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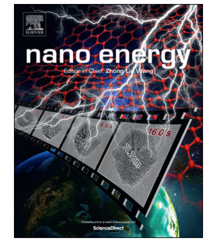

RAPID COMMUNICATION

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 morphologies 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/mm^2 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.

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

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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 nano-devices. 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 paper, 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 10/50 nm layer of chrome/silver was evaporated on the paper substrate to act as a contact. In the 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 Refs. [39,40]. The growth was terminated after 6 h. The paper sample was cleaned with deionized water and left to dry in an ordinary laboratory oven set at 80 °C 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 a 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.