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## Self-adhesive electrode applied to ZnO nanorod-based piezoelectric nanogenerators

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# Self-adhesive electrode applied to ZnO nanorod-based piezoelectric nanogenerators

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## **Abstract**

ZnO nanorod-based piezoelectric devices have gained wide attention in energy harvesting systems as they can be processed at low temperatures onto flexible plastic substrates, giving a good potential for low cost. However, the vacuum-evaporated, precious metal contacts remain a high-cost element of the devices. This paper discusses the use of transparent conductive adhesives (TCAs) as an alternative top contact that is free from both vacuum-evaporation and precious metals. TCA films of various thicknesses were tape-cast onto nickel microgrid on PET substrates and adhered using low-pressure cold-lamination to bond the adhesive component of the TCA to piezoelectric generators with the final device structure of PET/ITO/ZnO-seed/ZnO-nanorods/CuSCN/PEDOT:PSS/TCA. The piezoelectric performances of the devices were compared by measuring output voltage in open-circuit and maximum power output across a range of resistive loads. The voltage output was observed to rise with increasing TCA thickness, reaching a maximum value of 0.72 V generated with 110  $\mu\text{m}$  of TCA as top contact. However, the higher resistance due to increased TCA thickness led to decreased power output; a maximum calculated power of 0.25  $\mu\text{W}$  was obtained from the device with the thinnest TCA layer of 22  $\mu\text{m}$ . Finally, the performance of piezoelectric nanogenerators with TCA contacts were compared to a control device with an evaporated gold contact.

## **1. Introduction**

Piezoelectric energy harvesters have been of interest for some time as one of a class of vibration/kinetic energy harvesters that includes electrostatic and electromagnetic energy harvesters [1,2]. These have a wide range of potential applications where localised, generally low-level power can be harvested from the environment to power portable devices and sensors, removing or reducing the need for batteries or complex and expensive wiring. In particular, the growth in interest in the Internet of Things has driven a renewed interest in energy harvesting, as the proposed network of

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3 miniaturised and distributed sensors would be most effective if removed from the dependency on  
4 batteries and their necessary replacement.  
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6 For more than ten years there has been widespread development of ZnO nanorods for piezoelectric  
7 energy harvesting (nanogenerators) due to their low-cost and simple, solution-based fabrication. This  
8 enables the coating of a wide range of substrates, including polymers, in nanorod arrays that can be  
9 used for energy harvesting [3], offering the potential for low-cost and adaptable energy harvester  
10 fabrication. In our previous work, we have demonstrated an alternative ZnO nanogenerator, which  
11 uses a semiconducting polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)  
12 (PEDOT:PSS) to coat the surface of the ZnO nanorods [4], producing a lower impedance and higher  
13 output power than alternative designs with insulating polymer coatings [5]. We have also shown that  
14 a surface passivating layer of the semiconductor CuSCN produces large increases in output power [6].  
15 However, a serious hindrance remains to the low-cost, mass fabrication of these devices: the need for  
16 a vacuum-evaporated gold top contact. Such evaporated (or sputtered), precious metal contacts are  
17 also found in many other nanostructured energy harvesting devices [7–14] and therefore a viable,  
18 low-cost alternative would be extremely attractive for the energy harvesting, and wider community.  
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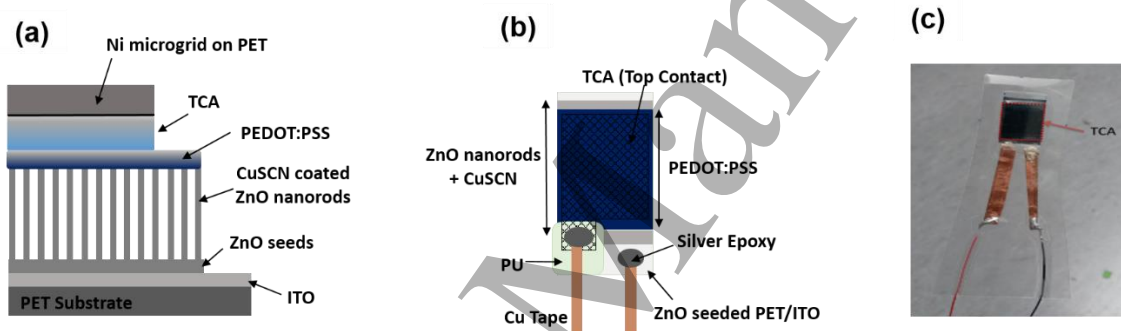
23 Here we report the innovative use of transparent conductive adhesives (TCAs) as top electrodes  
24 instead of conventional gold contacts. TCAs can be good alternatives to replace gold by omitting the  
25 vacuum deposition step and precious metal content of gold evaporation. These TCAs have been  
26 demonstrated to work as effective top contacts for hybrid organic-inorganic lead halide perovskite  
27 photovoltaics [15,16] and electroluminescent devices [17], but have never been demonstrated in a  
28 kinetic energy harvester. The PEDOT:PSS layer in our devices – to which the TCA has been shown to  
29 adhere well and form a good electrical contact [15,16] – offers a good opportunity to demonstrate  
30 this alternative contact material. The influence of TCA contacts was investigated for devices with TCA  
31 thickness ranging from 22 to 134  $\mu\text{m}$ . The devices were characterised by DC current-voltage  
32 measurements, AC impedance spectroscopy (IS), and open-circuit voltage output of the devices was  
33 measured by bending them to 45° and releasing. Maximum power output across a range of loads was  
34 also assessed by oscillating the devices on a permanent magnetic shaker. Functioning nanogenerators  
35 with varied TCA contact thickness were successfully produced where a voltage output was obtained  
36 responding to a strain change. The results were compared to study the optimum thickness of the TCA  
37 layers and how the thickness impacts on the overall properties and performance of the nanogenerator  
38 devices. The piezoelectric performances of TCA devices were also compared with a control device  
39 which has the same device structure but with a gold layer as top contact. Our study has shown that  
40 thicker TCA films generate higher open circuit voltage but lower power output due to the increased  
41 device resistance with greater TCA thickness. Open-circuit voltage over 0.5 V was obtained from  
42 devices with 110 and 134  $\mu\text{m}$  thick TCA layers. A TCA thickness of 22  $\mu\text{m}$  gave a maximum power  
43 output of 0.25  $\mu\text{W}$ . These results were lower compared to the control device with open circuit voltage  
44 output of  $\sim 0.7$  V and maximum power of 4.67  $\mu\text{W}$ . However, TCA devices still hold a good promise for  
45 a potential use in nanogenerator applications thanks to their low cost and easier processing methods.  
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## 52 **2. Experimental Methods**

### 53 **2.1. Fabrication of Piezoelectric Devices**

54 The piezoelectric device was fabricated by synthesizing layers of the following structure: PET/ITO/ZnO  
55 seeds/ZnO nanorods/CuSCN/PEDOT:PSS/TCA. ZnO nanorods were grown using an aqueous solution  
56 method on 2 x 1 cm<sup>2</sup> PET/ITO (polyethylene/indium-tin oxide) substrates (Sigma Aldrich, surface  
57 resistivity 60  $\Omega/\square$ ). These had previously been coated with a 100 nm-thick ZnO seed layer by  
58 magnetron sputtering [18]. An equimolar precursor solution of 25 mM Zn(NO<sub>3</sub>)<sub>2</sub> (Alfa Aesar, 99%) and  
59  
60

25 mM hexamethylenetetramine (HMT) (Alfa Aesar, 99%) in deionised water was used for ZnO nanorod synthesis. The synthesis was carried out for 24 hours at 90°C without any further treatment. ZnO nanorods were then spray coated with a thin layer of 0.15 M CuSCN (Aldrich, 99%) solution in dipropyl sulphide (Alfa Aesar, 98+%) by using a spray gun. An optimised amount of 8 ml of CuSCN solution was sprayed per three substrates, which were mounted on a hotplate at 100°C to evaporate the dipropyl sulphide. A further layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, Aldrich, 1.3 wt% in water, conductive grade) was deposited on CuSCN-coated ZnO nanorods by similar spray coating method. The insulating polyurethane (PU) resin was coated on the left side of the device before attaching the top contacts to avoid short circuit between the opposite contacts. The “transparent conductive adhesive” (TCA) top contacts were prepared by tape casting the PEDOT:PSS-acrylic adhesive blend onto the transparent conductive film (nickel microgrid on PET: Epigem, Epimesh) in accordance with established methods [15]. The height of the tape-casting guide was varied, using between 2 and 10 layers of adhesive tape to produce TCA films with a dry thickness ranging from 22 to 134  $\mu\text{m}$ . The PET/nickel microgrid/TCA Top contacts were adhered to the devices using low-pressure cold lamination to bond the adhesive component with the PEDOT:PSS surface of the nanogenerator. Devices were completed by bonding copper strips to each contact using silver epoxy with final encapsulation using PET laminating pouches to seal the whole device (**Figure 1**). Three devices were fabricated for each TCA thickness.



**Figure 1.** (a) Cross section and (b) top view schematics of the device. (c) Complete nanogenerator device.

## 2.2. Testing of Devices

Impedance spectroscopy (IS) was conducted using a Gamry Interface 1000 Potentiostat. The input frequency range used was from 0.1 Hz to 1 MHz. Open-circuit voltages were measured with an oscilloscope (Tektronix TDS 2012C) by manually bending the devices to 45° and releasing. For assessment of power outputs, the devices were mounted on a thin 1 cm x 4 cm spring-steel cantilever which was fixed on a permanent magnetic shaker (Brüel & Kjær, LDS V406) (Schematics in Supporting Information **Figure S1**). The root-mean-square (RMS) voltage outputs were measured across a range of resistive loads introduced by resistance box connected to the devices when the device/cantilever was oscillating at its resonant frequency (~300 Hz) with a peak acceleration of 12.4g. RMS power outputs were correspondingly calculated from the following equation:

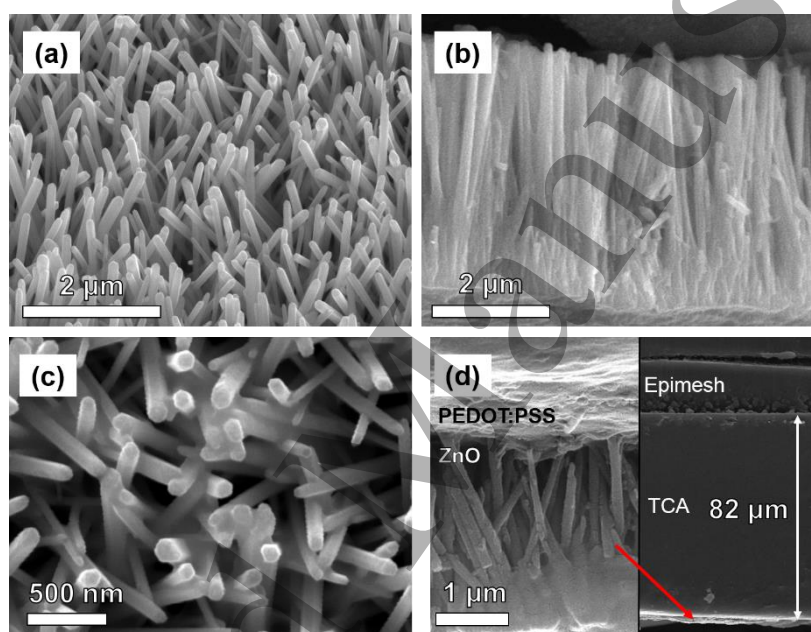
$$\text{Power (W)} = \frac{(\text{Voltage Output (V)})^2}{\text{Resistive Load } (\Omega)} \quad (1)$$

## 3. Results and Discussion

### 3.1. Device Structure

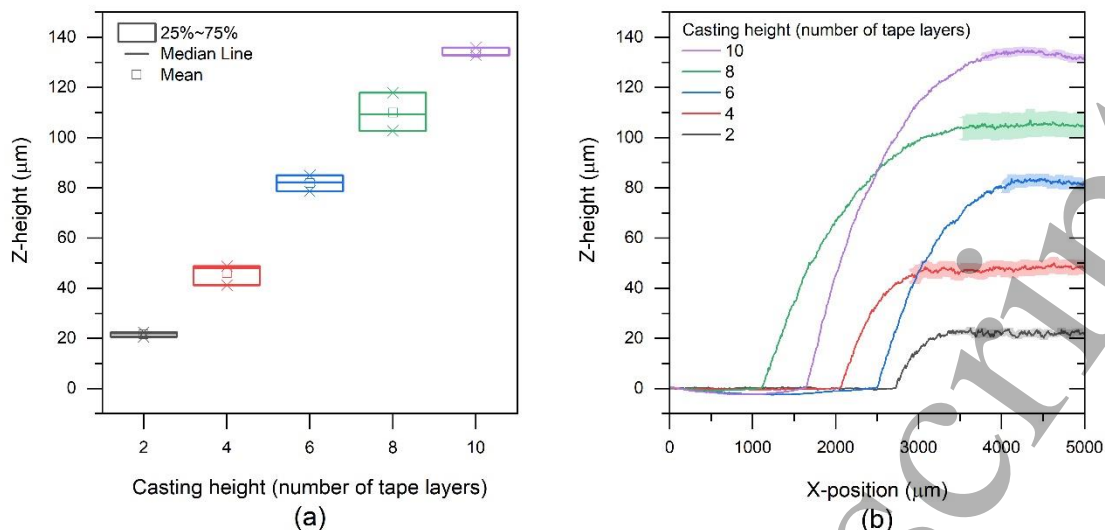
The morphology and dimensions of each layer of the device structure were analysed using scanning electron microscopy (SEM). The aqueous solution synthesis method at low temperature of 90°C

provided a uniform and densely packed array of ZnO nanorods growth on PET substrates (**Figure 2a-b**). The nanorods were approximately 4  $\mu\text{m}$  in length and 80 nm in diameter on average. CuSCN coating can just be seen as a thin layer on the surface of the nanorods, in some cases filling between rods which are close together (**Figure 2c**). The CuSCN coverage was  $\sim$ 5-10 nm thick, however was not completely uniform (**Figure 2c**). A layer of PEDOT:PSS was spray-coated onto the nanorod surface to provide a capping layer to allow addition of a top contact. The PEDOT:PSS layer was found to be  $\sim$ 2  $\mu\text{m}$  thick by SEM analysis of material removed from the device surface (**Figure S2**). In order to analyse the full device structure, complete devices were cryogenically fractured and analysed by SEM (**Figure 2d**). The ZnO nanorod array can be seen embedded in the thick PEDOT:PSS/TCA layer. No interface could be found between the spray-coated PEDOT:PSS layer and the TCA layer, indicating excellent adhesion. The thickness of the TCA layer for this device (cast using 6 tape layers) was measured to be 82  $\mu\text{m}$ , in excellent agreement with the profilometer measurement (see below). Overall, this analysis demonstrates the excellent adhesion of the TCA to the PEDOT:PSS surface, and in turn the PEDOT:PSS to the ZnO nanorods.



**Figure 2.** (a) Tilted and (b) cross section SEM image of ZnO nanorods grown on ITO-coated PET substrates. (c) Tilted SEM image of CuSCN coated ZnO nanorods. (d) Cross section SEM images of full device showing close-up of ZnO nanorods embedded in PEDOT:PSS layer (left), and cross-section of full, 82  $\mu\text{m}$  TCA film on nickel microgrid/PET with ZnO layer at bottom. Thickness of TCA layer indicated, with Ni microgrid layer and edge of PET layer visible above.

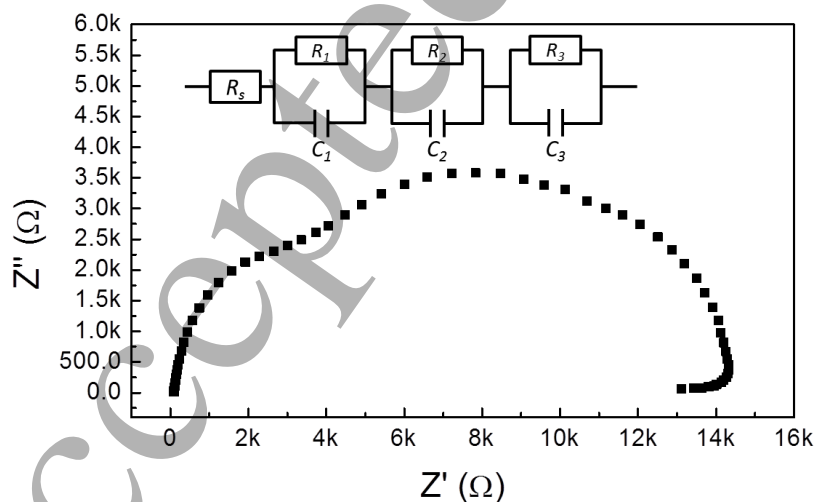
The thickness of the TCA films was measured using a stylus profilometer (Dektak, D150); predictably, an approximately linear trend between film thickness and casting height was found (**Figure 3**). The mean TCA thickness were 22, 46, 82, 110, and 134  $\mu\text{m}$  for nominal casting heights of 2, 4, 6, 8, and 10 tape layers. The overlaid profilometer scans (**Figure 3b**) show the region at the edge of each film used for the thickness measurement. The standard error of the mean for each sample is indicated by the shaded region; this error generally increases with the number of tape layers used to form the casting guide. The variation in film thickness is typical of the inconsistency exhibited by the tape casting process and can be eliminated with a scalable coating technique such as doctor blading or screen-printing.



**Figure 3.** (a) Summary of the TCA thickness data. (b) Topography of TCA film-edge used for the thickness measurement, the shading represents the standard error of the mean thickness.

### 3.2. Electrical Impedance Characteristics

Impedance spectroscopy (IS) measurements were performed to understand the charge transfer kinetics occurring at the interfaces of the layered structures. The impedance spectra generally appear to comprise three semi-circular elements (**Figure 4**). More information, including the nature of these elements, and their capacitance, can be obtained by fitting an equivalent circuit to the data. Due to the presence of three semicircles, it is assumed that the equivalent circuit comprises of three RC elements in series, with additional series resistance (**Figure 4 inset**). These would logically correspond to: 1. the main device structure of ZnO/CuSCN/PEDOT:PSS, which generally gives a single semicircle in a Nyquist plot [5]; 2. The PEDOT:PSS/TCA interface; 3. The TCA layer itself. A fit was therefore performed on these impedance data using this equivalent circuit. The full fit is shown in the supporting information (**Figure S3**), which gave the parameters shown in **Table 1**. The high capacitance of the RC element  $R_2-C_2$  suggests that this may correspond to the TCA film, which would be expected to have high capacitance. However, further control experiments of various combinations of each element would be needed to confirm this for certain.



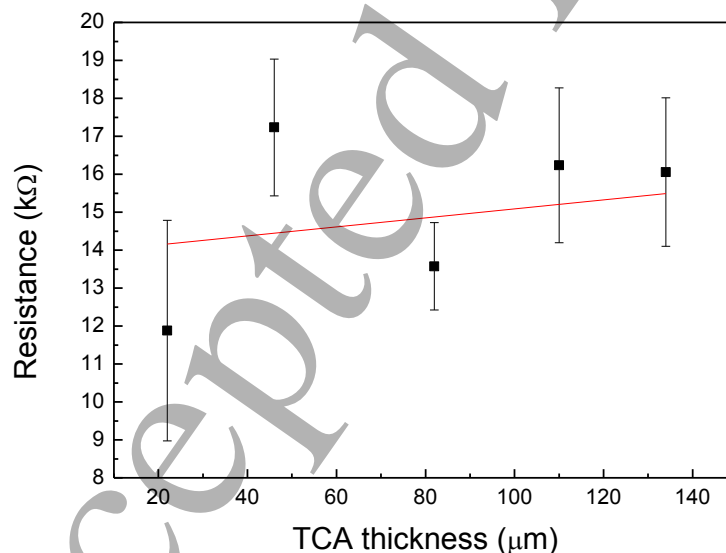
**Figure 4.** Example Nyquist plot for 6-layer device. Suggested equivalent circuit is shown in inset.



**Table 1.** Parameters obtained from fitting equivalent circuit model to impedance data shown in **Figure 4**.

Element	Resistance, k $\Omega$	Capacitance, $\mu$ F)
$R_s$	$0.16 \pm 0.03$	
$R_1, C_1$	$3.69 \pm 0.10$	$0.114 \pm 0.004$
$R_2, C_2$	$4.34 \pm 0.14$	$10.9 \pm 0.8$
$R_3, C_3$	$5.92 \pm 0.13$	$0.92 \pm 0.04$

Total device resistance was assessed from the maximum real component of the complex impedance. When plotted against the thickness of the TCA layer a weak trend was observed between device resistance and thickness, with a large error for the resistance of each layer (**Figure 5**). This seems to suggest that there is a slight increase in the device resistance as the TCA thickness increases. This is to be expected as the TCA is a relatively poor conductor when compared to the ITO electrode and nickel microgrid on PET materials between which the device is formed ( $60 \Omega/\square$  and  $1.2 \Omega/\square$  respectively). The linear trend has a slope of  $11.8 \Omega/\mu\text{m}$ , with an intercept of  $13.9 \text{ k}\Omega$ . This suggests an increase of  $11.8 \Omega$  per  $\mu\text{m}$  of TCA (bulk TCA film resistance), with a basic device resistance of  $13.9 \text{ k}\Omega$ . This basic resistance would correspond to the resistance of the ITO/ZnO/CuSCN/PEDOT:PSS structure, as well as the PEDOT:PSS/TCA interface and nickel microgrid resistances. This agrees well with a device resistance measured for our previous devices of  $\sim 12 \text{ k}\Omega$  [5], with the additional  $1.9 \text{ k}\Omega$  originating from the PEDOT:PSS/TCA interface and nickel microgrid on PET substrate. Also, comparing the estimate of  $11.8 \Omega$  per  $\mu\text{m}$  to RC element 2 from the fit above (**Table 1**) – which gave a resistance of  $4.34 \text{ k}\Omega$  for a 6-layer ( $82 \mu\text{m}$ ) device – gives  $\sim 53 \Omega$  per  $\mu\text{m}$ . This is within a factor of 5 of that obtained from the slope in **Figure 5**, which, considering the large error in the data points, suggests that a TCA resistance per thickness in this range is reasonable. The large error originates from large device-to-device variability, most likely from the quality of the bond to the TCA layer. Reduction of this variability is the subject of ongoing work.

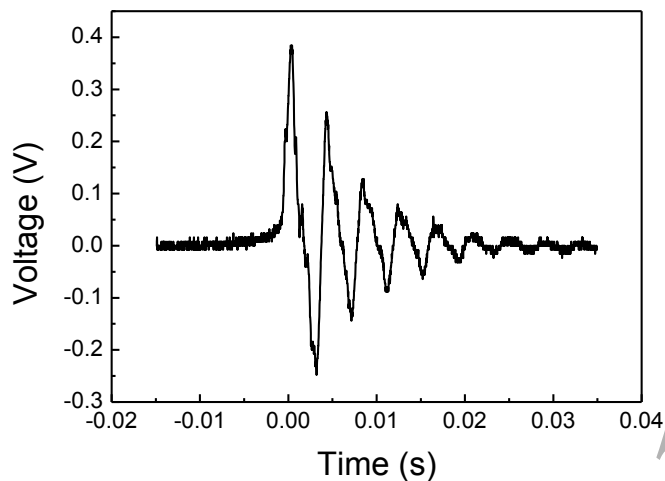


**Figure 5.** Average resistance values for the nanogenerator devices depending on TCA layer thickness.



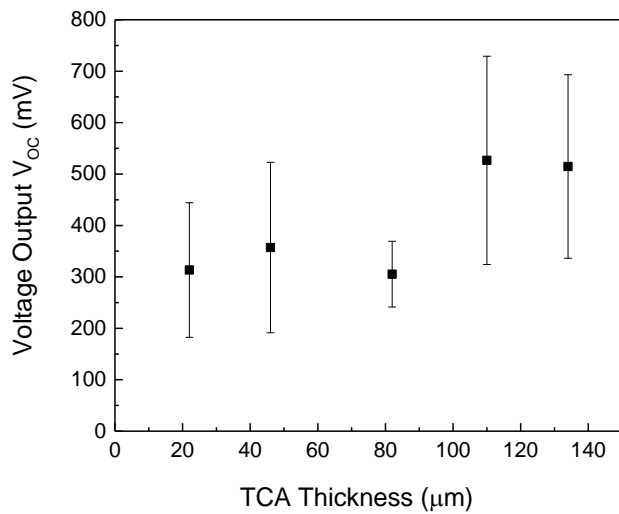
### 3.3. Device Output

It can be seen from **Figure 6** that functioning nanogenerators with TCA top contacts were successfully produced where an output voltage was obtained upon applying strain (45° bend and manual release); this example device with a 46  $\mu\text{m}$  TCA layer produced a peak open circuit voltage around  $\sim 0.4$  V. Full device performance testing was conducted by measuring maximum open-circuit output voltage from such traces, and average (RMS) power output across a range of resistive loads when vibrated using a mechanical shaker (see methods).



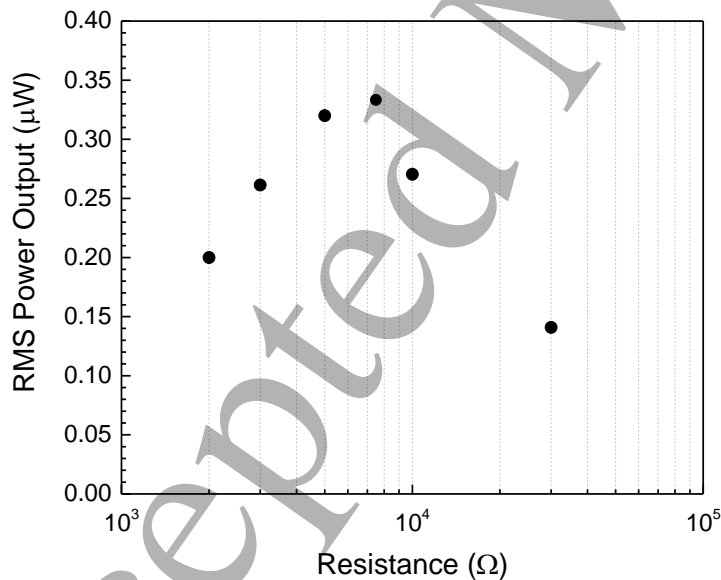
**Figure 6.** Open circuit voltage output of a nanogenerator device with a 46  $\mu\text{m}$  thick TCA layer when bent and released manually.

**Figure 7** shows the peak open-circuit voltage output of all nanogenerator devices plotted against the TCA layer thickness with each data point representing the average of three devices. The measured voltage output was higher for nanogenerators with a thicker TCA layer: the 110 and 134  $\mu\text{m}$  devices gave an average value of more than 0.5 V. This could be expected due to the increasing resistance of the device with increased TCA thickness, as calculated by the IS measurements; we have shown in our previous work that these devices are strongly affected by polarisation screening from the circuit, and that this can be slowed by increasing the  $RC$  time constant ( $\tau = RC$ ), giving higher voltage outputs with higher internal resistance [6]. Hence the need for electrical impedance matching to maximise power transfer [19,20], as investigated below.



**Figure 7.** Peak open circuit voltage output of all devices with different thicknesses of TCA layers.

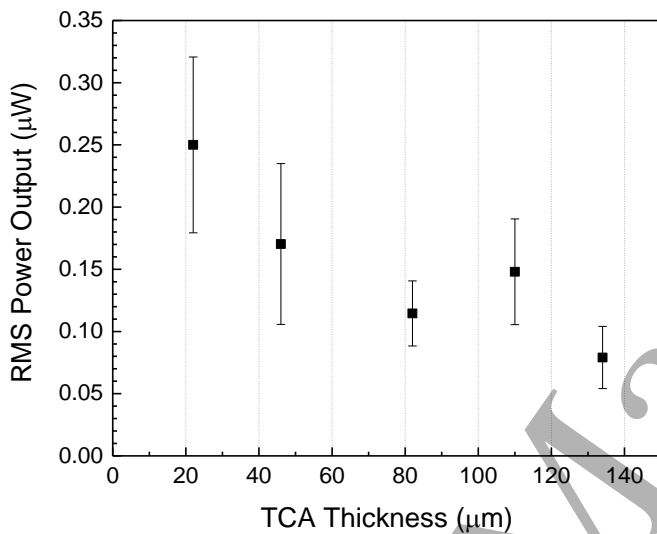
To more accurately assess the useful output from the devices, RMS voltage output was measured across a range of resistive loads. Correspondingly, RMS power output obtained by the devices at different resistive loads were calculated. These measurements were conducted when the devices were mounted on an oscillating cantilever fixed on a magnetic shaker at an acceleration of 12.4g. The RMS voltage output was then measured from the sinusoidal oscillation of the cantilever at resonant frequency ( $\sim 300$  Hz). An example plot of power versus resistive load for a device with a 22  $\mu\text{m}$  TCA layer is shown in **Figure 8** (See Figure S4 for plots of all devices).



**Figure 8.** RMS power output calculated by measuring RMS voltage outputs across a range of resistive loads for an example 22  $\mu\text{m}$  TCA layer device. Maximum power was obtained at a resistance load of 7500  $\Omega$ .

Using this method, the maximum RMS output power and optimum load were obtained for all nanogenerator devices. The average of this maximum power versus TCA layer is reported in **Figure 9**,

which was calculated by taking an average of the maximum powers obtained by the devices of same TCA thickness. The highest power output was obtained devices with a 22  $\mu\text{m}$  TCA layer reaching an average value of 0.25  $\mu\text{W}$ . The power output decreases with increasing TCA thickness. This is related to the higher internal (series) resistance of devices with a thicker TCA component causing a reduction in power output. This suggests a thin TCA film is desirable to reduce resistive losses for an increased power output despite the increased open-circuit voltage with increasing TCA thickness. We previously demonstrated that open-circuit voltage is a somewhat misleading measure of device performance, as it will generally increase with increasing internal resistance (due to the principle of a resistive divider), but power output will decrease where this resistance is added externally to the piezoelectric element [5].



**Figure 9.** Maximum RMS power obtained at different TCA layer thickness. The power increases with decreasing TCA thickness, where the average power for nanogenerator devices with a 22  $\mu\text{m}$  thick TCA layer was the highest at 0.25  $\mu\text{W}$ .

The output open-circuit voltage and RMS power output on a range of loads of a control device were also measured for comparison (**Figure S5**). The control device had an identical basic device structure as the TCA-containing devices (PET/ITO/ZnO seeds/ZnO nanorods/CuSCN/PEDOT:PSS) but with  $\sim 150$  nm of evaporated gold as top contact. The peak open-circuit voltage of the control device was found to be higher than all the TCA devices, reaching an average value of  $\sim 686$  mV (**Table 2**). Although the internal resistance of this device was lower than the TCA devices, the losses are also expected to be lower, accounting for the higher output. In addition, the mechanical resonance of the device clearly has a longer duration (Figure S5b). This is related to the different mechanical properties of the device, as the TCA-containing devices are mechanically stiffer due to the nickel microgrid on PET films on which TCA layer is deposited. To demonstrate, a simple stiffness test was conducted to calculate and compare the flexural constants ( $k$ ) of the devices (which is proportional to the modulus of elasticity) by measuring the maximum displacement upon applying the equal force. It was found that a 2 layer TCA containing device has a higher flexural constant, with ratio of  $k_{\text{TCA}}/k_{\text{Gold}} = 1.43$  compared to the device with gold contact, which implies less flexibility and explains the stronger damping of oscillation with TCA devices (See Figure S6 for experimental details and detailed calculations). To alleviate this in future a more compliant conductive substrate could be used as a basis for the TCA layer since in this application the transparency of the Ni microgrid is not needed, unlike the photovoltaic applications for which it was developed [15,16].

**Table 2.** Piezoelectric performance parameters for all TCA devices with different thickness of TCA layers and control device with Au layer as top contact

Contact	Open Circuit Voltage, mV	Peak Power, $\mu\text{W}$
TCA - 22 $\mu\text{m}$	$69 \pm 32$	$0.3 \pm 0.1$
TCA - 46 $\mu\text{m}$	$360 \pm 170$	$0.2 \pm 0.1$
TCA - 82 $\mu\text{m}$	$305 \pm 64$	$0.1 \pm 0.03$
TCA - 110 $\mu\text{m}$	$530 \pm 200$	$0.15 \pm 0.04$
TCA - 134 $\mu\text{m}$	$520 \pm 180$	$0.08 \pm 0.03$
Au	$690 \pm 210$	$4.7 \pm 2.6$

## 4. Conclusions

The use of transparent conductive adhesives (TCAs) as top-contact electrodes in piezoelectric devices has been demonstrated for the first time. The top-contacts were prepared by tape-casting the TCA at different thicknesses on nickel microgrid on PET substrates and applied to the devices using low-pressure cold-lamination. The piezoelectric performance of the devices was evaluated by measuring output voltage in open-circuit and maximum power output across a range of resistive loads. It was found that the peak voltage output increased for thicker TCA layers, where a maximum voltage output of 0.72 V was generated when a device with 110  $\mu\text{m}$  of TCA was bent and released manually. However, higher internal resistance introduced by increasing TCA thickness led to a reduced power output; a maximum calculated power of 0.25  $\mu\text{W}$  was obtained from the device 22  $\mu\text{m}$  of TCA. Devices with TCA contacts were also compared to a control device, where the top contact was  $\sim 150$  nm of evaporated gold. The control device generated a higher power reaching an average value of 4.67  $\mu\text{W}$ . This was expected due to the lower resistance of the gold layer and higher strain induced due to its less stiff structure. However, the piezoelectric performances of TCA devices are still within one order of magnitude of the control device, therefore, they have good promise for replacing the expensive and difficult-to-produce gold contacts. These results suggest that further lowering of the TCA resistance, for example by increasing the PEDOT:PSS content, may improve nanogenerator output power further. This is possible for this application, where transparency is not needed, unlike previous applications of the TCAs in optoelectronic devices. Furthermore, this utilisation of the TCA contacts beyond the initial demonstrations in optoelectronic devices indicate there may be many more applications to which these contacts could be applied to facilitate low-cost and high-throughput device manufacture.

## 5. Acknowledgements

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