUCTION

Suspended particulate matter (PM) has been identified as one of the primary components of air pollution with protocols [1] to limit PM exposure in industrial and public environments. The effective implementation of such protocols requires proper quantification of PM content and is performed using air quality monitoring systems strategically located within the assessed environment. Such systems require bulky instrumentation, repeated calibration and are often incapable of real-time sensing or field deployment [2] [3]. This gap is currently being filled by wall-mountable and portable systems for increasingly localized air quality monitoring of niche environments. However, these systems primarily use optical scattering [4] [5] [6] as the sensing method and thus, cannot be used as PM measurement standards according to EPA regulations which require measurement of the actual PM mass per volume of air [7].

Gravimetric PM mass detection is the standard adopted by the EPA, which makes the development of such a PM sensor a critical milestone towards the realization of a compact gravimetric-based air quality monitoring system. Different types of substrates are used as filters for PM trapping that can be broadly divided into membrane filters and fibre filters. Common membrane filters include PTFE [8], nylon [9], PVC-acetonitrile [10] and polycarbonate [11] with PTFE filters preferred for mass detection. Despite its resistance to moisture and chemicals, such membrane filters suffer from limited loading capacities with the bulk of the trapped PM deposited on the surface. This can often lead to measurement inaccuracies due to fractional loss of the PM deposits under heavy loading conditions. Fibre filters perform better than membrane filters in terms of loading capacity as well as PM retention. While glass [12], quartz [13] and cellulose [14] fibre filters have been demonstrated, they are impacted by other deficiencies like moisture sensitivity and typically low sampling efficiencies [15]. These effects can be minimized and compensated through signal conditioning within the PM sensor instrumentation, especially in scenarios where trade-offs between extreme accuracy (unrealistic outside laboratory environments) and sensor portability are acceptable.

Paper-based substrates not only provide requisite PM trapping functionality but also the potential for end-of-life recyclability and biodegradability through an economically mass-producible sensing platform. Despite reports of PM gravimetric sensing using paper-based (cellulose fibre) filters [16] [17], none of them were capable of *in situ* PM mass measurement. In this work, we present the first gravimetric PM sensor based on piezoelectric paper that has potential for integration within handheld or wearable devices with real-time signal conditioning and readout. Quantification of PM loading within the calibrated piezoelectric paper filter therefore does not require handling of the paper sample each time a measurement is taken. The paper acts as a filter as the air sample is drawn through it and the PM particles are deposited within the paper matrix. With the circular paper membrane vibrating at its fundamental mode, its mechanical resonant frequency shifts as the mass of deposited particles increases. The rate of frequency shift is therefore a measure of PM concentration in air. Further discussion on the PM sensor development is split into these sections: substrate manufacturing, sensor fabrication and sensor characterization.

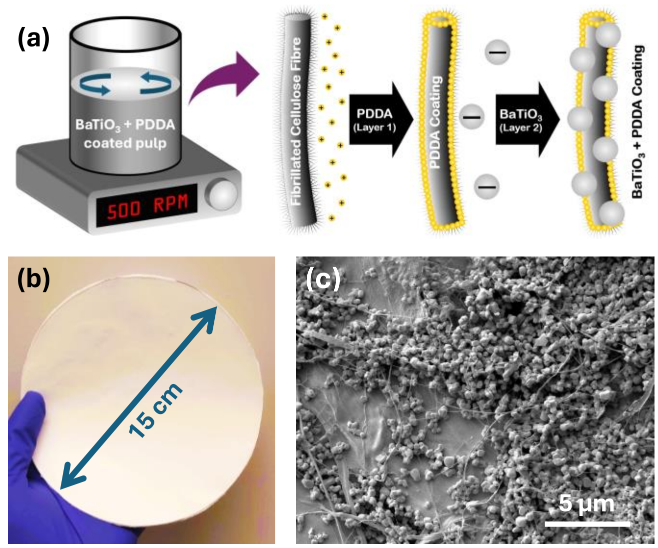

Figure 1: (a) Wood pulp-PDDA-BT slurry preparation (~20°C, 500 RPM) showing BT-functionalized cellulose fibres using electrostatic layer-by-layer deposition method, (b) piezoelectric nanocomposite paper substrate, and (c) its microstructure showing the fibrillation of the cellulose fibres, the PDDA distribution and BT loading.

SUBSTRATE MANUFACTURING

Our prior work on the protocol development for manufacturing piezoelectric paper [18] was simplified here to use highly refined cellulose fibres (specific refining energy: ~400 kWh/t) as the paper matrix from northern bleached softwood kraft (NBSK) pulp. A layer-by-layer deposition process was used to electrostatically prime the fibrillated cellulose fibres with a thin polymer layer (poly(diallyl dimethyl-ammonium chloride or PDDA). Barium titanate (BT) nanoparticles (~300 nm diameter) were then bonded to the fibrillated cellulose fibres using the adhesive PDDA interlayer to impart piezoelectric functionality. Figure 1 schematically illustrates the wood pulp-PDDA-BT slurry formulation comprising BT-loaded cellulose fibres. This slurry was processed according to TAPPI-standards [19] in order to produce sample handsheets of the nanocomposite paper. Each handsheet is ~15 cm in diameter with a thickness range of 150 µm to 250 µm. Figure 1b shows one such sample along with its microstructure comprising a fibrillated cellulose fibre matrix heavily intercalated with BT nanoparticles, forming a paper-based nanocomposite (Fig. 1c). The PDDA is seen to form an adhesive web, strongly binding the BT nanoparticles to itself and the fibrillated cellulose fibres, both electrostatically and mechanically.

SENSOR FABRICATION

In order to implement the electrostatic driving electrodes, electron beam evaporated gold thin films were patterned on either surface of the piezoelectric paper substrate using laser cut aluminum foil shadow masks. These 100 nm thick electrodes, patterned into 3 mm wide ring-like geometry (inner diameter = 10 mm), are designed to excite the primary "drum" mode of vibration in the substrate. Gold electrode deposition was followed by corona poling of the BT nanoparticles to impart significant piezoelectric response to the paper substrate. The applied electric fields are perpendicular to the substrate, and the corona discharge is generated using an 81-needle electrode array for ~4 hours at ~8 kV at ~120ºC, which is close to the Curie temperature [20] of the BT nanoparticles.

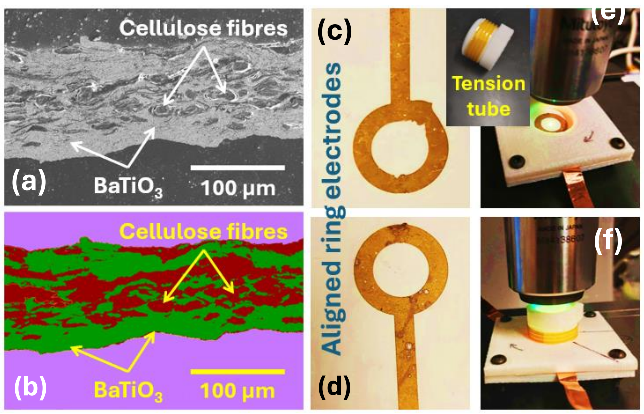

Figure 2: Highly connected BT nanoparticles loaded throughout the cellulose fibre matrix seen in the (a) cross-sectional SEM and (b) its pseudocolour rendering (lilac: background, red: cellulose fibre, green: BT nanoparticles); views of the (c) top and (d) bottom surfaces of a PM sensor strip showing aligned ring electrodes used for driving the "drum" modes of vibration, and PM sensor strips mounted on the tunable fixture (e) without and (f) with radial tension provided by the screw-mounted tension tube (inset).

Rectangular strips (3.5 cm × 2.5 cm) of the piezoelectric paper sensor with driving electrodes were cut from these substrates and mounted on a custom fixture designed to allow for tuning the in-plane tension of the membrane *in situ* during electromechanical tests. 3D printed plates with concentric central cylindrical cavities sandwich the PM sensor with the paper membrane clamped along the circular circumference of opposing annular extrusions. The 1 mm-thick annular extrusion of the upper plate cavity is also threaded by a hollow 3D printed tension tube that allows the tension in the membrane to be directly tuned through rotation of this tube. Figure 2 illustrates the two surfaces of one of the PM sensor strips with the ring electrodes aligned, their extensions at 180º orientation with respect to each other, and mounted on the fixture. The precision and accuracy of the tuning depends on the quality and pitch of the thread. We estimated that with our 3D printed prototype a 90º turn on the tension tube resulted in in-plane stress change of ~16 MPa. It is also important to note that the removal of any residual slack in the mounted but unstressed PM sensor paper is necessary before any in-plane tension can be imparted. An estimated maximum of 31 MPa in-plane stress was applied to the sensor paper before loss of structural integrity in the membrane. Cross-sectional views and the mode of operation of the mounting fixture are shown in Figure 3. The threads on the tension tube were covered by ~40 µm thick polyimide tape to reduce backlash of the tension tube due to the reaction force from the PM sensor strip. Any loss of grip due to external or internal thread imperfections was compensated by the additional grip provided by the polyimide tape. Copper (Cu) tape of ~36 µm thickness served as the electrical connections from the piezoelectric driver (amplifier) to the driving electrodes during the dynamic testing of the mounted PM sensor.

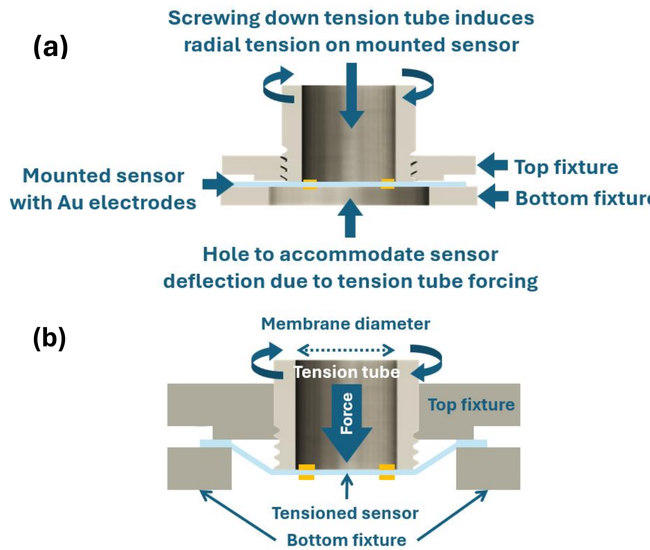

Figure 3: (a) Cross-sectional view of the sensor mounting fixture showing its different components and (b) mode of operation of the tension tube when in-plane stressing the mounted sensor strip.

SENSOR CHARACTERIZATION

The pristine piezoelectric paper substrates were measured to have an average BT mass loading of approximately 75% of the total nanocomposite sample mass with thermogravimetric measurements and an out-of-plane piezoelectric coefficient $d_{33} \approx 25.4$ pC/N with piezoelectric measurements. The average Young's modulus of these substrates was measured to be approximately 1.8 GPa. Scanning laser Doppler vibrometry (LDV) was used to examine the dynamic membrane behavior of the mounted PM sensors upon electrical excitation under varying membrane stress levels. The frequency response as a function of driving peak-to-peak voltage and in-plane stress is shown in Figure 4. The fundamental frequency is tunable through the in-plane tension where the quality factor increases with increasing membrane tension, reaching up to 20 at 31 MPa. It was noted that without any in-plane tension to the paper, its resonant response was either not present or barely noticeable above the background. The vibration frequency f of the PM sensor paper

$$f = \frac{1}{2\pi}\sqrt{\frac{Dk^4+Tk^2}{\rho h}} \quad (1)$$

depends upon the flexural rigidity of membrane D, the tension per unit membrane perimeter T, the wave number corresponding to the fundamental mode k, the density of membrane material ρ and the membrane thickness h. The piezoelectric paper membrane velocity increases almost linearly with the applied driving voltage, as expected for excitation using the inverse piezoelectric effect. The mode shapes of the simulated and observed resonant frequencies in Figure 4e, with respect to the applied tension on the membrane, demonstrate good agreement.

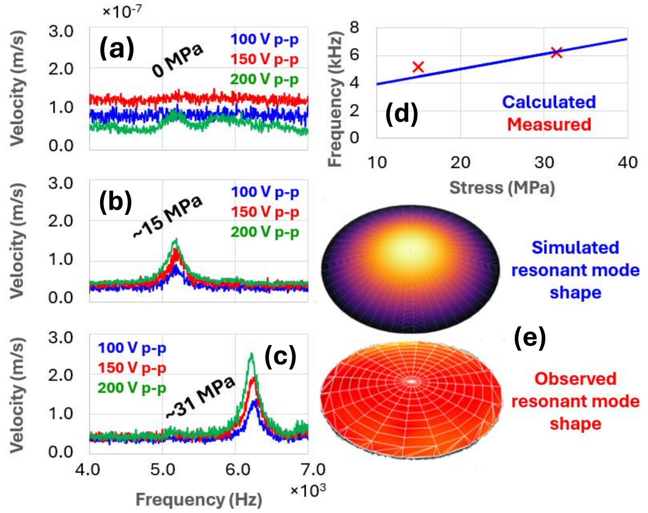

Figure 4: Surface velocity response of the paper membrane center using peak-to-peak driving voltages of 100 V, 150 V and 200 V for (a) 0 MPa, (b) 15 MPa and (c) 31 MPa in-plane stresses; (d) the measured frequency changes with applied in-plane stress similar to the model prediction; (e) the simulated and observed resonant mode shapes

For the verification of PM sensing, tobacco smoke was directed at the paper sample from either side to load it with particulates, and the resulting added mass was measured with an analytical balance. Smoke particulates are typically smaller than 1 µm, and PM at that size can penetrate deep into the lung [21]. Mass loading tests were conducted on electroded piezoelectric paper samples (sensor 1 and sensor 2) where the resonant peak shifts of the paper surface velocity due to PM loading were measured. The paper thicknesses were 240 µm and 190 µm for sensors 1 and 2 respectively, and they were both tuned to an in-plane stress of 31 MPa to maximize the sensor quality factor. Each sensor was loaded by directing about 25 liters of tobacco smoke towards both paper surfaces combined. We assume that the particulate mass loading by smoke-borne PM primarily affects the density term in Equation (1) and we assume that the changes in the flexural rigidity of the sample is negligeable at these low particle loadings. Change in the sensing substrate density translates to a change in the resonant peak frequency which, when calibrated for a particular PM sensor, enables the direct *in situ* estimation of added mass and also eliminates a critically sensitive step from the traditional gravimetric method: the need for collecting the PM filters followed by proper storage protocols and subsequent transportation to off-site measurement facilities.

Sensors 1 and 2 were loaded with 2.0 mg and 2.4 mg of tobacco smoke particulates respectively, resulting in a decrease in frequency consistent with Equation (1). Figure 5 illustrates the resonant frequencies of sensors 1 and 2 that broadly follow the expected sensing behavior, demonstrating some level of PM measurement reproducibility across different samples. The insets show the resonant surface velocity as a function of frequency, with the resonant peaks shifting with mass loading. The difference in peak heights for each sensor before and after mass loading can be attributed to a number of possible factors in handling the sample to collect mass. As seen in Figures 1 and 2, the BT loading within the cellulose fibre matrix is quite high (~75%) but there is variability in distribution along the thickness and planar directions of these nanocomposite substrates. This causes some regions of the piezoelectric paper surface to be of higher reflectivity (higher BT fraction) than others (lower BT fraction) which directly affects the laser signal reflected back to the LDV for the paper surface velocity measurement.

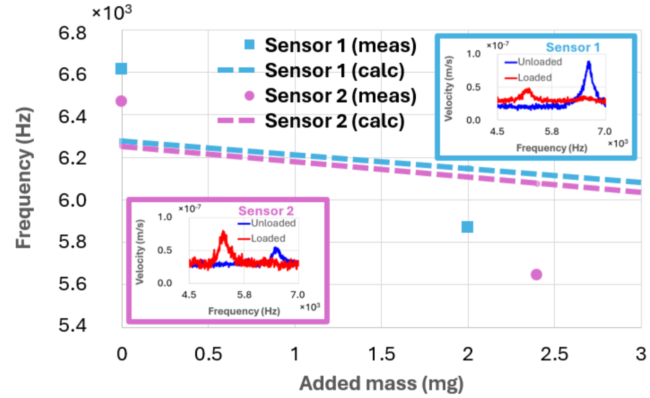

Figure 5: Calculated (dashed line) and measured (markers) variation of paper resonant frequency with the added mass of tobacco smoke particles for sensors 1 (blue) and 2 (pink). Resonant velocity peak shifts shown in inset.

Particulate mass sensitivities of 0.37 Hz/µg and 0.34 Hz/µg were measured for sensors 1 and 2 respectively which seems quite promising for a low-cost paper-based real-time gravimetric device. These values are higher compared to the calculated values for the two sensors of 0.1 Hz/µg which can be attributed in part to the addition of moisture and aerosol particulates which gets absorbed by cellulose fibres, affecting their structural integrity and the overall stiffness of the membrane. This potential softening of the cellulose fibres within the nanocomposite is unaccounted for in theoretical mass sensitivity calculations and results in higher estimated resonant frequencies after loading when compared with the experimentally calculated values and needs to be studied further.

CONCLUSION

We have demonstrated a novel gravimetric PM sensor based on piezoelectric paper nanocomposites prepared using a layer-by-layer method adjacent to large-scale paper manufacturing processes. Such paper-based nanocomposite substrates demonstrated stable average piezoelectric coefficients around 25 pC/N consistently. Thin film driving electrodes were fabricated on these substrates to excite them at their fundamental frequency. This resonant frequency changes with the amount of particulate mass added. A custom tuning fixture was used as the sensor mount to vary the in-plane tension of the nanocomposite substrate and improve the signal-to-noise ratio of the response. Laser Doppler vibrometry was performed on pristine piezoelectric paper as well as unloaded and particle-loaded sensors. Their mechanical response was almost linearly proportional to the electrical excitation magnitude and increased with applied in-plane tension. The resonant frequencies decreased with the addition of mass for the two sensor prototypes that were electromechanically tested, thus validating their potential for real-time gravimetric PM measurement. Mass sensitivities of the order of 0.3 Hz/µg were achieved by both sensors. The discrepancy between the theoretical and experimental values was attributed to factors unaccounted for in the analytical model of the PM sensor and requires further analysis. Our first experimental results demonstrate the utility of paper-based nanocomposites in the domain of mass sensing but further work is needed to obtain more insights into the long-term electromechanical behavior of such multi-component materials. They also open up greener avenues for applications in microphones, speakers, energy storage devices, tactile sensors and nanogenerators, among others.

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