Flexible ZnO–Cellulose Nanocomposite for Multisource Energy Conversion

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Materials with the ability to harness multiple sources of energy from the ambient environment could lead to new types of energy-harvesting systems. It is demonstrated that nanocomposite films consisting of zinc oxide nanostructures embedded in a common paper matrix can be directly used as energy-conversion devices to transform mechanical and thermal energies to electric power. These mechanically robust and flexible devices can be fabricated over large areas and are capable of producing an output voltage and power up to 80 mV and 50 nW cm^{-2}, respectively. Furthermore, it is shown that by integrating a certain number of devices (in series and parallel) the output voltage and the concomitant output power can be significantly increased. Also, the output voltage and power can be enhanced by scaling the size of the device. This multisource energy-harvesting system based on ZnO nanostructures embedded in a flexible paper matrix provides a simplified and cost-effective platform for capturing trace amounts of energy for practical applications.

1. Introduction

The growing need for alternative and portable sources of energy has motivated significant effort to develop new forms of energy-conversion and storage devices.[1–5] The capability of harnessing various forms of ambient energy present in the environment (e.g., mechanical vibrations, heat, water flow, wind, and human activities)[6] is an attractive feature for such energy-conversion devices. Powering small electronic devices with energy harvesters would make them independent of external power sources, which are generally bulky and expensive. Ambient energy is mostly dominant in the mechanical and thermal forms[6] and their conversion into electrical energy could play a key role in developing technologies, such as remote access electronics, self-powered sensors, or implantable medical devices. Considerable attention has been focused on using piezoelectric materials to capture ambient mechanical vibrations. Thermal energy is another potential source of energy, widely available in the environment, which can also be converted to electrical energy using thermoelectric or pyroelectric modules.[7–13] Moreover, if a single device has the capability to harvest energy from multiple sources, such as mechanical and thermal, it can lead to a new and more efficient platform for energy conversion.

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Both mechanical and thermal energy can be harvested using piezoelectric materials. Several types of piezoelectric materials, such as ceramics, polymers, and macrofiber composites, have been successfully used for harvesting thermal as well as mechanical energy.[14–17] Ferroelectric ceramic/polymer composites have been used in piezoelectric and pyroelectric sensor applications, as they combine the mechanical compliance and flexibility of polymers with the high piezoelectric and pyroelectric properties of ceramics.[18] Among these, zinc oxide (ZnO) is a unique material that has both semiconductor and piezoelectric properties[19] and has an added advantage of low cost.[20–23] Wang and others have developed aligned arrays of ZnO nanowires by a vapor–liquid–solid process on GaN and sapphire substrates, and utilized them for energy generation by deflection/vibration of the nanowires.[20,21] The reported procedure involves complicated material processing and device fabrication (using precise manipulators), which are hurdles for scalability and cost.

Although these reports have made significant contributions and set benchmarks, it is important to explore innovative, inexpensive, scalable technologies based on new materials and engineering approaches wherein a single device can be used to transform multiple sources of energy. Cellulose (the main constituent of paper) is an appropriate flexible platform for the fabrication of energy-harvesting devices as it is lightweight, abundant, environmentally benign, recyclable, and economically viable.[24–27] We have previously demonstrated a simple procedure for the synthesis of ZnO nanostructure-embedded paper (ZnO–cellulose nanocomposite, hitherto termed NC-paper), which has been demonstrated to be an efficient candidate for flexible strain-sensing devices.[28] Building upon the same material, we show here that by increasing ZnO density on one side of the NC-paper, it can be used for multisource energy harvesting.

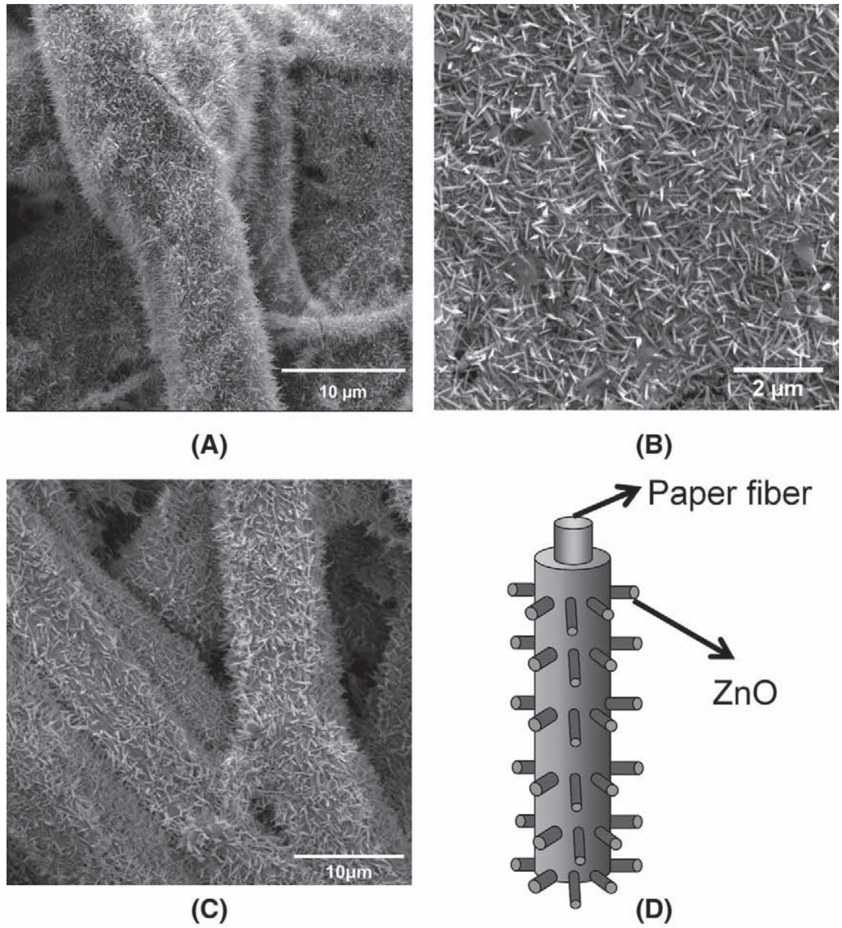

Figure 1. A,B) SEM images of ZnO-coated paper formed by a hydrothermal process showing the ZnO–paper composite morphology. C) SEM image of the ZnO paper made using a slightly different solvothermal method that has been previously reported. D) Schematic depiction of the structure of the composite. A thin film of ZnO is formed around the paper fiber, and nanorods grow radially out from it.

2. Results and Discussion

NC-paper synthesis is described in the Experimental Section; we have slightly modified the synthesis protocol from the one used previously[28] for strain-sensing applications. We introduced a second hydrothermal step for ease of synthesis without altering its quality. The NC-paper can be bent and the deformation is fully recoverable, which is critical for energy-harvesting devices. The morphology and chemical composition of the NC-paper were observed by scanning electron microscopy (SEM; **Figure 1**A,B). ZnO nanorods grew uniformly on the surface of the cellulose fibers. Although the synthesis method has been modified, the morphology of the fibers is similar to the one we have previously reported (Figure 1C).[28] The ZnO nanorods have a typical diameter in the range of 40–100 nm and lengths between 500 and 1000 nm. The low-magnification and cross-sectional images shown in Figure S2 (Supporting Information) clearly reveal the uniform coating on the NC-paper over large areas. Energy-dispersive X-ray (EDX) analysis of NC-paper (see Supporting Information Figure S3) confirms the presence of ZnO. X-ray diffraction (XRD) has been used to confirm the structure of the ZnO phase present in the paper. Figure S4 shows the XRD spectra of the NC-paper revealing the zinc oxide wurtzite structure.

The device fabrication process consists of sputtering gold on the surfaces of the NC-paper for charge collection, which also induces rectification due to Schottky effects. The gold-coated NC-paper, which is sandwiched between copper current collectors and laminated, is shown in **Figure 2**A. The typical configuration of the device is shown in Figure 2B, in which I_p is the piezoelectric current produced, C_p is the internal capacitance of the device, and V_p is the voltage produced. R_e and C_e are the resistance and capacitance between

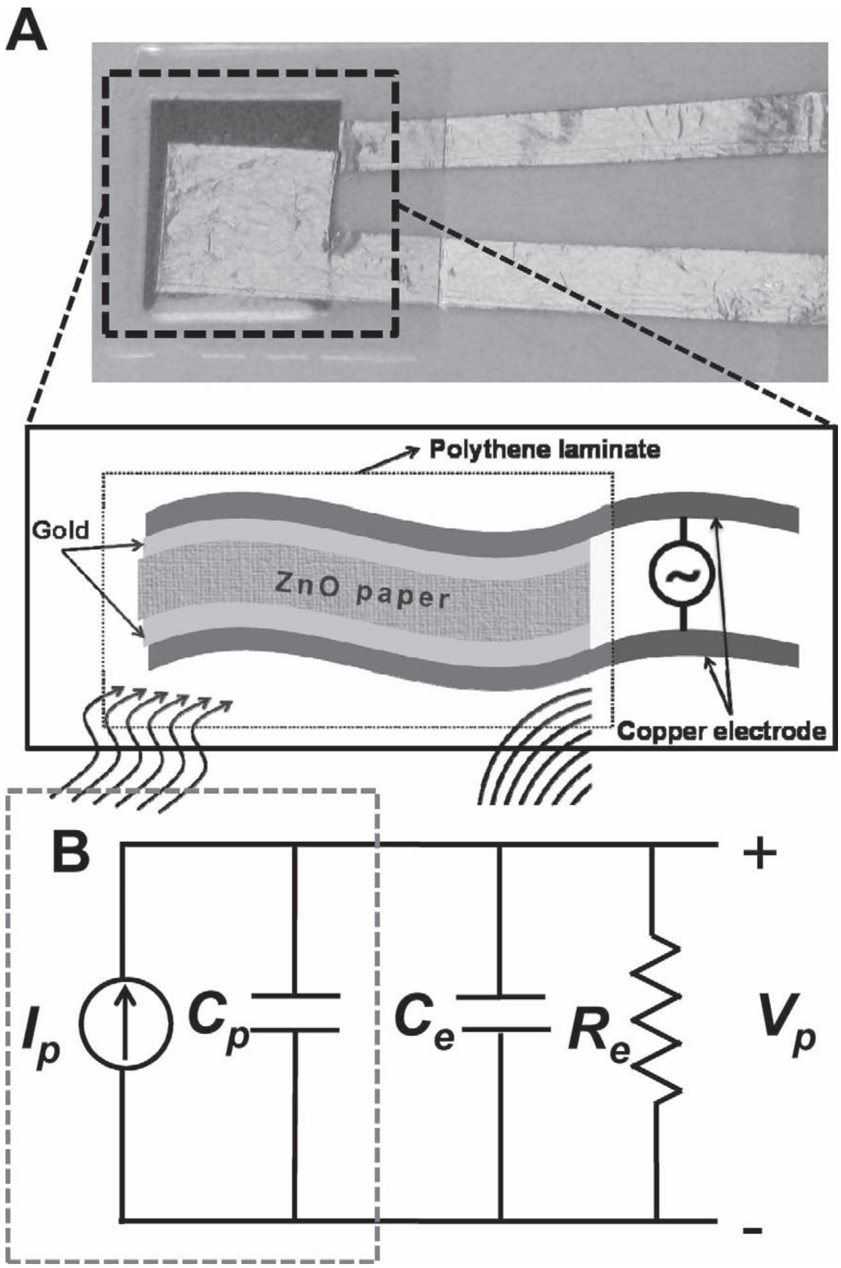

Figure 2. A) Photograph of gold-coated NC-paper sandwiched between current collectors (copper foil) and laminated with polyethylene sheet. The schematic diagram represents a cross section of devices showing the simplicity of the device. B) Equivalent circuit of the NC-paper energy-harvesting device.

the electrical contacts, respectively, caused mainly by the copper current collectors and the connecting wires.

2.1. Thermal Energy Harvesting

The NC-paper device was tested for thermal energy conversion by measuring the closed-circuit current and open-circuit voltage of the device by placing it on a heating plate maintained at 150 °C for 15 s and allowing it to cool for 45 s in air. The output voltage and current from the device follow the heating cycles. The peak current (I_p) and voltage (V_p) observed were ≈1.25 μA and ≈80 mV, respectively. **Figure 3**A shows the closed-circuit current of devices with repetitive heating and cooling cycles along with the corresponding temperature profile. The data clearly indicate that the output current originated from the NC-paper as a result of heating, as it follows the working cycle (Figure 3A). Furthermore, measurements were recorded under both polarities to rule out any possible artifact caused by the measurement setup. The output signal switched in sign from positive to negative when the polarity was switched from forward to reverse connection (Figure 3B). A similar pattern in the open-circuit voltage output was also observed, as shown in Figure 3C,D. Higher output currents of ≈20 and ≈46 μA were achieved using 4 and 9 cm^2 size devices, respectively, thus proving the scalability of this NC-paper (Figure S5).

The maximum power output for a single-layer (1 cm^2) device presented in this work is ≈50 nW cm^{-2} when subjected to a temperature difference of around 80 °C at a rate of approximately 5.8 °C s^{-1}. The response of the composite can be attributed to a combination of three different mechanisms. Firstly, the initial increase in the voltage can be attributed to the pyroelectric behavior of ZnO since there was a steep change in temperature, whereas the stable output observed after heating is essentially due to the other two corresponding factors. The first is the temperature gradient between the two terminals, as one side of the NC-paper is in contact with the hot-plate while the other is exposed to air. The other predominant factor is the local strains created due to the unequal expansion of cellulose and ZnO when the composite is heated. This results in local strains acting radially outwards in the fibers thereby causing piezoelectric currents from the ZnO thin film.

2.2. Mechanical Energy Harvesting

The NC-paper can also be used (as it is) for harvesting energy from other sources, for example, the energy from mechanical vibrations through the piezoelectric phenomenon. The response of the NC-paper was tested by measuring the closed-circuit current when the device was immersed in an ultrasonic bath (frequency ≈40 kHz; **Figure 4**). The current response of a typical device (0.5 cm^2) when exposed to ultrasonic waves, in pulsed intervals, is ≈350 nA (Figure 4A) leading to a current density of 0.7 μA cm^{-2}. The forward current (Figure 4A) and the reverse current (by inverting the

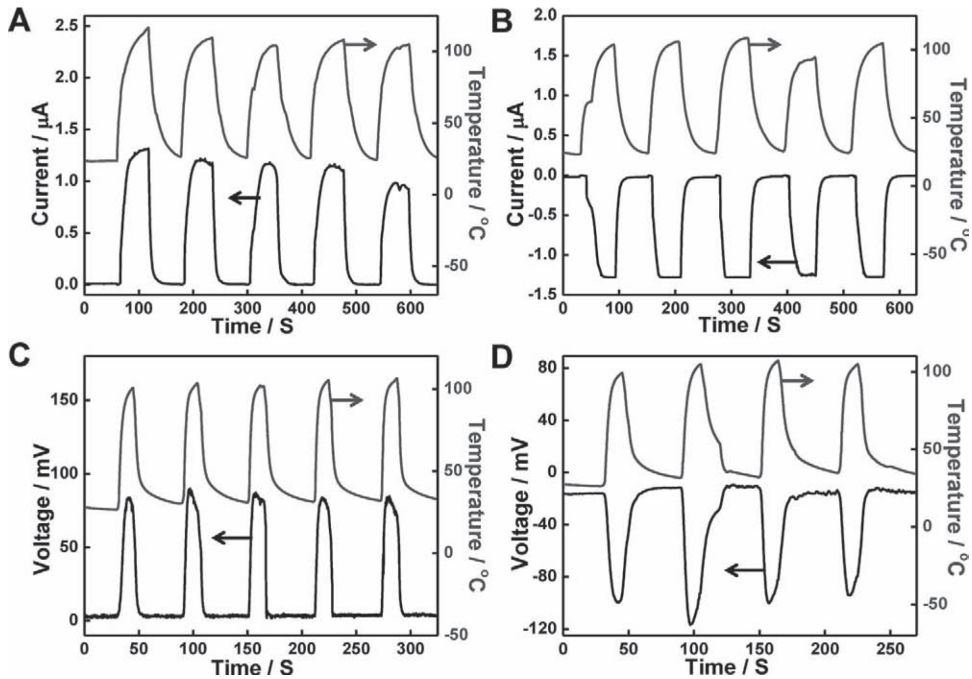

Figure 3. Performance of NC-paper as a thermal energy harvester, as characterized by the electric signal. The current output of the NC-paper in cycles of repetitive cooling and heating is shown in forward (A) and backward (B) polarity. The voltage response of same device was measured under similar experimental conditions in both in forward (C) and backward (D) polarity. The reverse polarity negates any artifact from the instrument setup. The size of the NC-paper device is ≈1 cm^2 in effective area.

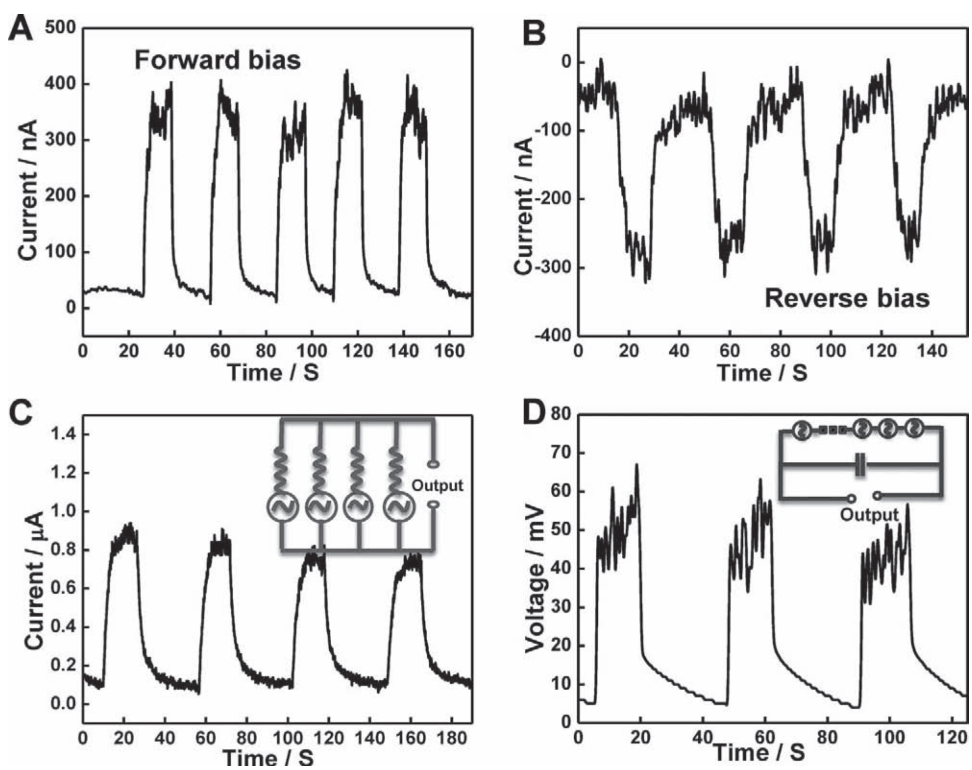

Figure 4. Output showing the performance of the NC-paper device when exposed to pulsed excitations of ultrasonic waves. The current was measured in forward (A) and reverse (B) polarity, when the ultrasonic wave was turned on and off. C) Closed-circuit current response of stacked NC- paper devices. The response of a single 0.5 cm^2 device (≈350 nA) is improved when four similar devices are stacked in parallel, as shown in the inset (≈800 nA). D) Open-circuit voltage response of ten devices connected in series, as shown in the inset.

probes of the multimeter; Figure 4B) were measured to verify that the observed response was not an artifact.

In order to probe the scalability of the proposed device, we stacked N number of single devices (0.5 cm^2) either in series or in parallel, named N-stack. The inset of Figure 4C shows a schematic of a four-stack device. Before stacking, each individual device was poled and tested to make sure it was defect free. For a four-stack device connected in parallel, the output current response was found to be additive, giving a total of ≈800 nA when excited with ultrasonic waves (Figure 4C). In another measurement, a device having ten stacks of individual NC-paper connected in series was used to measure the scalability of output voltage, as shown in the inset of Figure 4D. The device was excited for a pulse of 15 s at regular intervals of 30 s. The arrays of NC-paper devices gave ≈50 mV voltage output (Figure 4D).

The mechanism for charge collection in the vapor-grown ZnO nanogenerator has been proposed by Wang et al.[20] In the NC-paper device we fabricated here, the mechanical waves made the fibers vibrate, thus creating two types of stresses on the ZnO-coated paper: 1) as contiguous fibers vibrate, the nanorods on their surfaces are rubbed against each other, causing them to deflect, and generating a potential difference (or piezoelectric potential) along the nanowire diameter; and 2) since the fibers are coated with a ZnO thin film, there is a strain due to the vibration of the fibers. The ion displacement due to this strain creates a difference of potential along the thin film, therefore increasing the time for potential screening due to the intrinsic carriers in the ZnO film. This increase in the time for potential screening allows the current to flow through the external circuit.

3. Conclusion

We have shown that a simple, flexible platform comprising ZnO nanostructures embedded in a paper matrix can be utilized for harvesting of energy from both ambient thermal and mechanical sources. The multisource energy-harvesting nanocomposite devices can be easily scaled and stacked up to increase the output responses, thereby allowing enhanced harvesting capabilities. Our results open up a new fabrication approach for the realization of low-cost, lightweight, and flexible energy-scavenging systems.

4. Experimental Section

The detailed synthesis of the NC-paper is described in the Supporting Information. In short, solvothermal and hydrothermal methods, which have been previously demonstrated for growth of ZnO nanostructures, were employed.[28–33] This method yields the uniformly ZnO-coated paper with aligned growth of ZnO nanorods. Unlike existing approaches that involve modifying the cellulose surface with a parylene coating to grow ZnO nanostructures,[34] our approach does not require any surface modification. We found that by employing a two-step synthesis protocol, the optimization of the seed layer did allow for uniform growth of the ZnO nanostructures throughout the surface of the cellulose paper (see the Supporting Information). Thermogravimetric analysis carried out on plain paper and NC-paper showed ≈35% (w/w) ZnO in the paper (Figure S1).

For the fabrication of devices, gold was sputtered on both sides of the NC-paper to give a ≈500 nm continuous film. A small piece (1.0 × 1.0 cm^2) of the gold-coated NC-paper was sandwiched between copper electrodes and laminated with a commercial ID-card laminating sleeve for preventing damage and to hold the contacts in place.

The current and voltage responses of the devices were measured with a Yokogawa multimeter (model 7562). For current measurements, a DL Instruments current-to-voltage preamp (model 1211) was also used. The measurements were also confirmed using a different multimeter (Keithley 2400) with a 10 pA resolution. A cement-on type K surface thermocouple from Omega Inc. was attached to the laminated NC-paper to measure the temperature of the device, and the temperature was monitored using a Lakeshore 331 temperature controller.

Before performing any measurement, an I–V test was performed on the devices with a voltage of 20 V to verify contacts and to align the otherwise randomly polarized domains in the material. The contacts were then short-circuited for 30 min to drain out any residual charge accumulated due to such polling.

The voltage measurement circuit involved a capacitive filter (0.22 μF) in parallel to the device, to smooth the output and to obtain a stable dc voltage as shown in Figure 4C. The initial output from the device without capacitive filtering was observed to be a series of highly fluctuating pulses of single polarity. By introducing the capacitive filter, these pulses were averaged out to produce a stable dc voltage. The voltage was measured in differential mode for better accuracy.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. It includes details of the synthesis of the composite, and device fabrication and testing; thermogravimetric measurements that confirm the composition of the composite to be 35 wt% of ZnO; and SEM images, XRD, and EDX analysis results, which show the structural and elemental characterization.

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