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Self-Powered pH Sensor Based on a Flexible Organic–Inorganic Hybrid Composite Nanogenerator

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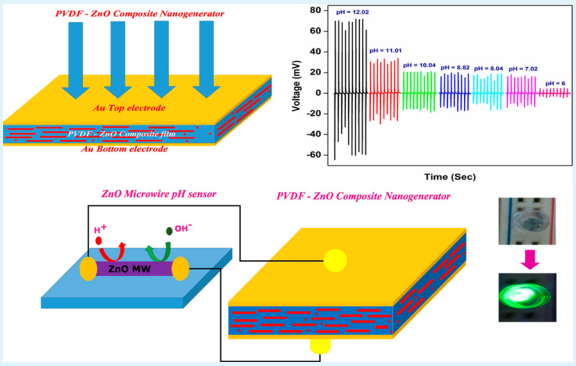
Supporting Information

ABSTRACT: In this study, we developed an innovative, flexible, organic–inorganic hybrid composite nanogenerator, which was used to drive a self-powered microwire-based pH sensor. The hybrid composite nanogenerator was fabricated using ZnO nanowire and piezoelectric polymer poly(vinylidene fluoride), through a simple, inexpensive solution-casting technique. The fabricated hybrid composite nanogenerator delivered a maximum open-circuit voltage of 6.9 V and a short-circuit current of 0.96 μA, with an output power of 6.624 μW under uniaxial compression. This high-performance, electric poling free composite nanogenerator opens up the possibility of industrial-scale fabrication. The hybrid nanogenerator demonstrated its ability to drive five green LEDs simultaneously, without using an energy-storage device. Additionally, we constructed a self-powered pH sensor, using a ZnO microwire powered with our hybrid nanogenerator. The output voltage varied according to changes in the pH level. This study demonstrates the feasibility of using a hybrid nanogenerator as a self-powered device that can be extended for use as a biosensor for environmental monitoring and/or as a smart, wearable, vibration sensor in future applications.



KEYWORDS: *hybrid nanogenerator, pH sensor, PVDF, self-powered device, solution-casting, ZnO nanowire*

INTRODUCTION

Recently, energy requirements have escalated exponentially due to increasing populations and industrial growth, while at the same time, fossil fuel availability has steadily decreased. Thus, scientists have been focused on increasing the utilization of renewable energy sources in an effective way. The commonly available renewable energy sources, such as solar, wind, hydro, geothermal, and biomass, are place- and time-dependent.[1] Numerous irregular energy sources that are available in the living environment include sound, friction, motion, wind, and noise;[2,3] these energies exist enormously everywhere, which are small and have the potential for use as future power sources for smart, wearable electronic devices. The tremendous growth in the electronics industry has resulted in the steady reduction of the operating voltages and sizes of electronic devices, which opens up the possibility for new self-powered (no batteries required) electronic systems for environmental monitoring and sensing, or as implantable biomedical devices in small, wearable electronic applications.[4−7]

For the past few decades, energy harvesting from environmental noise and friction and from biomechanical, thermal, and low-frequency mechanical deformation has had a huge impact on the energy sector of the scientific community.[8] One such device is the nanogenerator, which converts low-frequency vibration and environmental activities (e.g., wind, sound, friction, and thermal energy) into electrical energy through piezoelectric, triboelectric, and pyroelectric effects.[5] The harvested energy is sufficient for the operation of small electronic devices in an aperiodic manner, using an energy-storage device. However, in real time, the nanogenerator is required to have higher electrical output and longer cycle stability to support continuous operation for environmental monitoring, defense, and implantable device applications.

Many research groups have attempted to fabricate high-performance nanogenerators using different materials and architectural forms (e.g., films, fibers, and composites). A variety of piezoelectric materials, such as perovskites ($BaTiO_3$,[9,10] $PbZr_xTi_{1-x}O_3$ (PZT),[11,12] Na, K-Nb_2O_3,[13] PMN-PT,[14]), ZnO,[8,15] $ZnSnO_3$,[16,17] GaN,[18] CdS,[19] CdTe,[20] and piezoelectric polymers,[3,21] have been examined in diverse forms. Among them, ZnO is an appealing material for a broad spectrum of the field, because it possesses higher exciton binding energy,[22,23] it is biocompatible and nontoxic, and it can be used to formulate many nanostructures at an elevated condition on all substrates.

The coexistence of semiconducting and piezoelectric properties in ZnO has germinated a new field of piezotronics, which take this material into further dimensions. Furthermore, it is

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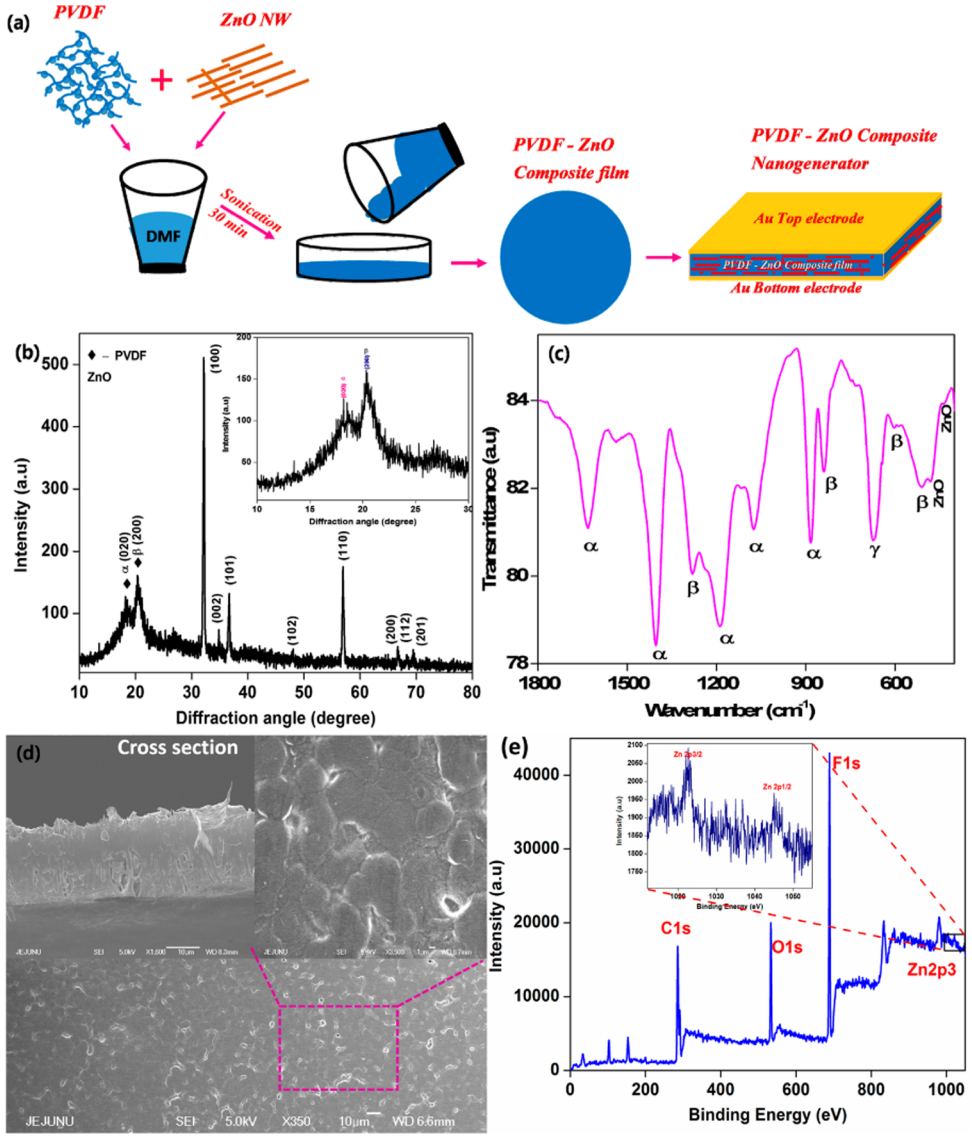

Figure 1. (a) Schematic diagram of the fabrication process of the hybrid composite nanogenerator. The composite film: (b) X-ray diffraction (XRD) pattern (the inset shows an enlarged view from 10 to 30°), (c) Fourier-transform infrared (FTIR) spectrum, (d) field-emission scanning electron microscopy (FE-SEM) image (the inset shows a higher magnification and cross-sectional view), and (e) X-ray photoelectron spectroscopy (XPS) survey spectrum (the inset shows the Zn 2p core-level spectrum).

utilized for harvesting the solar, thermal, and mechanical energy in hybrid forms.[24] There are many reports on the fabrication of piezoelectric nanogenerators using vertical, laterally aligned ZnO micro/nanowires, nanotubes, and micro/nanobelts using a variety of device tectonics.[5] However, the utility of these piezoelectric materials in this form is limited due to the brittleness and reduced strain levels, which limit large-scale fabrication. The first nanocomposite-based nanogenerator was proposed by Park et.al,[25] which overcomes the problem discussed earlier. However, the performance of this nanogenerator was not sufficient to self-drive the wearable electronic devices and sensors. Further explorations were required to improve the performance of the nanogenerator, which inspired us to design a flexible, paper-like, lightweight, large-scale nanogenerator that offered higher performance.

There have been several reports of composite nanogenerators based on polydimethylsiloxane (PDMS) and piezoelectric pervoskites, such as $BaTiO_3$,[10] PZT,[11] $NaNbO_3$,[13] $ZnSnO_3$ nanostructures,[17] and ZnO nanoparticles.[26] As of now, only a few reports are available for fabricating composite nanogenerators that use organic and inorganic piezoelectric materials.[27] The ferroelectric organic polymers, namely, poly(vinylidene fluoride) (PVDF),[28] and its copolymers with trifluoroethylene (TrFE)[3] are used for energy-harvesting applications because these materials possess both piezoelectric and pyroelectric properties. The main advantages of using polymers are their low cost, chemical stability, flexibility, ease of fabrication in various forms, and durability under an applied strain. Among these, the PVDF polymer has a higher piezoelectric coefficient[21] and has been used in a variety of applications (e.g., soft-touch switches, strain gauges, piezoelectric transducers, actuators, and ultrasound transducers) for more than two decades.[29−31]

In this paper, we report a novel, flexible, paper-like organic−inorganic composite-based hybrid nanogenerator, using ZnO nanowire and PVDF. Surprisingly, the fabricated hybrid nanogenerator showed higher performance under uniaxial compression, without electric poling. This result suggests that

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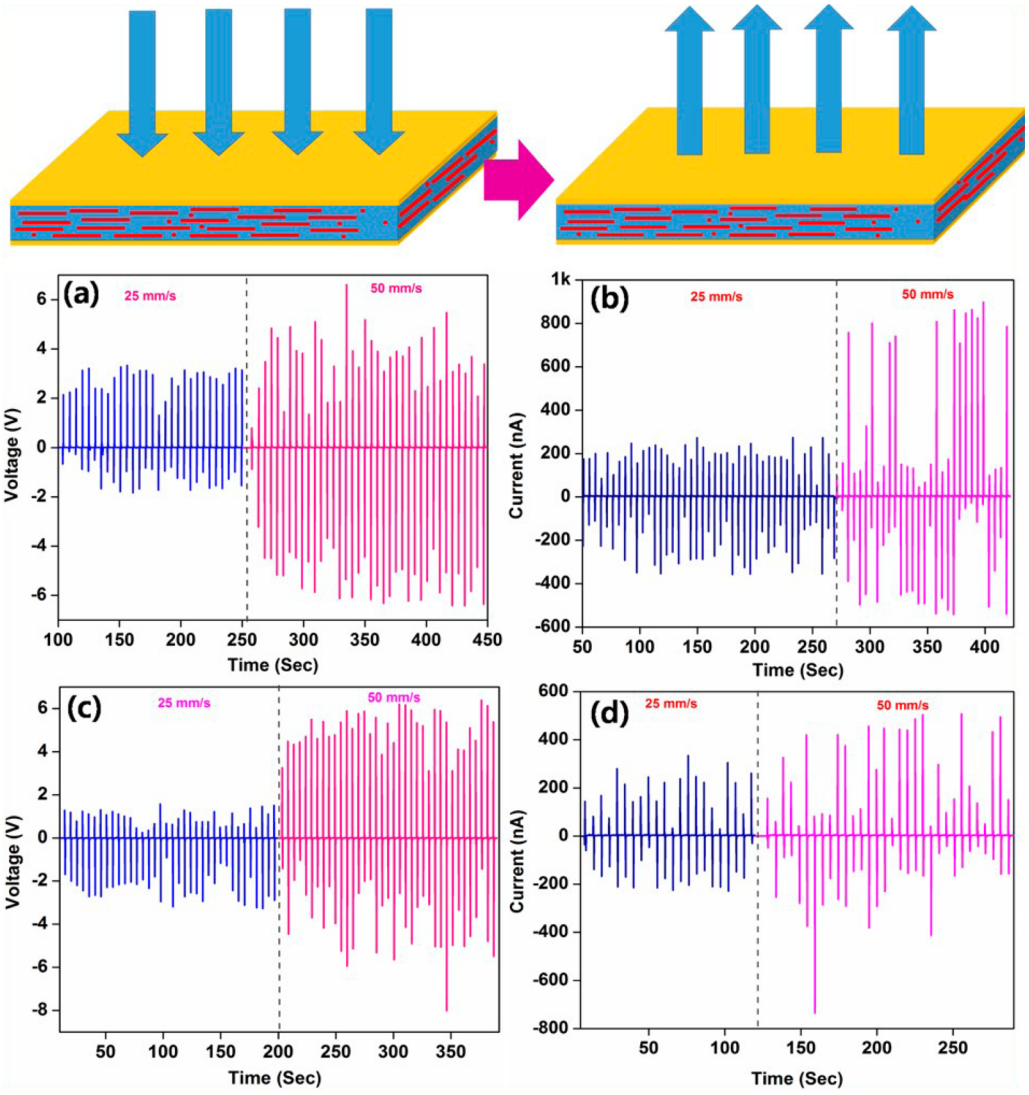

Figure 2. Measured open-circuit voltage and short-circuit current of the hybrid composite nanogenerator under different speeds of uniaxial pressing/release conditions: (a, b) forward and (c, d) reverse connection.

the fabricated hybrid nanogenerator is a good candidate for real applications, due to its easy fabrication process and the availability of a large number of vertical compression systems, such as road transport, footpaths, bridges, vehicle tires, and shoes. The fabricated hybrid nanogenerator was capable of operating five green LEDs simultaneously, without any storage device, and successfully harvested biomechanical energy. Additionally, we demonstrated a self-powered ZnO-based pH sensor that operates based on energy obtained from the hybrid nanogenerator.

EXPERIMENTAL SECTION

Fabrication of the Hybrid Composite Nanogenerator. The ZnO nanowire (see the Supporting Information) and poly(vinylidene fluoride) (PVDF) (Sigma-Aldrich) were dispersed in 15 mL of *N*,*N*-dimethylformamide at the weight percentage of 0.1/1 (w/w). The homogeneous mixture was prepared by the sonication process, using a probe sonicator for 30 min, and was poured into a Petri dish and dried in a hot-air oven overnight at 80 °C. The dried film was peeled off from the Petri dish. The nanogenerator was fabricated by coating Au electrodes on the top and bottom of the composite film through thermal evaporation. The electrical contact was taken from the top and bottom sides of the gold-coated composite, with Cu wires connected with silver paste. Finally, the entire device was covered with polydimethylsiloxane (PDMS) to avoid physical damage while under operation.

Characterization. The crystallinity and surface morphology of the as-grown nanowire and composite film were analyzed using X-ray diffraction (XRD, Rigaku) and field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) correspondingly. The chemical and surface composition of the composite film was analyzed through Fourier-transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific) and X-ray photoelectron electron spectroscopy (XPS, Theta Probe, Thermo Scientific). The electrical measurement was carried out under continuous uniaxial pressing condition, using a picoammeter (Keithley 6485) and nanovoltmeter (Keithley 2182A). A bending tester (JIBT-200, Junil Tech) provided the uniaxial pressing for the experimental testing.

Fabrication of the pH Sensor. The pH sensor was fabricated using a ZnO microwire, which was grown using the vapor transport method (see the Supporting Information).[32] A single ZnO microwire was positioned across a glass substrate, and both ends of the wire were affixed with silver paste. A very thin poly(methyl methacrylate) (PMMA) layer of around 100 nm was coated on the microwire surface to protect the microwire from dissolving in the buffer solution. Electrical contact was made through Cu wires; both electrical contacts were covered with epoxy. The buffer solution pH was varied from 12 to 6 by adding sodium dihydrogen phosphate (5 M NaH_2PO_4). The

fabricated pH sensor was connected in parallel with a hybrid composite nanogenerator to measure the response as a function of pH value.

RESULTS AND DISCUSSION

We fabricated a simple, low-cost, flexible hybrid composite nanogenerator, using PVDF and ZnO nanowire. PVDF plays a crucial role in this device, not only as a piezoelectric, but also by restricting aggregation between the ZnO nanowires. Figure 1a shows a schematic diagram of the detailed fabrication process. A simple solution-casting process was used to fabricate the composite film; this technique is applicable to large-scale nanogenerator fabrication for real-world applications.

X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FE-SEM), and X-ray photoelectron spectroscopy (XPS) were used to verify the crystallinity, phase, morphology, and composition of the composite film (Figure 1b−e), respectively. The XRD pattern of the composite film confirmed the presence of ZnO and PVDF. The ZnO diffraction peaks in the composite film were in good agreement with standard file 3-1457, and also with as-grown ZnO nanowires[32] (Figure S2a, Supporting Information). The inset shows an enlarged portion over 10−30°, corresponding to the crystalline phase of the PVDF film. XRD results showed a strong peak at 2θ = 20.7°, corresponding to the (200) plane of the β phase, and a small peak at 2θ = 18.4°, corresponding to the (020) plane of α-PVDF.[31] FTIR results confirmed the existence of the β phase of PVDF[31] at 512, 606, 838, and 1282 cm^{-1}, and ZnO stretching vibration mode peaks at 518 and 420 cm^{-1}; the remaining peaks were related to other phases of PVDF. The peaks that appeared in the composite film were in good agreement with the bare PVDF and ZnO nanowire results (Figure S3, Supporting Information). Figure S2b (Supporting Information) shows an FE-SEM image of the as-grown ZnO nanowire (diameter: 60−80 nm; length: 6−8 μm).

The microscopic surface morphology of the composite film was investigated by FE-SEM, as shown in Figure 1d; the magnified image shows a homogeneous distribution of ZnO nanowires in crystalline superulites of the PVDF matrix.[33] For clear observation, we also measured the cross-sectional view of the composite film, from which we obtained the composite film thickness (~30 μm) (inset of Figure 1d and Figure S4, Supporting Information). The homogeneous and disaggregated ZnO nanowires in the film are a good sign to ensure the highest performance. The surface composition of the film was investigated using XPS. Figure 1e shows the XPS spectra, which confirmed the presence of O, C, F, and Zn in the composite film, as well as the high purity of the fabricated film. The inset shows the Zn 2p core-level spectra of the ZnO nanowire. The core-level spectrum of C 1s consisted of three peaks at 284.57, 286.02, and 290.67 eV, which corresponded to C═C, C−H, and C−F species, respectively (Figure S5a, Supporting Information). O 1s and F 1s peaks were observed at 532.27 and 688 eV, respectively, which corresponded to the C−O and C−F bonds[33] (Figure S5b,c).

To show the potential of the composite film, we fabricated a nanogenerator with gold as the top and bottom electrodes, having an active device area of 3 × 3 cm^2. Most practical nanogenerator applications are based on uniaxial compression, such as walking, running, transportation, etc.... We tested our device under the periodic uniaxial compression force through a bending tester. The open-circuit voltage and short-circuit current of the hybrid device were measured under periodic uniaxial pressing and release conditions (Figure 2). At a compression speed of 25 $mm{\cdot}s^{-1}$, we measured an average output voltage and current of 2.9 V and 0.263 μA, respectively. The switching polarity test was used to verify the measured electrical output generated from the hybrid device. To check the polarity test, we connected the nanogenerator under reverse connection conditions. The measured outputs were the same; however, the polarity of the output signal was reversed in the case of the reverse connection. The results conclude that the measured electrical signal generated from the nanogenerator during compression and release condition. The output voltage and current of the device were not uniform for both forward and reverse connection conditions, which may be attributed to different strain rates.[5] The nanogenerator delivered an output voltage and current of 2.9, 1.46 V and 0.193, 0.263 μA with an output power of 0.56, 0.384 μW for forward-connection conditions, and 1.15, 2.45 V and 0.174, 0.186 μA with an output power of 0.20, 0.456 μW for reverse-connection conditions, under compression and release, respectively.

To verify the effect of compression speed on the output performance of the nanogenerator, we measured the performance as a function of the compression speed. Increasing the compression speed up to 50 $mm{\cdot}s^{-1}$ increased the output; however, further increases in the compression speed reduced the electrical output. The maximum output voltage and current of 6.9 V and 0.96 μA with an output power of 6.624 μW was measured at a compression speed of 50 $mm{\cdot}s^{-1}$. These results were higher than the values presented in previous reports based on composite nanogenerators, as summarized in Table S1 (Supporting Information).[25,28,34,35]

In our daily life, activities related to human body movement, such as walking, running, arm movements, finger typing, blood flow, and heartbeats, are ideal mechanical energy sources for human-based self-powered devices. To develop a human-based self-powered device, we tested the feasibility of our hybrid nanogenerator to harvest biomechanical energy. Figure S6 (Supporting Information) shows device output testing under folding and pressing of fingers. When folding or pressing, the finger produces stress on the hybrid composite nanogenerator, which generates a piezopotential across the device. The developed piezopotential drives the electrons in the external circuit through Au electrodes. The measured average voltage and current under folding and pressing were 0.33 V, 0.062 μA and 1.3 V, 0.177 μA, respectively, which is higher than values cited in an earlier report.[36] The higher output may be due to the equal distribution of applied strain over the nanowire surface. The device performance was higher under uniaxial compression than bending (Figure S6c,d), which suggests that this device could be used to harvest the biomechanical energy while walking and running.

The proposed working mechanism of the hybrid composite nanogenerator is the combined effect of PVDF and ZnO nanowire. In the hybrid nanogenerator, ZnO nanowires are uniformly distributed in the PVDF polymer matrix, which prevents agglomeration. The presence of an oppositively charged polar surface in the nanowire during the process, which actively interacts with CF_2/CH_2 groups in PVDF, builds negative and positive charge densities over the surface. The formation of a dipole promotes the formation of the piezoelectric PVDF β phase through surface charge induced polarization[37] and nanoconfinement.[38] Both nanoconfinement and surface charge induced polarization results in the self-

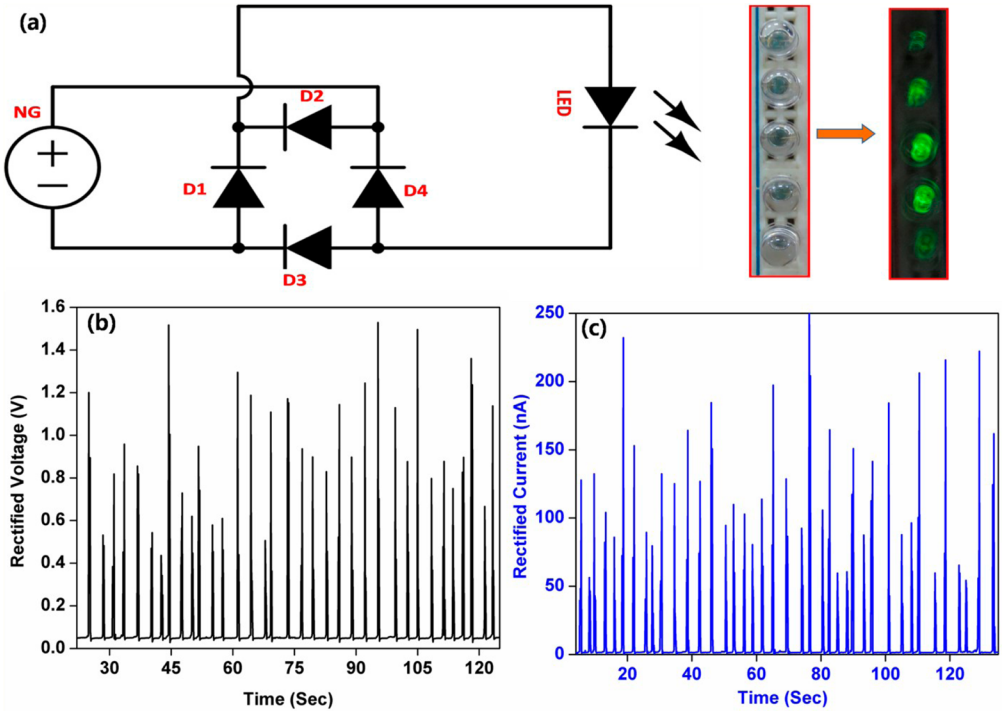

Figure 3. (a) Schematic diagram of the full-wave bridge rectifier circuit. (b) Measured rectified open-circuit voltage. (c) Short-circuit current by pressing the fingers. The rectified output was used to drive five green LEDs, which is shown in the top left corner.

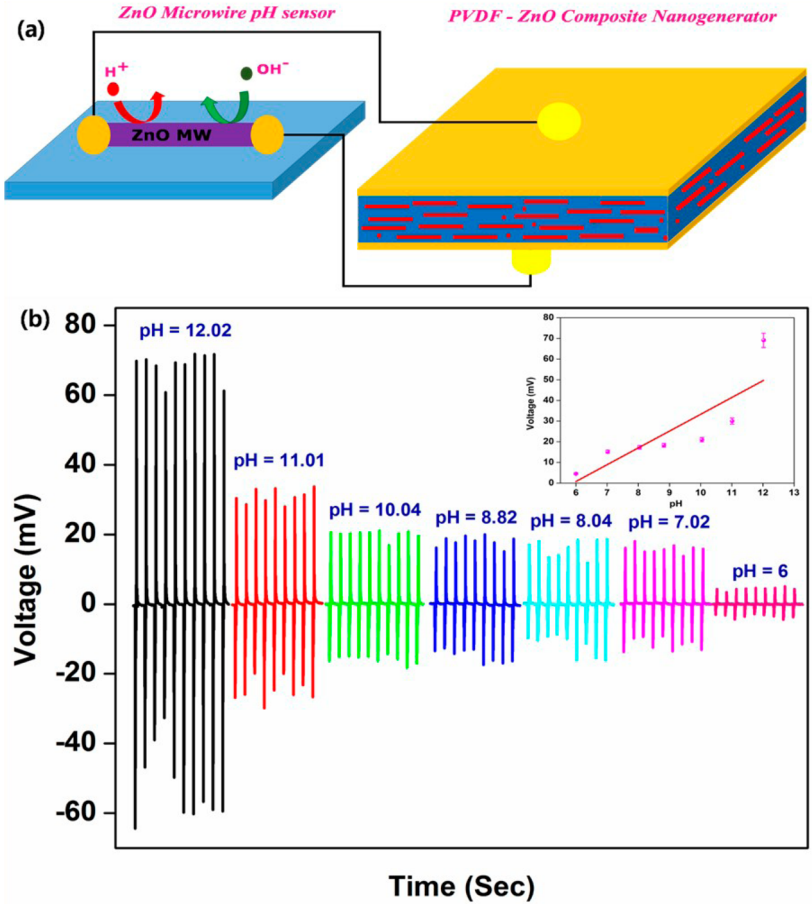

Figure 4. (a) Demonstration of the self-powered device, which consists of a ZnO microwire pH sensor and a hybrid composite nanogenerator. (b) Electrical output as a function of pH across the pH sensor. The inset shows the voltage as a function of different pH values.

polarized film. In addition to that, the applied external mechanical force builds a potential in the nanowire, which aligns the PVDF electric dipole further along the unidirection through stress-induced polarization.[17] Finally, PVDF molecules are self-polarized along a single direction from the results of stress and surface charge induced polarization without external electric potential. The self-polarization mechanism in piezoelectric and ferroelectric materials is unclear due to its complex nature. The self-polarization eliminates the complexity of the poling process in MEMS and microstructure based energy-harvesting devices, which is the additional advantage. Under bending/compression, the hybrid composite device experiences a strain over the surface, which produces the piezopotential in ZnO nanowires' surface and as well as from the PVDF film, and this combined effect contributes in the final output. The produced piezopotential on either side of the composite film induces an inductive charge on the top and bottom electrodes. This potential difference will drive the electron in the external circuit. To prove the self-polarization of the fabricated film, we have tested the device after electrical pole (5.5 kV, 36 h). The result suggested that the electrical output was not much improved than the unpoled device, which defends the self-polarization behavior of PVDF−ZnO film (Figure S7, Supporting Information).[38] To check the effect of ZnO nanowires on the performance of the hybrid nanogenerator, we measured the electrical output voltage and current of the PVDF nanogenerator; voltage and current values of 60 mV and 30 nA were observed, respectively (Figure S8, Supporting Information). The measured output is low due to the random orientation of molecular dipoles in the PVDF film. To show the potential of the hybrid device, we further compared with the ZnO nanoparticle-based hybrid device. The results are clearly indicating that the fabricated hybrid device displayed higher performance than the bare (PVDF) and ZnO nanoparticle-based device (Figure S9, Supporting Information).

To demonstrate the application of the hybrid composite nanogenerator, we fabricated a full-wave bridge rectifier circuit (Figure 3a). Using this circuit, we rectified the electrical signal generated in the nanogenerator, shown in Figure 3b,c. The rectified electrical signal generated by one press/release cycle was directly used to drive five green LEDs simultaneously, without any storage device; see Figure 3.

The performance of the hybrid composite nanogenerator inspired us to develop a self-powered device. In this study, we fabricated a pH sensor using a ZnO microwire, connected in parallel to a hybrid nanogenerator. Figure 4a shows a schematic diagram of the pH sensor. The fabricated hybrid composite nanogenerator was used to drive the ZnO microwire-based pH sensor without external power. When there was no buffer solution, the measured potential drop across the microwire pH sensor was ∼0.34 V (Figure S10, Supporting Information), due to the high resistance across the ZnO microwire. The introduction of a buffer solution changed the chemical environment (H^+, OH^-) around the microwire, which altered the output voltage by changing the depletion region.[39] The measured output voltage as a function of pH value is presented in Figure 4b; the change from basic to acidic conditions reduced the output voltage. At higher pH (base) values, the existence of negatively charged species increased the depletion region at the ZnO surface and increased the resistance of the microwire. This leads to developing a potential drop across the microwire for a pH value of 12.2. Under lower pH conditions (acidic), the PMMA surface was surrounded by H^+ ions, which led to a reduction of the depletion region thickness. The pH changed from basic to acidic (12.2 to 6.02), which reduced the output voltage by lowering the resistance across the microwire.[40−43] Nonlinear behavior was observed in the response voltage as a function of pH value, which may be due to small variations in the depletion layer at lower pH levels. To validate the results, we measured the current−voltage ($I-V$) characteristics of the ZnO microwire as a function of pH at a bias voltage of 5 V (Figure S11, Supporting Information). Under normal conditions, the device showed a very low current (in the pA range), which confirmed the existence of higher resistance. When the solution pH changed from basic to acidic, the chemical environment around the ZnO surface become altered, which led to an increase in the output current. The output of the self-powered device was directly related to the resistance change in the ZnO microwire during the pH changes. A similar behavior was observed in the self-powered device, as well as in the bare ZnO device, indicating that the fabricated self-powered device could be used as a pH sensor. To show the stability of the pH sensor, we have measured the current at constant bias condition for different pH values. The observed results confirmed that the fabricated device was stable under different pHs, which is shown Figure S12 (Supporting Information). This study demonstrates the potential of the hybrid composite nanogenerator as a self-powered device for portable, wearable electronic device applications.

The fabricated hybrid composite nanogenerator exhibited several advantages. First, the fabrication process was simple, cost-effective, and easily transferred to mass production. Second, electric poling was not required to align the piezoelectric domains, which increases the possibility for mass production. Third, the device is nontoxic, flexible, and lightweight. Finally, a higher output performance was observed under uniaxial compressive stress, which facilitates real-life applications of the device. The integration of other piezoelectric nanomaterials with PVDF polymer gives the new research area to enhance the output performance.

CONCLUSIONS

In summary, a hybrid composite nanogenerator was developed with ZnO nanowires and a PVDF polymer, using a simple, low-cost solution-casting method. The simplicity of the process and electric poling free composite nanogenerator provided the possibility of producing a thin, large-scale, lightweight nanogenerator of any shape. The hybrid composite nanogenerator delivered a maximum voltage, current, and output power of 6.9 V, 0.96 μA, and 6.624 μW, respectively. Finally, we used the hybrid composite nanogenerator to build a self-powered ZnO microwire-based pH sensor and that was capable of operating five green LEDs simultaneously, without the need of a storage device. The higher performance of the device under uniaxial compression provides a new platform for harvesting biomechanical energy and vehicle transportation energy.

ASSOCIATED CONTENT

Supporting Information

The following are provided in the Supporting Information: figures showing a schematic diagram of the experimental setup and growth of the ZnO micro/nanowire; an XRD pattern and FE-SEM image of the as-grown ZnO nanowire; FTIR spectra of the ZnO nanowire and PVDF film; XPS core-level spectra of C 1s, O 1s, and F 1s of the composite film; the electrical output after electrical pole; measured open-circuit voltage and current

of the hybrid composite nanogenerator under folding and pressing by fingers; the measured electrical output of the PVDF film under bending and uniaxial compression conditions; the electrical output of PVDF−ZnO nanoparticle device; the output voltage across the microwire pH sensor; *I*−*V* characteristics of a ZnO microwire as a function of pH; and stability test of the sensor at different pHs; and a table containing a comparison of this work with reported composite nanogenerators. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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