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PAPER

Control of naturally coupled piezoelectric and photovoltaic properties for multi-type energy scavengers†

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In this paper, we present a simple, low-cost and flexible hybrid cell that converts individually or simultaneously low-frequency mechanical energy and photon energy into electricity using piezoelectric zinc oxide (ZnO) in conjunction with organic solar cell design. Since the hybrid cell is designed by coupled piezoelectric and photoconductive properties of ZnO, this is a naturally hybrid architecture without crosstalk and an additional assembling process to create multi-type energy scavengers, thus differing from a simple integration of two different energy generators. It is demonstrated that the behavior of a piezoelectric output is controlled from alternating current (AC) type to direct current (DC)-like type by tailoring mechanical straining processes both in the dark and under light illumination. Based on such controllability of output modes, it is shown that the performance of the hybrid cell is synergistically enhanced by integrating the contribution made by a piezoelectric generator with a solar cell under a normal indoor level of illumination. Our approach clearly demonstrates the potential of the hybrid approach for scavenging multi-type energies whenever and wherever they are available. Furthermore, this work establishes the methodology to harvest solar energy and low-frequency mechanical energies such as body movements, making it possible to produce a promising multi-functional power generator that could be embedded in flexible architectures.

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Broader context

Energy conversion from the environment is a core technology for future wireless/portable electronics and global environmental problems. To harvest the energy at anytime and anywhere, it is important to explore innovative technologies that utilize diverse forms of energy such as mechanical vibrations, acoustic energy, thermal gradients and electromagnetic waves, including solar energy. Furthermore, the multiple-type energy scavenger based on flexible soft materials could have a variety of implications on flexible electronics. In this paper, we present a simple, low-cost and flexible hybrid cell that converts individually or simultaneously low-frequency mechanical energy and photon energy into electricity using ZnO with coupled piezoelectric and n-type conductive properties. The work establishes the methodology to harvest solar energy and low-frequency mechanical energies such as a light-wind and body movements, making it possible to produce a promising power generator that could be embedded in flexible architectures such as “flag/shirt/bag/curtain”. This is also of critical importance for its future applications in defense technology, environmental monitoring and personal electronics. Therefore, such a hybrid energy generator is expected to be a novel multi-functional power supply that could provide electricity at anytime and anywhere which is likely to be the most conventional case for mobile electronics.

1. Introduction

Seeking renewable energy is critical in meeting the world's need for energy in construction, transportation, homes, electronics, and other areas.[1] With the reduction in size of portable electronics, the search for thin and light energy generation/storage units with a high efficiency has also become important.[2–4] Over the years, green energy technologies for energy conversion into electrical power from ambient sources have been developed using light (photovoltaic),[5,6] heat (thermoelectric),[7] mechanical energy (wind, water, and piezoelectric),[8–13] and biological energy (biofuels).[14] However, because of the completely different physical principles utilized for scavenging different types of energies, each type of conversion involves an independent unit wherever it applies.[15,16] A solar cell, for example, can provide electrical energy only in an area with appreciable light illumination. An innovative approach in the design of effective energy harvesting systems would comprise a multiple-type energy generator utilizing two or more energy sources at once, so that electrical energy can be provided whenever and wherever at least one of them is available.[2,17,18] However, since a simple integrated form usually causes crosstalk problems such as the increase of a device series resistance and total volume resulting in degraded efficiency and could not support any synergetic effect on the performance, the design and the development of an integrated architecture that harvests multiple types of energies without crosstalk and with synergetic effects is critically necessary for effective exploitation of the energies available in nature.

Traditionally, it has been believed that harvesting solar energy is sufficient because it has a high efficiency. Such a judgment was made based on a hypothesis that all of the operations are under one full sun illumination (100 mW cm^{-2}). In reality, however, many mobile electronics are operated indoors and possibly in a hidden area with very dim light. In such a case, the power that can be harvested from available light drops probably by 2–3 orders of magnitude in comparison to full sun illumination. In such a case, harvesting the energy contributed by other types of stimulation becomes viable.

Herein, we report a flexible hybrid architecture designed to harvest mechanical and solar energies, either separately or simultaneously. By using zinc oxide (ZnO) with intrinsically coupled piezoelectric and n-type conductive properties, a flexible hybrid energy scavenger is naturally created without any crosstalk and an additional assembling process, thus totally differing from a simple integration of two different energy generators. We demonstrate that the piezoelectric output signals from our hybrid cells are originally alternating current (AC) type, but they can be controlled to direct current (DC)-like type by tailoring mechanical straining processes both in the dark and under light illumination. Based on such controllability of piezoelectric output behavior, the performance of the hybrid cell is synergistically enhanced by the contribution of a piezoelectric generator, compared with the output power generated independently from the solar cell part under a normal indoor level of illumination ($\sim$1 mW cm^{-2}). We further present and discuss the synergetic effects and the mechanism of a power generation from our natural hybrid cells. Our work provides a promising approach for scavenging multi-type energies whenever and wherever they are available as well as a potential way for realizing multi-functional energy devices.

2. Experimental section

2.1. Fabrication of hybrid cells

Our hybrid cell is based on an integration of a piezoelectric generator and an organic solar cell. To achieve a fully flexible power generating device, we prepared an indium tin oxide (ITO)-coated polyethersulfone (PES) substrate as a cathode window in terms of a solar cell. A ZnO thin film layer was first sputtered to 50 nm thickness on the ITO/PES substrate.[19] ZnO nanorods on the sputtered ZnO film were then formed by continuously supplying zinc ions and hydroxyl radicals in aqueous solution, using zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 0.025 M], hexamethylenetetramine (0.025 M), and de-ionized water (250 ml). The main growth of the ZnO nanorods took place at 95 °C for 30 min.[11–13] As a photoactive layer, poly(3-hexylthiophene) (P3HT):(6,6)-phenyl-C_{71}-butyric acid methyl ester (PCBM) polymer blend (1 : 1 vol%) was spin-coated to a thickness of about 250 nm, and a few nm thick molybdenum oxide (MoO_x) layer and a gold (Au) anode of thickness about 70 nm were then deposited.[20,21] The P3HT:PCBM polymer blend was infiltrated between the ZnO nanorods (see ESI Fig. S1a†), which were used as the electron channel conductor for transporting the electrons generated by the organic solar cell. The entire structure is flexible, packaged in a single platform and can be easily integrated with any flexible electronics. Thus, our hybrid device can structurally harvest solar energy from light and mechanical energy created by mechanical straining. To minimize the variation of the photo-induced voltage and current by bending of the device, it was designed such that the "active area" (*AA*) of the size 4 × 5 mm^2 was located at the center of the substrate, which was about 7 cm long (ESI Fig. S1b†). Furthermore, the wires connecting to measurement instruments are positioned on both sides far from the *AA* on the substrate so as not to generate high noise signals by bending.

2.2. Measurement and characterization

Solar *J*–*V* measurements (CompactStat, IVIUM Technologies B. V.) were carried out by using a solar simulator (Peccell Technologies) under the irradiation intensity of air-mass (AM) 1.5 global (G) (100 mW cm^{-2}). A nanovoltmeter and a picoammeter (model 2182 and 6485, respectively, Keithley Instrument) were used for detecting the output signals generated from the hybrid cell.

3. Results and discussion

ZnO was chosen as a piezoelectric material for the mechanical energy converter as well as an electron transport layer in a solar cell (see the inset in Fig. 1a). As shown in Fig. 1a, the power conversion efficiency (PCE) of about 1.5% on average from our hybrid devices was obtained with an open circuit voltage (V_{oc}) of 0.55 V and a short circuit current density (J_{sc}) on 9.2 mA cm^{-2} in a standard AM 1.5 G illumination condition (100 mW cm^{-2}) without any mechanical strain (*i.e.* independent solar cell performance). The low PCE on our hybrid device might be attributed to the uneven surface due to the ZnO nanorods which can cause insufficient nanomorphology for a P3HT:PCBM blend. Since this work focuses on the conceptual demonstration which simultaneously and individually harvests solar and mechanical energies and on the controllability of output signals, the PCE of our hybrid devices was not further optimized through post-treatments.[22] In order to improve the PCE of our flexible hybrid device in terms of solar cell performance, we can suggest additional post-processes such as solvent annealing, surface energy engineering, and new materials for internal or photoactive layers.[6,23]

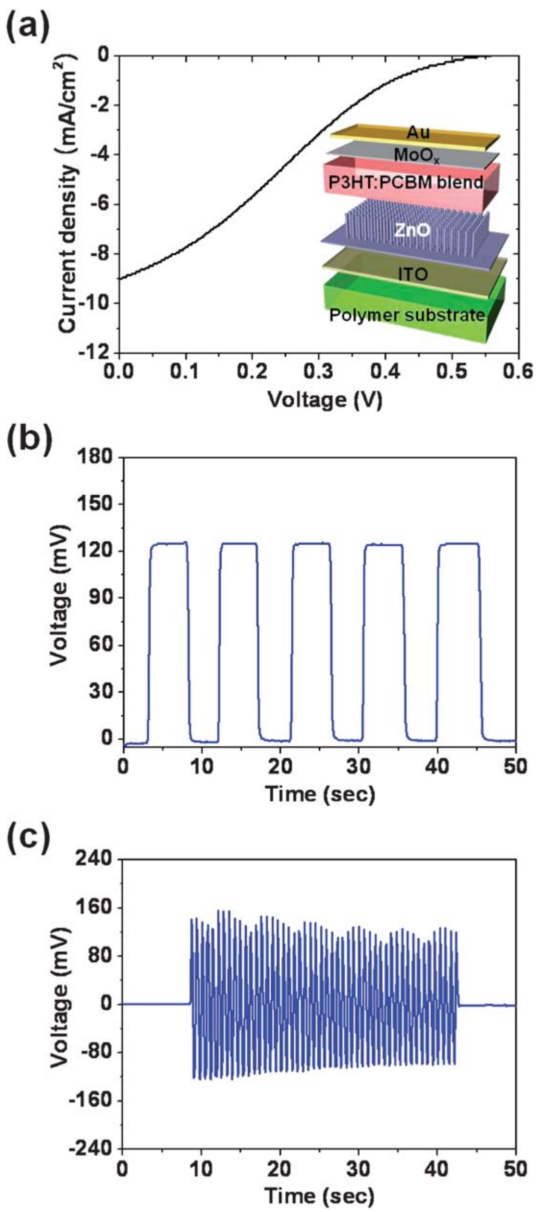

Fig. 1 Naturally hybrid architecture of a piezoelectric and photovoltaic power generator. (a) *J–V* characteristic under AM 1.5 G illumination (100 mW cm^{-2}). The inset shows schematic illustration of our hybrid device based on ZnO. To provide mechanical energy by bending, we applied a transparent flexible polymer substrate. (b) Step-functioned photovoltaic voltage under an indoor level of illumination (about 1 mW cm^{-2}). (c) Piezoelectric voltage induced only by mechanical energy such as bending in the dark. Fast bending and fast full releasing process was repeated.

Fig. 1b shows the output voltages that were measured from our hybrid cell under indoor level illumination (~1 mW cm^{-2}) without mechanical energies. DC-type step-functioned photovoltaic voltages were measured by repeating turn on and off. In order to clearly investigate and compare the output behaviors generated by solar and mechanical energies from our hybrid cells, the solar cell power was intentionally adjusted to a level comparable to that of piezoelectric power generation from mechanical energy by decreasing the intensity of the illuminating light, because the output of the piezoelectric power generation is much lower than that of the solar cell under AM 1.5 G illumination. This is also for the indoor illumination condition for practical applications. The photovoltaic voltages under indoor level illumination ranged from tens of mV to about 120 mV. Fig. 1c presents the piezoelectric output voltages by a periodic mechanical straining process of a hybrid device in the dark. The output mode showed an AC type power generation by repeating fast bending and fully fast releasing (where 'fast' is defined as an angular bending rate of ~230° s^{-1} at a bending radius of 3 cm). Based on the individual operating performance, it can be confirmed that our hybrid device can independently generate electricity.

Fig. 2a shows a typical p–n junction diode characteristic of our hybrid device in the dark together with the definition of forward connection with the measurement instruments. We performed 'switching-polarity' (Fig. 2b and c) tests which can verify that the measured piezoelectric signals are generated from the devices rather than the electrical measurement instruments.[24,25] When the instruments were forward connected to a hybrid device, positive voltage pulses (the black line in Fig. 2b and c) were first generated under the fast bending (*FB*) of the device, and corresponding negative voltage pulses for fast releasing (*FR*).

In the case of reverse connection, the output voltage was also reversed (the red line in Fig. 2b and c). When a hybrid device is subjected to dynamic bending, as shown in the inset of Fig. 2b, the ZnO layer undergoes a compressive straining in the direction of the thickness (the details of mechanical analysis of the strain distribution in the hybrid device is set out in Fig. S2 and S3 and Table S1 in the ESI†), so that the piezoelectric field is generated mainly across the thickness of the ZnO layer. In the thickness direction, the polymer blend layer undergoes much less stress than the ZnO film, so that the piezoelectric field is generated mainly from the ZnO film.

Based on the previous report,[9] a mechanism for the independent piezoelectric power generation in our hybrid device can be proposed in terms of the band structure of the system, with a p–n junction at the interface between ZnO and P3HT, and Schottky barrier at the interface between P3HT and Au. When the ZnO in a hybrid device undergoes compressive strain, a piezoelectric field is created in the ZnO thin film due to polarization of atoms in the crystal that creates ionic charges. When the piezoelectric potential in the ZnO thin film is positive (V^+) at the interface with the polymer blend and negative (V^-) at the side facing ITO, piezoelectric-induced electrons flow from the ITO electrode to Au through an external load resistor, because the resistance of the p–n junction barrier is very high for voltages below a threshold value, blocking the flow of electrons through the ZnO/polymer layer. In our hybrid devices, the first pulse due to the piezoelectric potential from the bending was positive in the forward connection, which is the same direction as the current generated by solar energy. Consequently, we confirm the direction of the piezoelectric field (*i.e.* V^+ at the interface with the polymer blend and V^- at the ITO interface). The electrons accumulate at the interfacial region between Au and P3HT, due to the high Schottky barrier; this process continues until the potential created by the accumulated electrons balances/screens the piezoelectric potential, resulting in a new balanced state and no further flow of electrons. When the compressive strain is released, the piezoelectric potential immediately vanishes and the electrons accumulated near the Au electrode flow back through the external circuit to the ITO electrode, returning the system to its original state.

A piezoelectric element under mechanical load has been modelled as a current source in which the current response is proportional to the applied strain rate, described by $i \propto d(\partial F/\partial t) = dAE(\partial\varepsilon/\partial t)$ where i is the current, d is the charge constant, and E is the Young's modulus of the piezoelectric element, F is the applied load, A is the load area, and ε is the strain.[26,27] On the basis of Ohm's law in the equivalent circuit, the piezoelectric potential also increases with the strain rate ($\partial\varepsilon/\partial t$). In our hybrid devices, we could observe the dependence of the piezoelectric output on the strain and straining rate. Depending on the factors controlling strain and straining rate, the piezoelectric output

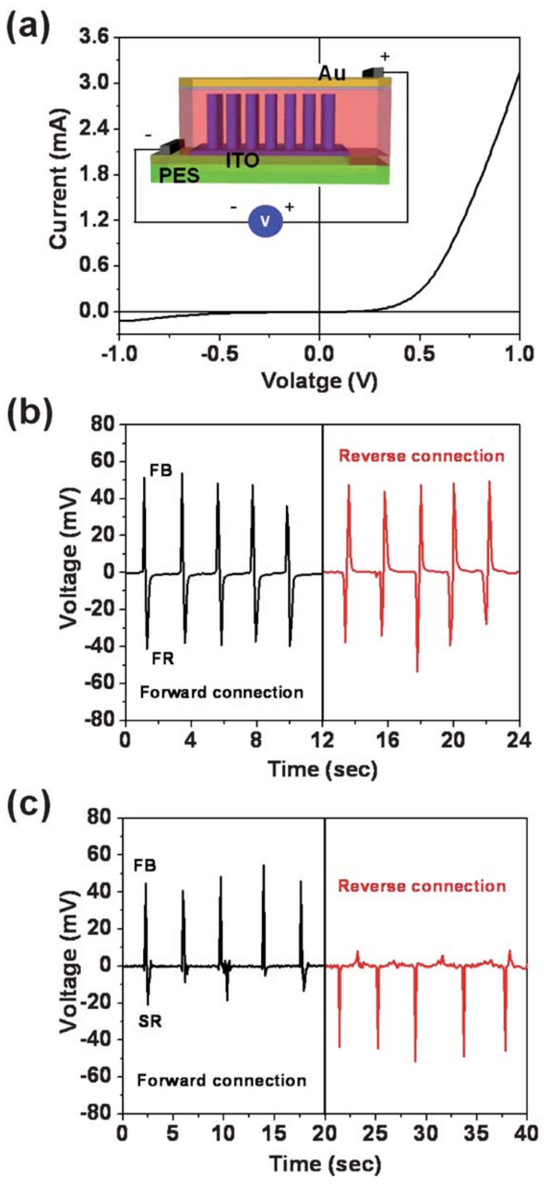

Fig. 2 Piezoelectric power generation under independent operation. (a) *I–V* characteristic of the hybrid device. The inset shows the definition of the forward connection with the measurement instruments. (b) Piezoelectric output voltage by fast bending (*FB*) and fast releasing (*FR*). (c) Controlled piezoelectric voltage by *FB* and slow releasing (*SR*). All data are taken under a dark condition.

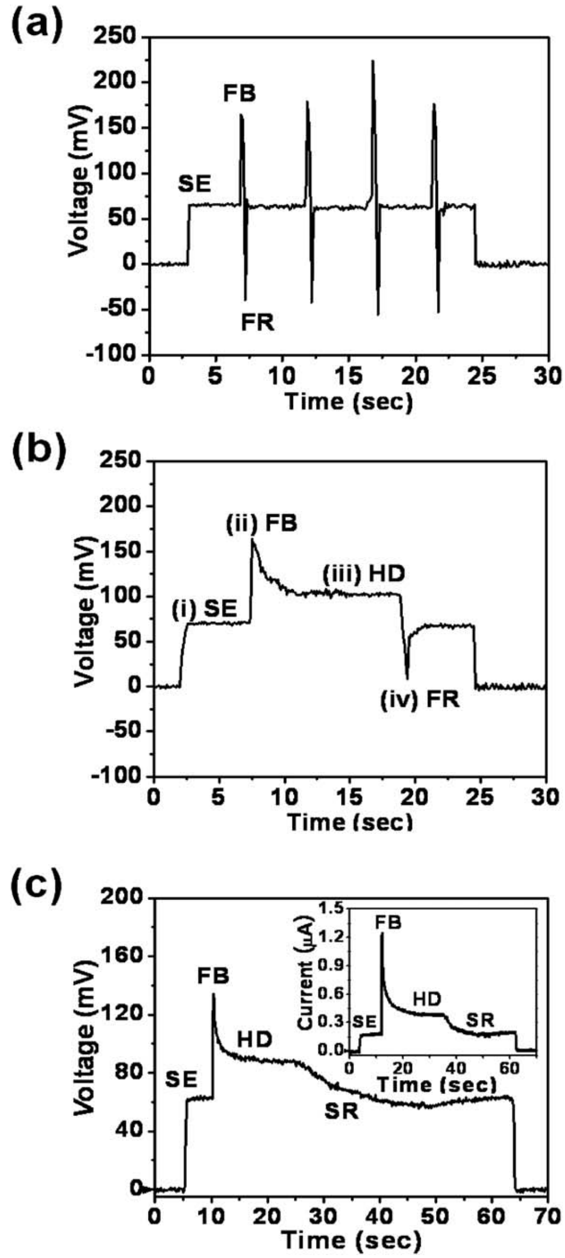

Fig. 3 Hybrid operation by solar energy (SE) and mechanical energy with controlled mechanical straining processes. Under the 'solar' energy given by indoor light, the overall output voltage by controlled mechanical straining processes of (a) fast bending (*FB*) and fast releasing (*FR*), (b) *FB*, holding (*HD*), and *FR*, and (c) *FB*, *HD*, and slow releasing (*SR*).

voltage was tens of mV up to ~150 mV, and the output current was hundreds of nA. We further controlled the piezoelectric output by adjusting the releasing rate after bending.[9] Under fast bending (*FB*) and fast releasing (*FR*) of a hybrid device, the peak values of positive and negative pulses for an output voltage are almost the same (Fig. 2b). However, when a hybrid device is subjected to slow releasing (*SR*) after *FB* (where 'slow' means an angular bending rate of $\sim 10^\circ\ s^{-1}$ at a bending radius of 3 cm), the peak intensity of the negative voltage can be significantly reduced, as shown in Fig. 2c. This result suggests that the piezoelectric output mode can be controlled from AC to DC-like simply by controlling the straining rate.

Based on the independent and controlled operations of our hybrid device in terms of piezoelectric potential, we have successfully created a dual-mode scavenging energy generator that employs both solar and mechanical energies, where it is demonstrated that the overall output signal from this hybrid device could be controlled by precisely adjusting the releasing configuration after bending (*e.g.*, programmed straining rate).[9,28] In hybrid operation, the ZnO layer including the ZnO nanorods and the ZnO thin film serves simultaneously as an electron transport layer and a piezoelectric power generator. Fig. 3 presents the various behaviors of the output voltage under different releasing configurations (see ESI, Fig. S6† for the corresponding detailed straining processes). When mechanical strain was applied *via FB* and *FR*, clear AC-type piezoelectric potentials were received in superposition to the solar power produced by an indoor level of illumination (Fig. 3a). When a holding (*HD*) was introduced between *FB* and *FR* (Fig. 3b), an increase in the output voltage of the solar cell was observed (the mechanism will be discussed in Fig. 4). Based on the controlled piezoelectric output behavior shown in Fig. 2c, we were able to greatly reduce the negative pulse in AC-type piezoelectric output by controlling the releasing strain rate (*i.e.* slow releasing) under the hybrid operation (*i.e.* both in light illumination and under mechanical straining). Fig. 3c and the inset show the overall output voltage and current under solar energy and controlled mechanical energy with *FB*, *HD*, and *SR*, where the negative pulse was greatly reduced in magnitude. Thus, it could be shown that the piezoelectric output under light illumination is controlled from AC type to DC-like type by simply adjusting the mechanical straining process.

The proposed mechanism for hybrid operation involving both solar and mechanical energies is shown in Fig. 4. When the hybrid cell is under light illumination alone (Fig. 4a), it generates continuous electrical output (e_{SE} or I_{SE}) according to the usual mechanism of solar power generation in bulk-heterojunction solar cells (Fig. 3b(i)).[19,20] When dynamic mechanical straining is applied to the device together with photon energy (Fig. 4b), the sharp piezoelectric output signal adds to the overall output signal as a result of the instantaneous high piezoelectric field created in the ZnO layer. The X-ray diffraction (XRD) profile from an as-sputtered ZnO thin film (ESI, Fig. S4†) showed that ZnO (002) diffraction peak was predominant, indicating that the ZnO thin

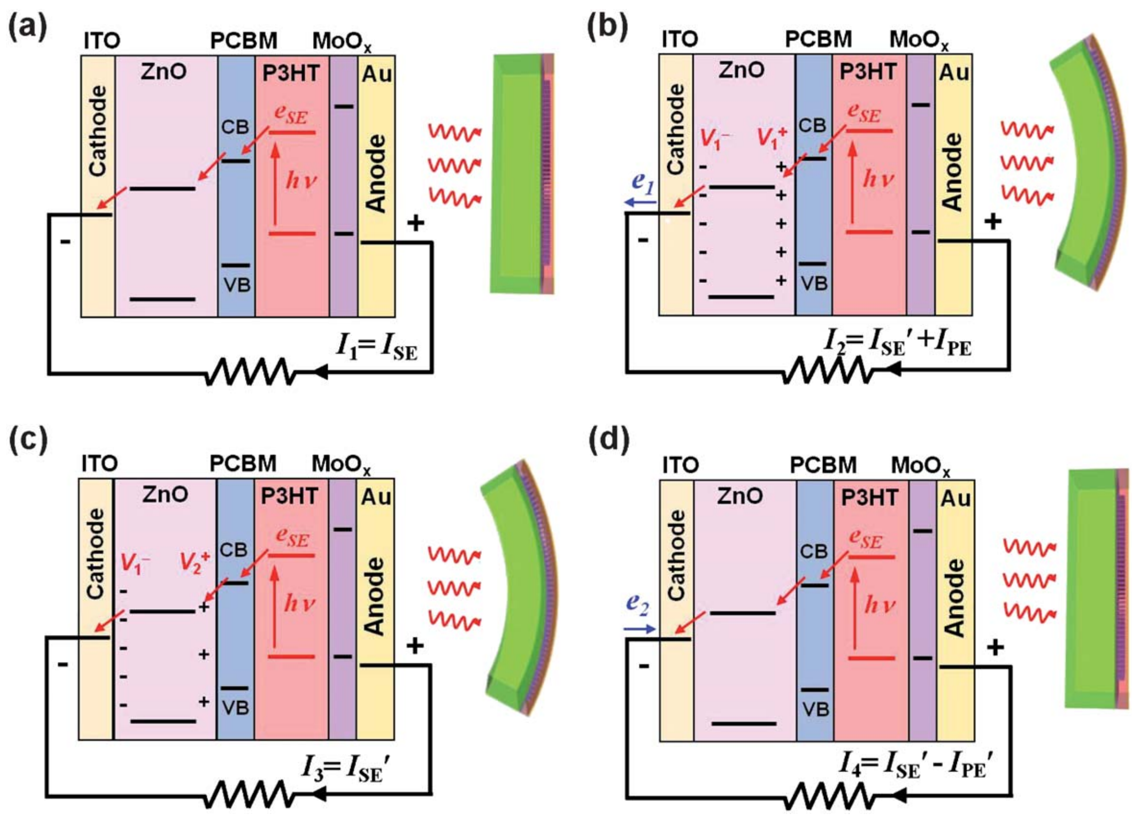

Fig. 4 Proposed mechanism of hybrid operation by solar and mechanical energies in the hybrid device. (a) Under solar energy alone. (b) Applying dynamic mechanical straining to the device together with solar energy. (c) In the static holding position with bending under solar energy. (d) Device fully released under *FR*.

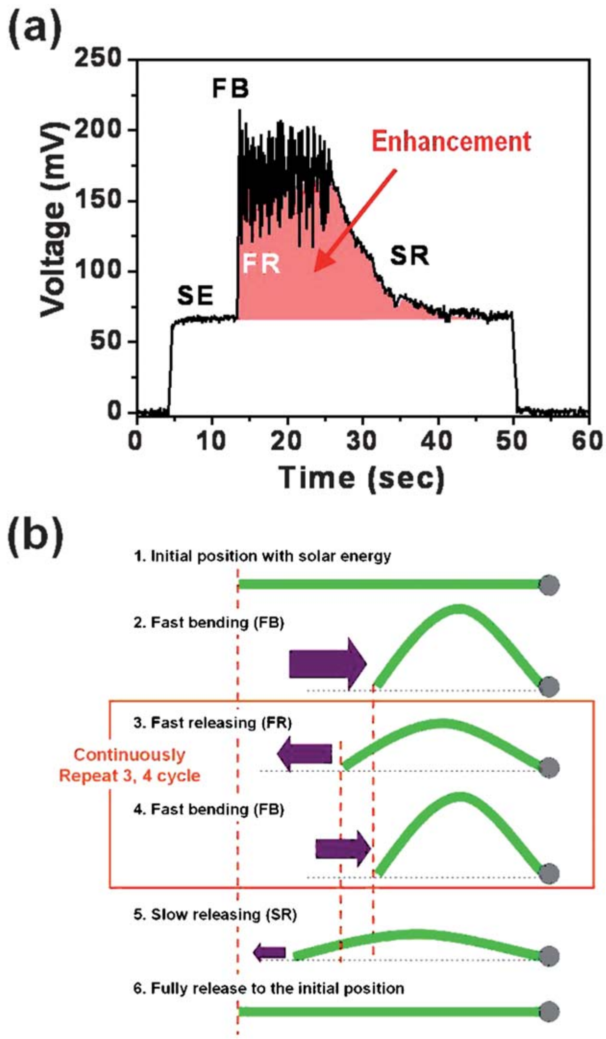

Fig. 5 Synergetic enhancement by the contribution of the piezoelectric element during solar power generation. (a) Output voltage measured by controlling straining processes under solar energy (*SE*) with fast bending (*FB*), fast release (*FR*), but not fully release, and slow releasing (*SR*). (b) The detailed straining process. The green part is our hybrid device.

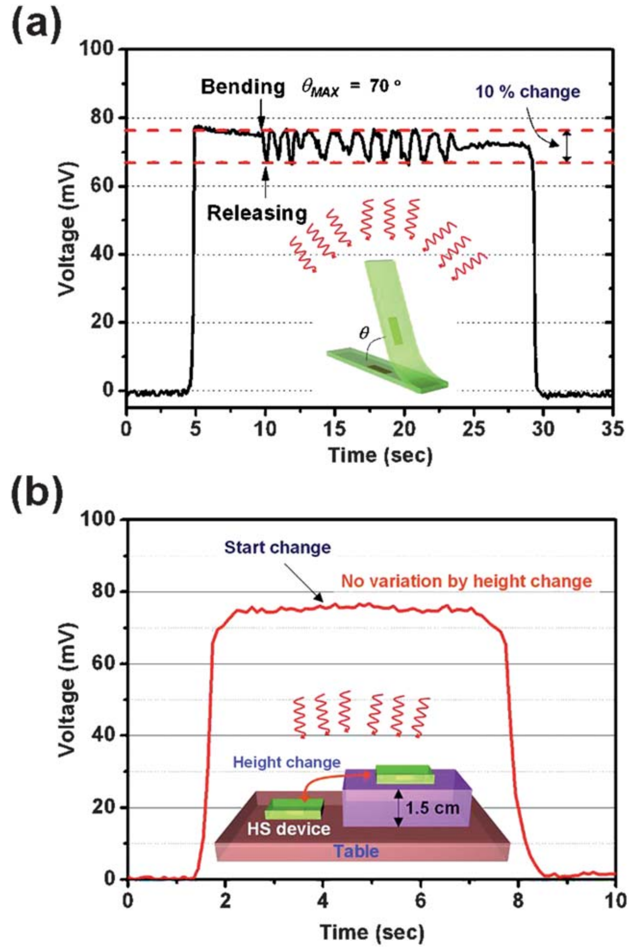

Fig. 6 Verification of solar power variation according to the angle and height changes of a device (a) output voltage by solar energy according to the angle change of a hybrid device and (b) output voltage by solar energy according to the height change of a hybrid device. We can clearly confirm that the sharp output responses (see Fig. 3) by bending together with solar energy originated from the piezoelectric field in ZnO.

film was deposited along a preferred *c*-axis orientation with a textured structure, which leads to the strong piezoelectric alignment to the external mechanical stimuli. Based on the polarity of the output voltage from photon energy and mechanical energy under independent operation, the piezoelectric potential in the ZnO thin film under mechanical bending is positive (V^+) at the interface contacting with polymer blend and negative (V^-) at the side facing ITO. Thus, the piezoelectric-induced electrons (e_1 or I_{PE}) flow out from the ITO electrode through an external load resistor, and the flow of photo-induced electrons is also enhanced (I_{SE}') due to the piezoelectric potential, demonstrating an overall enhanced output signal ($I_2 = I_{SE}' + I_{PE}$ in Fig. 4b; see also Fig. 3b(ii)).

When the hybrid cell is held in a static bent position (Fig. 4c), there is no dynamic straining, so that the momentarily 'static' strain produces no more additional current from the mechanical unit, thus, the output current is only contributed by photons (I_{SE}'). Based on the previous report,[29] the piezoelectric potential created in ZnO holds for an equivalent length of time before being screened by external electrons, giving sufficient time for experimental observation of the effect of the piezoelectric potential across ZnO. Thus, it is important to note, a static piezopotential in ZnO can be partially preserved within a short time. The photon-generated electrons screen only the positive piezopotential region, thus the potential drops locally from V_1^+ to V_2^+, but leave the negative piezopotential almost unchanged[28] as V_1^-. Due to V_1^-, the output voltage (I_{SE}') is, therefore, higher than that (I_{SE}) generated only by the photon energy (see Fig. 3b (iii)). This is why that the observed output voltage in Fig. 3c in the *HD* region is a higher flat plateau. As the device is released (Fig. 4d), electrons (e_2 or I_{PE}') flow through the external load into the ZnO layer to screen the piezoelectric potential, giving a negative pulse ($I_4 = I_{SE} - I_{PE}'$). If the device is fully released under *FR*, the piezoelectric potential instantaneously disappears and the AC-type sharp negative signal can be observed (Fig. 3b(iv)). Finally, the output voltage recovers to the original level (I_1) as contributed by solar energy.

With a controlled mechanical straining process applied to the device, the overall output voltages from both solar and mechanical energies were synergistically enhanced (Fig. 5a). After fast bending of a hybrid device, we quickly released the device, although not fully, and then the device was bent again (Fig. 5b for the details of the straining process). Since the device was not fully released, the negative piezoelectric pulse is much less than the positive pulse, so that we could obtain a DC-like enhanced output voltage (Fig. 5a). By using such a "programmed" straining process, the total output voltage was enhanced by up to about a factor of 2 compared to that produced only by solar energy. Of course, the enhancement factor by the contribution of piezoelectric part must be significantly changed by the reference solar power, the mechanical bending curvature, the straining rate and time, and so on. However, the hybrid device indeed demonstrates the concurrent scavenging of two types of energies, which can improve the PCE of solar cells especially in applications where there is a large amount of mechanical disturbance and the light intensity is rather low. This is a practical consideration for the applications of the devices in a variety of environments. We further controlled the behavior of the overall output voltage through stepwise *FR* (Fig. S7†) and repeated *FB* and *SR* (Fig. S8†) under hybrid operation. Such a high degree of controllability of the piezoelectric output behavior might support the potential design of multiplex hybrid energy devices with multi-sensing functions such as photo or strain sensors.

When mechanical bending is applied to the hybrid device together with solar energy, the output voltage and current from the solar energy unit is varied by changing the angle and position of the device, since the energy impinging on it depends on the angle of the incident light and the distance to the source. We tested this by varying the angle and position of the hybrid device, as shown in Fig. 6. As the angle changed, the variation of output voltage was found to be below 10% of the original output voltage generated by solar energy. Furthermore, there was almost no variation with the position change (1.5 cm) since the distance from the light source was about 2 m. We thereby confirm that the sharp output responses (Fig. 3) with magnitude significantly greater than the baseline set by the solar energy contribution are derived from the piezoelectric field in ZnO.

4. Conclusions

In summary, we have demonstrated a promising flexible hybrid energy scavenger that harvests diverse forms of energies in nature. By using ZnO with the coupled piezoelectric and photoconductive characteristics, a naturally flexible hybrid architecture of a piezoelectric power generator and an organic solar cell was successfully created as a new-type power cell that can harvest solar and mechanical energies, either separately or simultaneously. The key advantages of our natural hybrid device were no crosstalk, no volume increase, no additional assembly process, and the synergetic effects on the performance of each element. Furthermore, based on a programmed mechanical straining process, the output behavior of our hybrid cell could be facilely controlled. Such a hybrid energy generator is expected to be a novel multi-functional power supply that could provide electricity at anytime and anywhere, especially in an environment where solar light is weak, which is likely to be the most conventional case for mobile electronics.

Acknowledgements

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