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Handwriting enabled harvested piezoelectric power using ZnO nanowires/polymer composite on paper substrate

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Abstract

We here, present a flexible handwriting driven nanogenerator (NG) based on zinc oxide (ZnO) nanowires (NWs)/polymer composite grown/deposited on paper substrate. The targeted configuration is composed of ZnO NWs/PVDF polymer ink pasted and sandwiched between two pieces of paper with ZnO NWs grown chemically on one side of each piece of paper. Other configurations utilizing a ZnO/PVDF ink with different ZnO morphology on paper platform and others on plastic platform were fabricated for comparison. The mechanical pressure exerted on the paper platform while handwriting is then harvested by the ZnO NWs/polymer based NG to deliver electrical energy. Two handwriting modes were tested; these were slow (low pressure) and fast (high pressure) handwriting. The maximum achieved harvested open circuit voltage was 4.8 V. While an out power density as high as 1.3 mW/mm² was estimated when connecting the NG to a 100 Ω load resistor. The observed results were stable and reproducible. The present NG provides a low cost and scalable approach with many potential applications, like e.g. programmable paper for signature verification.

Key words: Zinc oxide nanowires, polymers, paper substrate, piezoelectricity, energy harvesting, nanogenerators.

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Introduction

Self-powered systems are a new emerging technology, which allows the use of a system or a device that gives energy without the need for external power like a battery or any other type of source [1]. This technology can for example use harvested energy from sources around us such as ambient mechanical vibrations, noise, and human movement and converted it to electric energy using the piezoelectric effect [1].

For nanoscale devices, the size of traditional batteries is not suitable and will lead to loss of the concept of ‘‘nano’’. This is due to the large size and the relatively large magnitude of the delivered power from traditional source. The development of a nanogenerator to convert energy from the environment into electric energy would facilitate the development of self-powered systems relying on nanodevices. In recent years, various articles have reported the utilization of the piezoelectric properties of zinc oxide (ZnO) nanostructures, but most of these efforts have focused on studying single ZnO nanowire (NW) [3, 4]. A few investigations have discussed ZnO nanowire arrays with glass, sapphire, Si, or other hard substrates [3-5]. Other research groups have exploited the piezoelectric effect of various flexible substrates, such as paper, zinc foil, PET (polyethylene terephthalate), and some more [2, 6], because it is difficult to enhance the piezoelectric effect by transferring the mechanical energy into electrical energy using hard substrates such as glass, sapphire, Si, etc.

Zinc oxide is a II-VI wide direct bandgap (3.7 eV) semiconductor and has excellent piezoelectric properties. Hence it exhibits potential for novel applications since we can couple the fields of electronics, photonics and piezoelectricity [7, 8]. This is one of the reasons why ZnO has attracted a lot of interest for developing nanogenerators [1]. The synthesis of aligned ZnO NW arrays has been studied [9, 10] during the past several years due to the various potential applications of aligned ZnO NW arrays in light emitting diodes [11-13], lasers [14,15], solar cells [16-18], nanogenerators [19-21] and piezotronics [22, 23], etc. Various methods have been reported for synthesizing ZnO NW arrays, mainly including physical vapor phase transport and deposition [24-26], metal organic chemical vapor deposition (MOCVD) [27, 28] and the low temperature hydrothermal approach [29-31]. Nevertheless, the hydrothermal is advantageous when compared to other methods because the growth temperature is suitable for soft substrates like e.g. paper substrate. Furthermore, the hydrothermal method is low cost and can be adopted for mass production [32]. Recently, ZnO NWs have received more attention for their ability to convert mechanical energy to
harvestable electrical energy [33–36]. In addition to the development of systems depending only on ZnO NW arrays, ZnO composite structures have been suggested. As a polymer piezoelectric material and owing to the good optical transparency and mechanical flexibility, poly (vinylidene fluoride- trifluoroethylene) (P(VDF-TrFE)), has been exploited [37, 38].

In the present letter, we demonstrate a handwriting driven piezoelectric nanogenerator (NG) based on ZnO NWs/PVDF polymer hybrid structure grown on paper substrate. We demonstrate the applications of P(VDF-TrFE)/ZnO NWs ink sandwiched between two pieces of paper coated with vertically aligned ZnO NWs grown on silver electrodes to act as an actuator. Two different P(VDF-TrFE)/ZnO NWs ink configurations have been fabricated. The first is based on hydrothermal ZnO NWs filtered from growth solutions and the other is based on ZnO tetrapods. After processing of the NG, pressure from handwriting is used to harvest electrical energy. The demonstrated NG exhibited good mechanical durability, high sensitivity, and provides scalable simple low cost approach.

**Experimental section**

In the fabrication of the handwriting enabled piezoelectric nanogenerators, basically two different configurations of ZnO NWs/polymer composite grown on a paper substrate were used. A third sample was prepared on a PEDOT:PSS coated plastic substrate for comparison. In addition another comparison fourth sample was prepared using pure PVDF ink without ZnO nano powder. The choice of paper as a platform in this work is basically due to two reasons. The first is the possibility to introduce devices with low cost, while the second is due to the softness and porous nature of the paper that allow efficient transfer of pressure forces and consequently the possibility of efficiently harvesting mechanical energy into electrical energy.

In all fabricated configurations used ZnO NWs were first grown on paper substrate. The paper substrates used in our experiments were cut from a large piece of common packing paper with high flexibility (Invercote G from Holmen AB, Sweden). After being cleaned ultrasonically in acetone and ethanol, a 10/50nm layer of chrome/silver was evaporated on the paper substrate to act as a contact. In a second step we grow ZnO NWs on this paper substrate using the low-temperature chemical growth technique. Usually after two steps, well aligned ZnO NWs can be grown using this method. The details of this growth can be found in [39, 40]. The growth was terminated after 6 hrs. The paper sample was cleaned with deionized water and left to dry in an ordinary laboratory oven set at 80 ºC for ten minutes. The growth
nutrient solution which was transparent when mixed becomes blurry and full of ZnO nanostructures after the termination of the growth. This solution was kept and filtered and the collected powder was used later. The resulting white powder was composed of ZnO NWs [39]. This powder was kept and used later to fabricated a ZnO/polymer composite NGs. Depending on the nutrient growth solution concentration and the duration of the growth period, different sizes and amounts of NWs can be obtained by filtering the growth nutrients solution [41]. For the extraction of the filtered ZnO NWs we have performed many experiments with nutrient solutions having different concentrations. From these experiments we have achieved ZnO powder in a range between 0.1 mg/mL and up to 20.0 mg/mL. This chemically grown ZnO NWs powder was used for the first piezoelectric NG configuration. While for the second configuration another commercial ZnO tetrapod material prepared by physical method was used [42].

The electrical harvested energy measurement was performed using a Keithley 2400 source meter. The Keithley 2400 is also interfaced to a computer to plot the data. For estimating the open circuit output voltage, the two end contacts of the nanogenerator were connected to the source meter. The mode of measurement used was voltage versus time. For the case of the current measurement (short circuit current), a load resistor is connected in parallel to the nanogenerator and the voltage across this load resistance versus time was measured. To measure and estimate the exerted pressure when handwriting is performed a simple setup is arranged. In this setup the paper substrate is fixed on top of a balance in such a way that the exerted pressure is only transferred to the paper/balance table i.e. the rest of the hand supported parts are not in contact to the paper/balance table. The weight exerted during handwriting is then transferred to pressure by using the surface area of the pen tip. This was performed for both fast and slow handwriting modes, and was repeated several times and the mean value was used.

**Result and discussion**

The structural properties of the grown nanostructures were performed using scanning electron microscopy (SEM) and powder X-ray diffraction (XRD). Figure 1a shows a low magnification SEM micrograph of the ZnO NWs grown on paper substrate. As clearly seen dense ZnO NWs arrays were achieved. Figure 1b shows a high magnification SEM image indicating a hexagonal NWs with a diameter ranging between 0.8 – 1.5 µm. X-ray diffraction pattern from this sample is shown in Figure 1c. As can be seen only diffraction peaks from
ZnO and Ag were observed. While Figure 1d shows a SEM image of ZnO NWs grown on the PEDOT:PSS coated plastic and used as mentioned above for comparison purpose.

The fabrication of the present NG proceeded as follows: 0.01g of the filtered ZnO NWs powder (or from the commercial ZnO tetrapods) was added to 1 mL of P(VDF-TrFE) (70:30). The mixture was stirred at 60°C for 6 hours to form a homogenous ink. The addition of the ZnO nano powder to the PVDF-TrFE will lead to enhance the stability of the piezoelectric polymer [43, 44]. A small drop from the ink was applied on top of the paper substrate with chemically grown ZnO NWs (Stencil print method). Then the paper was dried for 15 min. at room temperature and then heated at 80 °C for 10 minutes. Typically different pieces of paper of a size of around 4.2 cm x 2.0 cm were used. After this two similar paper pieces were attached face to face and electrical wires were connected from both faces and handwriting was performed on one face while monitoring the electrical output on a computer screen. Figure 2a shows a digital photograph of the final fabricated NG. While in Figure 2b a schematic diagram displaying the structure of the general configuration used for the piezoelectric NG is shown. Finally Figure 2c-d show photographs during the measurement. The electrical characterization of the NG grown on paper using ZnO NWs/PVDF polymer was performed using a Keithley 2400 source meter and the measurement data was transferred to a computer (as shown in Figure 2c). The measurement was performed for two modes; fast and slow handwriting modes as different mechanical energy are applied for these two different modes. The handwriting speed and the corresponding pressure vary from person to person and depend on the type of pen used. The slow mode corresponds to low applied pressure, while the fast handwriting mode corresponds to high applied pressure. The handwriting was performed using a ball pen with a tip spatial area of about 0.16 cm². In our experiments the handwriting speeds were estimated to be about 100-120 letters/minute and about 200-240 letters/minute for the slow and fast handwriting modes, respectively. The corresponding pressures were measured to 8.2 N/cm² and 28.4 N/cm², respectively. The harvested electrical voltage and current were recorded for a handwriting period of around 1 minute.

Figure 3 (a) shows the open circuit output voltage of the NG fabricated using the ZnO tetrapods/P(VDF-TrFE) ink pasted on ZnO NWs grown on paper substrate. The maximum harvested output voltage achieved was 1.8 mV for fast speed handwriting and was down to around 0.3 mV for slow speed handwriting. The corresponding electrical open circuit output voltage for the other configuration using the chemically grown ZnO NWs is shown in Figure 3b. As it is clearly seen the output voltage is increased to a maximum value of 2.0 V for slow
speed handwriting and reached a maximum of 4.8 V for fast speed handwriting. This indicates an enhancement when using ZnO NWs grown chemically compared to commercial ZnO tetrapods grown using high temperature physical approach [42]. To estimate the short circuit current delivered from this NG, a 100 Ω load resistance is connected as shown in Figure 3c. The voltage across this 100 Ω load resistance was measured and the current is then estimated. As shown in figure 3d, a maximum current of 14.4 mA was measured for high speed handwriting while the corresponding value was 2.8 mA for low speed handwriting. These values are higher than results published from configurations having ZnO NWs with pure PVDF grown on fiber [42], and even higher than NG fabricated from ink of a mixture of polar ZnO NWs with PMMA grown on flexible polystyrene plastic substrate [44]. This high value is attributed to the relatively high pressure exerted by the pen tip. To separate the effect of the ink mixture (Figure 3a, b) from that of a pure polymer ink with no ZnO nano powder, a sample with only pure P(VDF-TrFE) sandwiched between two pieces of paper with ZnO NWs grown chemically on their surface is fabricated. This configuration showed relatively lower output voltage compared to the results of Figure 3a-b. This is shown in Figure 3e where a maximum of 0.2 V was achieved when performing high speed handwriting. To investigate the effect of the substrate, we have also fabricated a NG using our ink sandwiched between two ZnO NWs grown by the chemical methods on PEDOT:PSS coated plastic (see below).

According to theoretical calculations, the output voltage from a nanowire is linearly proportional to the magnitude of the deformation caused by the external applied force or pressure [45]. Hence for maximizing the harvested mechanical energy an efficient transfer of the applied pressure would be preferable. While the ZnO NWs have a positive value of the piezoelectric coefficient d_{33}, the value for the PVDF gives a negative voltage when polarized [44]. Nevertheless, in a tri-layer based configuration similar to the one presented here (ZnO NWs/PVDF/ZnO NWs) the PVDF was poled to achieve maximum harvested output power [44]. In our case the PVDF is not poled and hence it acts as a dielectric layer. The crystallographic alignment of the ZnO NWs indicates their piezoelectric response to external pressure which is in our case due to handwriting. Generally when a ZnO NW is bent (due to external force) a separation of the static ionic charge centers in the tetrahedral coordinated Zn-O system results in a piezoelectric potential gradient along the c-axis. Because the c-axes of all the NWs are aligned parallel to one another, the piezoelectric potentials created along each NW would have the same tendency of distribution, leading to an enhanced macroscopic behavior [45]. Based on this, the working principle of the handwriting enables NG is as
follows: Figure 4 illustrates all possible bending situations of the two ZnO NWs layers (on the top or the bottom paper) with or without handwriting. When no handwriting is applied (Figure 4a) i.e. no bending, no c-axis potential gradient along the ZnO NWs will be observed. Nevertheless, when the NWs are bent, there will be two possible distinct situations. These two situations are illustrated in Figure 4b-c. In the situation of Figure 4b, the bending of the NWs leads to create a piezoelectric potential gradient in such a way that the top paper contact will have a positive potential while the bottom paper contact will have a negative potential. A situation similar to this but with reversed voltage polarity can also exist. In that case the harvested potential will be in the opposite direction to that of figure 4b. The last situation, shown in Figure 4c, is when similar voltage polarity exists at both top and bottom contacts. Assuming that the ZnO NWs are identical and upon handwriting they bent similarly, the harvested voltage from the top and bottom paper will cancel each other.

The efficient transfer of the applied external mechanical energy will also depend on the platform hosting the NG. A NG on plastic was fabricated for comparison with paper and hence it was having a configuration similar to that of the device of Figure 3b, i.e. polymer ink with ZnO NWs powder grown chemically and sandwiched between two pieces of paper having ZnO NWs on a surface grown over Ag/Cr thin layer. The ZnO NWs used for this plastic based NG are shown in Figure 1d. The result of the output voltage of the plastic platform based ZnO NWs NG is shown in Figure 5a together with the output voltage of the device of Figure 3b. As it is clearly seen, the delivered open circuit output voltage from this plastic based NG has reached a maximum value of around 0.04 V. This value is relatively much lower than the highest value obtained from similar ZnO NWs/polymer ink stacking configuration NG based on paper platform (4.8 V). This shows that the choice of the porous and soft substrate, i.e. paper, has led to an improvement of the output voltage by a factor of 100 compared to the case when using plastic as a platform. This is believed to be due to the more efficient transfer of handwriting pressure to the nanowires rather than being absorbed through bending of the whole platform.

To estimate the output power delivered from NGs different circuits can be used [46-49].The basic test is to connect the NG to a load resistance (R_L). By measuring the maximum voltage across this load resistance (V_R) the output power (P) can be estimated as [46].

$$P = \frac{V_R^2}{R_L}$$  \hspace{1cm} (1)

We have connected our NG that delivered the highest open circuit output voltage to different load resistors varying between 100 Ω and up to 3 kΩ. Then the pen tip spatial area
while handwriting is used to estimate the output power density. Figure 5b displays the output power density obtained from the ZnO NWs grown on paper platform and for a configuration with ZnO NWs/PVDF polymer ink pasted and sandwiched between the two pieces of paper with ZnO NWs grown chemically (configuration of figure 3b). As can be seen from Figure 5b, the maximum observed output power density has reached about 1.3 mW/mm² when a load resistor of 100 Ω is connected to the NG. This NG was then tested to operate a commercial light emitting diode (LEDs). The insert in Figure 5b shows a commercial red LED operated using the NG of figure 3b. From the presented results, it seems that the stacking ink layer (layer of PVDF with filtered ZnO NWs) in the middle contributes to increase the harvested output power. In the configuration with PVDF with the filtered ZnO NWs sandwiched between two pieces of paper covered with vertical ZnO NWs when handwriting pressure is applied on the surface of the NG we achieved the highest output due to two contributions. The first effect is from the bending of the vertical ZnO NWs grown on the paper coated with Cr/Ag. The second contribution is due to the filtered ZnO NWs which forms a composite with the PVDF polymer. More detailed study on the individual contribution, together with the estimation of the efficiency of harvesting mechanical pressure when handwriting in connection to the stacking sequence is under present investigations.

**Conclusion**

In summary, in this letter we demonstrate a ZnO NWs/PVDF polymer based hybrid handwriting driven NG fabricated on soft porous paper platform. From the different configurations studied, it was concluded that the highest harvested electrical output power was achieved when using a ZnO NWs/ PVDF polymer ink pasted and sandwiched between two pieces of paper with ZnO NWs grown chemically on the side of each piece of paper. This stacking configuration has delivered a voltage as high as 4.8 V and a current as high as 14.4 mA. A maximum spatial output power density of 1.3 mW/mm² was achieved for fast handwriting mode (200-240 letters/minute). The present approach is promising, scalable, and the principle of harvesting mechanical vibration on paper platform can be utilized from any machineries. The present piezoelectric NG can be used for many applications, like e.g. development of signature verification programmable smart paper, handwriting in dark paper when integrating light emitting diodes on the same paper etc..
References

[42] Pana-Tera is trade mark of Matsushita Electric Industrial Co. Ltd. (Japan).
**Figure Captions**

**Figure 1**: (a) shows a low magnification SEM micrograph of the ZnO NWs grown on paper substrate, (b) shows a high magnification SEM image indicating hexagonal NWs, (c) shows x-ray diffraction pattern from this sample, and (d) shows a SEM image of ZnO NWs grown on the PEDOT: PSS coated plastic and used for comparison purpose.

**Figure 2**: The setup of measurement (a) a digital photograph of the final fabricated NG is shown, and (b) shows a schematic diagram displaying the structure of the general configuration used for the present piezoelectric NG, (c) and (d) photographs during the measurement using the handwriting enabled harvested electrical energy, respectively.

**Figure 3**: The performance of ZnO NWs/PVDF paper based NG, (a) the output voltage achieved by using commercial ZnO tetrapod powder as a function of time for slow and high speed handwriting. (b) The output voltage achieved using ZnO NWs filtered powder as a function of time at slow and high speed handwriting. (c) Schematic diagram of the circuit used to estimate the short circuit current through a load resistance. (d) The short circuit output current through a 100 load resistor measured for the structure of (b) as function of time for fast and low speed handwriting. Finally in (e) the open circuit output voltage as a function of time of a NG fabricated by pure polymer ink sandwiched between two ZnO NWs grown on paper is shown.

**Figure 4**: Schematic diagram illustrating the different possibilities of the ZnO NWs bending due to pressure exerted while handwriting is applied. The expected voltage polarity on the paper contact (top and bottom) is also shown.

**Figure 5**: (a) The performance of ZnO NWs/PVDF NG fabricated on paper and on PEDOT:PSS plastic platforms for comparison, and finally in (b) the maximum output power density as function of load resistance for NG based on ZnO NWs/PVDF polymer ink pasted and sandwiched between two pieces of paper with ZnO NWs grown chemically on one side of each piece of paper is shown. The inset is a digital photograph showing a light emitting diodes operated by handwriting harvested power from the handwriting enabled paper nanogenerator.
Figure 1:
Figure 2:
Figure 3:

(a) 

(b)
(e)
Figure 4:

No handwriting pressure

With handwriting pressure

(a)

(b)

(c)
Figure 5:

(a)

(b)