ABSTRACT
For the first time, a 3D-printed flexible and wearable triboelectric energy harvester (TEH) is presented based on the 3D printing of polyurethane (PU) and a conformal coating process using Parylene AF4. The key advancements of this work include: (1) the usage of the stereolithographic (SL) 3D printing process for the prototype of a multiple-layer energy harvester to increase the active surface areas; (2) the deposition of the high surface charge density material of Parylene AF4 with a conformal coating process to act as the active layer. The experimental results for a prototype triple-layer device show a peak short circuit current (SCC) of 390nA and a peak power density of 5.5µW/cm². As such, this work can potentially open up a new class of energy harvesters based on 3D printing technologies for arbitrary geometries for applications such as shoe soles.

INTRODUCTION
The development of wearable electronics and portable devices ranging from healthcare monitors to tactile feedback systems have garnered great attention in recent years[1], [2]. These devices have been able to capture physiological and behavioral data that can be used in the healthcare industry. However, one key obstacle in the adoption of these devices is the power requirement and the replacement of batteries. To overcome this drawback various energy harvesters capable of converting mechanical energy into electrical energy have been investigated. Among these devices, triboelectric energy harvesters (TEH) have gained considerable interest. In laboratory settings, TEHs have been constructed by various processes using structural and active layers [1]. Two key features can affect the performance of the THEs: (1) the surface electrical charge capturing capability of the material; and (2) the mechanical properties of the material to sustain large mechanical deformations [3], [4].

Previously, several groups have reported TEHs by means of 3D printing processes using a post-assembly process and 3D printed components to assemble together the final device [3][5]–[7]. These include 3D printed hydrogel-based THEs [3] with the assembly of resin parts and an ionic hydrogel; and the assembly of structures fabricated via Fused Deposition Modeling (FDM) parts. [6]. However, these devices are not fully 3D printed as additional assembly steps are required to produce the functional devices. Furthermore, the FDM-based 3D printing processes have focused on the use of thermoplastic polymers, limiting the material selection. To overcome the material limitation and avoid the post-mechanical assembly step, we use the stereolithographic 3D printing process, which has a wider material spectrum, in this work. One such material is elastomeric PU (EPU) which is flexible and can sustain high deformations (>250% elongation before break [8]). Although large mechanical deformations can be achieved, 3D printed
DESIGN
The versatility of the 3D printing process enables a wide variety of structural designs to increase the system performance. Here, the design of various multi-layered structures, including single, double, and triple layers is shown in Figure 1. The surface charge density on the electrodes, \( \sigma_o \), is the most important parameter for TEHs and is modelled using equation (1):

\[
\sigma_o = \frac{\varepsilon \frac{\sum_{i=1}^{n} \sigma_i}{D_1} + \sigma_i}{D_2 + \varepsilon}
\]  

(1)

where \( \varepsilon \) denotes the relative dielectric constant of the active electret layer; \( n \) is the number of layers in the structure; and \( D_1 \) and \( D_2 \) are the thickness of the electret material and gap in between the layers, respectively.

From equation (1), it is observed that the thickness of the electret material, the gap distance between layers, and the deformation of the layers will affect the overall performance of the system. In order to maximize the mechanical deformation between the layers, a v-shaped support structure has been used to support the 500 \( \mu \)m thick 20x20 mm\(^2\) surface area square layers. These structures have been modelled in COMSOL Multiphysics to determine the optimum dimensions maximizing mechanical deformations.

FABRICATION
The fabrication process of the devices constitutes a major portion of the work presented here. In order to create the three-dimensional TEH structures optimized for maximum deformation, the 3D printing process based on stereolithography is utilized. This method allows the structures to be created in a one-step fabrication process and eliminates the need for extra assembly steps seen in other reports. The 3D printed structures are functionalized afterwards using a conformal coating process of Parylene AF\(_4\).

Figure 2 illustrates the fabrication process starting with the stereolithographic 3D printing (Figure 2a). In which the commercial Carbon3D M1 printer is used. As shown in the illustration, a UV-light source (385 nm) irradiates the uncured photopolymerizable polyurethane resin and a high resolution screen is used to project the required shape on to the resin to solidify it. This process is repeated many cycles until the desired structure is fabricated. As such, multiple layered devices can be created using this process, allowing for high flexibility for a variety of designs. Furthermore, numerous devices can be printed at the same time to reduce the manufacturing time.

After the structures are printed, a conformal layer of parylene AF\(_4\) is deposited (Figure 2b). In the prototype fabrication, a total amount of 4 grams of Parylene AF\(_4\) was coated using Specialty Coating Systems’ Parylene Deposition System 2010. This process results in a conformal layer that functionalizes the surface of the polyurethane structures to capture a large amount of surface charges due to the high surface charge density of Parylene AF\(_4\) (3.7mC/m\(^2\) [10]). This high surface charge density can be attributed to the fluorine atoms present in the polymer’s structure (Figure 2b).

Surface charges are then induced in between the layers using the corona charging technique. A high voltage power supply is used to deliver 15 kV to the tip of the corona needle (Figure 2c). This high voltage can produce an high electrical field to break down the air molecules in between the parylene layers, which then capture these charges. Lastly, the outer top and bottom layers are metallized using aluminum tape (Figure 2d).

DEVICE CHARACTERIZATION
The fabricated devices are first characterized by measuring device parameters that have the direct effect on the power generation efficiency. These parameters include: (1) the thickness of the Parylene AF\(_4\) layer, (2) the surface charge potential, and (3) the cumulative displacement of all active layers achieved by the different designs.

\[ \text{Figure 2: (a) The fabrication details of the stereolithographic 3D printing process with the continuous liquid interface printing for the energy harvesters. The UV LED is applied from the bottom of the system and the high resolution screen is used as the optical mask. The UV-curable resin is illuminated by the UV light and the cured structure is pulled by the build platform mechanism. Various and multiple-layer of 3D printed devices can be made in the same batch. (b) The conformal Parylene AF}_4\) coating process; (c) the corona charging process; and (d) metallization for the electrodes.} \]
First, the thickness of the parylene AF$_4$ layer is determined by SEM images (Figure 3a). The layer is measured to be about 100 nm. The surface seen in Figure 3b is the Parylene-coated polyurethane surface. The striations are the result of the layer-by-layer printing process in which each ridge corresponds to an approximate 16 µm layer in thickness.

Second, the surface charge potential is measured for 1 month after the corona charging process (Figure 3c). The surface charge potential initially decays rapidly; however, it reaches a steady state condition at approximately -12V and exhibits good stability afterwards. The surface charge potential can be further increased by increasing the thickness of the Parylene AF$_4$ layer. This increase in thickness will result in more charges being accumulated on the surface because higher potentials can be applied during the corona charging process.

Third, the average cumulative displacements of the three different designs of single, double and triple layers are calculated using the COMSOL simulations (Figure 3d). It is seen that the triple layer device exhibits 3 times the average total displacement as compared to that of the single layer device as expected.

EXPERIMENTAL RESULTS & DISCUSSION

Electrical outputs of the different designs were measured afterwards. Specifically the short circuit current and the power output of the devices were tested. The devices were mounted onto a dynamic mechanical test device (ElectroForce 3200, TA Instruments). The top layer of the energy harvesters were displaced under a constant amplitude actuator at a given frequency. The load exerted onto the harvesters was measured by a load cell placed underneath the bottom layer of the devices. The SCC output of the three different designs were compared as seen in Figure 4. The top layers of the devices were compressed with a 1 N force applied at 1 Hz. It was found that the SCC of the triple-layer device was approximately 20 times higher than that of a single-layer device. This difference in performance is due to the increase in surface area and the displacement under the external load as both factors directly affect device performance. We believe that this non-proportional 20 times increase in the response is due to active support structures. Unlike other TEH devices, the support structures are also coated with Parylene AF$_4$ and they contribute to the output of the device during the structural deformation process. However, further studies on the specific effects need to be conducted to fully understand the influence of the active support structures.

Finally, the power and current outputs over a range of different electrical loads were measured. Due to the high electrical impedance of the device, large impedance values were chosen for testing to find the optimum operating load. Figure 5a shows the SCC of a triple-layer device under an applied compressive force of 3 N at 1 Hz. This resulted in a peak SCC of 390 nA. The same device was then tested using the same experimental conditions under different electrical resistors. A peak power density of 5.5 µW/cm$^2$ was obtained at 900 MΩ.

![Figure 3: (a) Side-view SEM image of 3D printed elastomeric polyurethane coated with 100 nm-thick parylene AF$_4$. (b) Top-view SEM image of the 3D printed device after the parylene AF$_4$ coating process. The striations are the result of the layer-by-layer printing process in which each ridge corresponds to an approximate 16 µm layer in thickness. (c) Surface charge potential vs. time after the corona charging process. The surface charges stabilize at -12 Volts. (d) COMSOL simulations of the displacement under a force of 1 Newton for devices with single, double and triple layers.

![Figure 4: Short circuit current comparison of single-, double-, and triple-layer devices. Triple-layer devices show approximately 20× larger output current than that of single-layer devices.](image-url)
CONCLUSION

In conclusion, we have developed a fabrication method for triboelectric energy harvesters utilizing 3D printing and a robust conformal coating process for a fully 3D printed device. We have used the versatility of the method by designing and fabricating multi-layered structures. It is observed that a non-proportional 20× output current increase for the triple-layer device was achieved as compared with that of a single-layer device. This increase is thought to be due to the increase in displacement and surface area as well as the effects of active support structures. As such, the device and method presented here could directly impact the energy harvesting community by using 3D printing technology to make specific designs for wearable energy harvesting devices which require both good flexibility and soft structures.

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REFERENCES


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