Optical Fiber-Based Core–Shell Coaxially Structured Hybrid Cells for Self-Powered Nanosystems

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Searching for renewable and green energy resources is one of the most urgent challenges to the sustainable development of human civilization with the threat of global warming and energy crises. Meanwhile, in the nano-world, the development of a wireless self-powered system that harvests its operating energy from the environment is of great importance for sensing, personal electronic, and defense technologies.[1] Recently, conjunctional harvesting of energy from multiple sources available in our living environments using a single device has become highly desirable, representing a new trend in energy technologies, not only for powering personal electronics but also for future implantable sensor–transmitter devices for biomedical and healthcare applications.[2] Hybrid energy harvesting is now becoming a well-received approach, and several models have already been demonstrated, like hybrid cells for harvesting solar and mechanical energy,[3] biochemical and biomechanical energy,[4,5] thermal and solar energy,[6] and sound and solar energy.[7] Solar is probably the most abundant clean and renewable energy around us, but solar is not always available at the location the devices will be deployed, being strongly depending on day/night, the weather, and, especially, in those special cases that we want to utilize solar to power devices at concealed locations. On the other hand, mechanical energy is widely available in our living environment and can be a power source for electronic devices when solar is not available.

Here, we report an optical fiber-based three-dimensional (3D) hybrid cell (HC), consisting of a dye-sensitized solar cell (DSSC) for harvesting solar energy and a nanogenerator (NG) for harvesting mechanical energy; these are fabricated coaxially around a single fiber as a core–shell structure. A conventional optical fiber is flexible and allows remote transmission of light, which makes the DSSC suitable for solar power generation at remote/concealed locations, such as caves and basements, with applications in defensive technologies, smart construction, and environmental science. The widely available mechanical energy in our living environment will supplement the power need when the DSSC is not available, such as at nights and on rainy days. The output for the HC, with a diameter of 500 μm and a length of 2 cm, is 7.65 μA and 3.3 V, which is strong enough to power nanodevices and even commercial electronic components. Alternatively, an HC can also serve as a self-powered sensor, which will give the information about structures (such as a smart bridge, **Figure 1**a) where the HC is utilized to detect mechanical vibration. Our optical fiber-based HC is of great potential application as a power source for nanosystems in biological sciences, environmental monitoring, defense technology, and even personal electronics, especially for continually powering devices at remote/concealed locations.

A compact HC is fabricated based on a traditional optical fiber, consisting of a DSSC and a piezoelectric NG. The design of the DSSC is based on ZnO NWs arrays grown radially around the optical fiber,[8] with the *c*-axis pointing outwards, as shown in Figure 1 a–c. First, a 5 nm thick ITO adhesion layer followed by a 50 nm thick ZnO seed layer were deposited on the optical fiber in sequence. The ITO layer on the optical fiber not only served as a conductive layer, but also as a high-refractive-index material that allows light to escape the fiber and enter the DSSC. The ZnO seed layer was for growing ZnO NW array via a wet chemical method at 95 °C for 5 h. The nutrient solution for growing NWs was an aqueous solution of 0.02 M Zn(NO$_3$)$_2$ and 0.02 M hexamethylenetetramine (HMTA). In order to get separated ZnO NWs, which will increase the dye absorption surface, 0–5 mL ammonium hydroxide (Aldrich) was added per 100 mL solution. The ZnO NWs are then sensitized in a 0.3 mM cisbis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)bis-tetrabutylammonium dye (N-719; as received from Solaronix) solution in dry ethanol for 24 h. An approximately 500 μm stainless steel tube with Pt coated inner wall was used as the counter electrode. The optical fiber with ZnO NWs was inserted into the stainless steel capillary tube as the photoanode, then the liquid electrolyte (0.5 M LiI, 50 mM I$_2$, 0.5 M 4-tertbutylpyridine in 3-methoxypropionitrile) was injected into the tube by the capillary effect.[9] For such 3D DSSCs, light will enter the optical fiber from the end cross-section and experience multiple internal reflections inside the fiber during propagation, which will improve the performance of the DSSC (Figure 1d). Detailed experimental procedures and structure is given in a previous work by Weintraub et al.[8]

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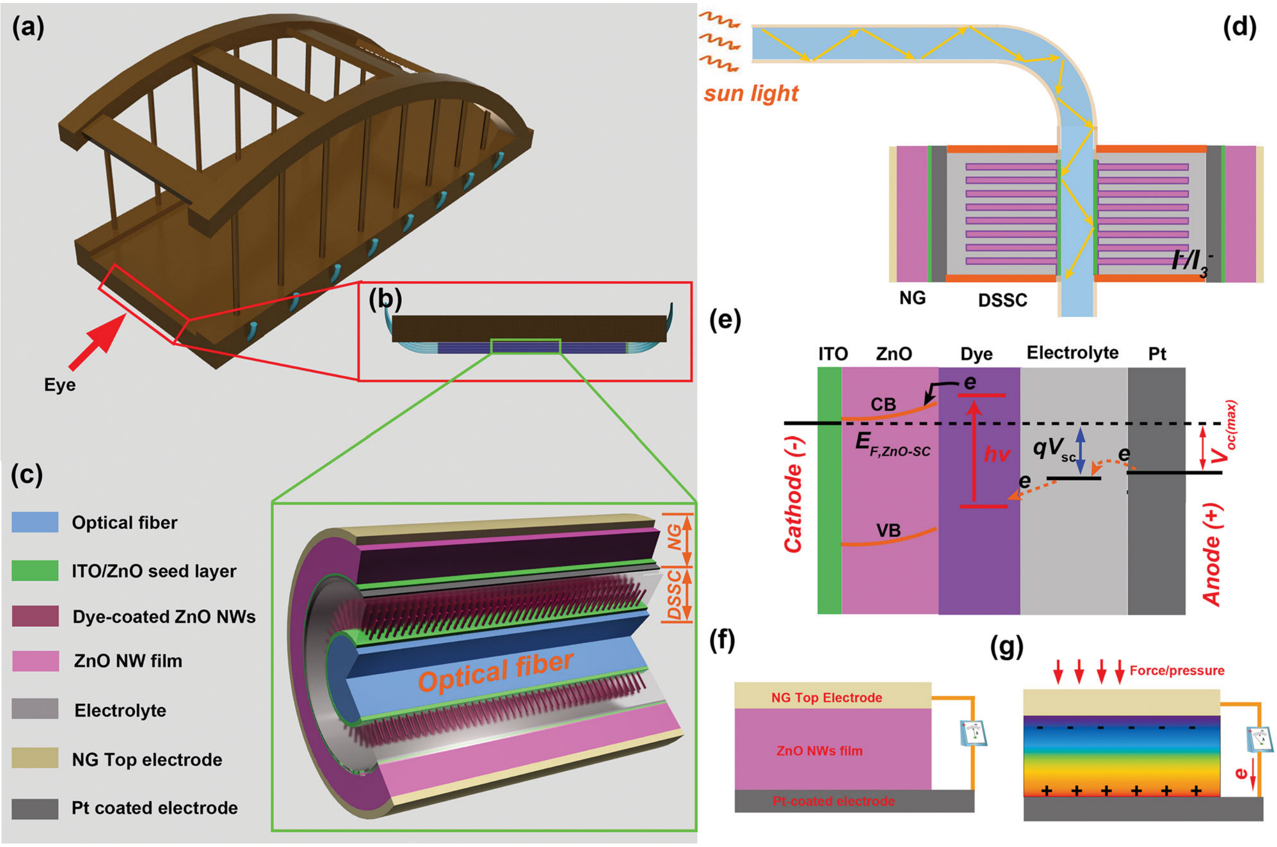

Figure 1. Design and principle of a 3D optical fiber-based HC consisting of a DSSC and an NG. a) Taking a smart structure (e.g., a bridge) as a demonstration, HCs are deployed for simultaneously or independently harvesting solar and mechanical energy for self-powered systems, which can monitor the conditions of these smart constructions without external power supply. The conventional optical fiber allows remote transmission of light, making the DSSC suitable for solar power generation at a remote/concealed location, with applications in defensive technologies, smart constructions, and environmental science. b) Enlarged view of the HCs mounted beneath the bridge. c) The 3D HC is composed of an optical fiber-based DSSC with capillary tube as counter electrode. d) Detailed structure of the 3D HC. e) Electron energy band diagram of the DSSC. f,g) The working principle of the NG. The +/– signs indicate the polarity of the local piezoelectric potential created on the inner and outer surfaces of the ZnO NW film as a result of the applied pressure.

The working principle of the DSSC is presented by the electron energy band diagram (Figure 1e).

An NG, which converts the mechanical energy into electricity, is based on a densely packed ZnO NW textured film grown by a wet chemical method on the outer wall of the stainless steel tube. Different from the aforementioned ZnO NW fabrication process, the concentration of the nutrient solution was increased from 0.02 to 0.15 M and no ammonium hydroxide was added. A conductive carbon tape was used as the top electrode, and the stainless steel tube was used as the other electrode. When the ZnO NW film is strain free, there are no piezopotential and piezocharges at the surface of the ZnO NW film (Figure 1f); when a compressive strain is applied, a separation between the static ionic charge centers in the tetrahedrally coordinated Zn–O units results in a piezoelectric potential gradient along the *c*-axis. An AC output is generated by applying a cycled pressure/deformation on the ZnO NW film owing to the piezopotential generated between the inner and outer surfaces of the shell[10] (Figure 1g).

Figure 2 shows scanning electron microscopy (SEM) images of the as-grown ZnO NWs on the optical fiber and dense ZnO NW film on the stainless steel tube (Figure 2e and f). The synthesized ZnO NWs are 20 µm in length. They are very well aligned in the vertical orientation and densely packed with great size uniformity (Figure 2a –d). The cross-sectional view of the ZnO NW film indicates that the ZnO nanowires are vertically grown from the substrate with a high packing density, like a textured film. The bottoms of these nanowires are bonded through the ZnO seed layer, and the growth direction is along the *c*-axis.[11] The ZnO NW film has length of approximately 2 µm and diameter of approximately 200 nm.

The performance of the HC is presented in **Figure 3**. A plot of current density against voltage (*J*–*V* curve) of the DSSC is presented in Figure 3a, irradiated via the cross-section of the optical fiber using a 1.5 AM solar simulator (300 W Model 91160, Newport), showing an open-circuit voltage V_{OC} of about 0.38 V and a short-circuit current density J_{SC} of about 2.8 mA cm^{-2}. The output of the HC in voltage is presented in Figure 3b. Due to the AC output of the NG, a current rectification was implemented using a commercial full-wave bridge rectifier composed of four diodes (**Figure** 4b), each of which had a threshold voltage of 0.3–0.4 V, to fully use the electrical energy

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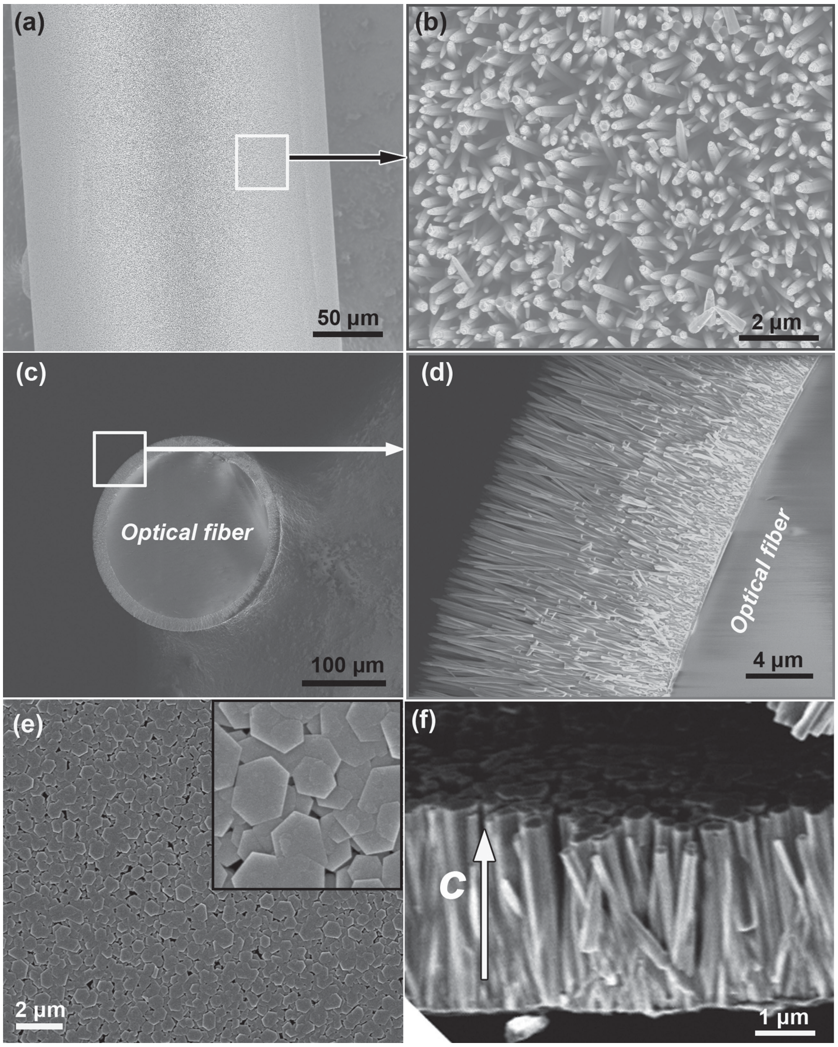

Figure 2. SEM images of ZnO NWs and ZnO NW film: a and b) are low and high magnified top views of ZnO NW arrays on optical fiber, respectively; c and d) are low and high magnified cross-sectional views of ZnO NW arrays on optical fiber, respectively; and, e and f) are top and cross-sectional views of compact ZnO NW film grown on the outer surface of tubular stainless iron electrode, respectively. The insert in (e) is the corresponding high-magnification SEM image. The *c*-axis of the ZnO NWs is pointing outwards.

harvested by the AC NG in one full cycle of mechanical deformation from both pressing and releasing processes. The V_{OC} of the DSSC is about 0.4 V, and the V_{OC} of the NG is about 2.9 V, resulting in a V_{OC} of the HC about 3.3 V, clearly demonstrating full-wave rectification. Figures 3c presents the output in current from the HC under a cycled compressive strain with an average frequency about 1 Hz. The enlarged views of the I_{SC} of a single NG and the HC, which are marked in blue and red rectangles in Figure 3c, are shown in Figure 3d and e, respectively. The I_{SC} of the DSSC is 7.52 µA and that of the NG is 0.13 µA; as a result, the I_{SC} of the HC is 7.65 µA when the DSSC and the NG were connected in parallel with the same polarity. It is noted that the output current of the HC is dominated by the DSSC, while the output voltage of the HC is dominated by the NG. Complementary contribution of the DSSC and NG is likely beneficial for the power output of the HC.

A totally self-powered nanosystem includes the functional unit (such as the sensor), a power harvesting unit, an electrical measurement system, a data processing system, and, possibly, a wireless communication unit (radio frequency, RF, technology).[12] A simply schematic view of a self-powered system is illustrated in Figure 4a. The power source in this system consists of an energy harvesting module and an energy storage module. The harvester first scavenges multiple types of energy (solar, mechanical, chemical, and/or thermal) from the environment, then stores it in the energy storage module (e.g., capacitors), which can be used to power the other parts of the system, like sensors (detecting the changes in the environment), the data processing unit, and the (wireless) communication unit. In this work, the HC harvested solar energy and mechanical energy simultaneously or individually, and the as-generated charges were stored consecutively into eight 22 µF capacitors that were connected in parallel, as shown in Figure 4b, with the switches set at position '1'. The entire charging process by individual DSSC, NG, and HC were recorded by monitoring the voltage/potential across capacitors, as presented in Figure 4d–f, respectively.

When the capacitors were charged only by the NG, the voltage across the capacitors increased two steps within each cycle of the energy conversion process, which was in accordance with the rectified output of the NG, as indicated by arrowheads in Figure 4d. This charging rate was very low; it usually took 3–4 h to reach the saturated value of the capacitors. When the capacitors were charged only by the DSSC, the charging rate was very high due to the high output in current of the DSSC; only 30 s was needed to reach the saturated value of the capacitors, and the charging curving was smooth – no steps were observed (Figure 4e and the insert enlarged view). When the capacitors were charged by the HC, an obvious adding up effect was observed, as seen in the inset enlarged figure in Figure 4e. The charging rate was high, which was contributed by the DSSC, and the stepwise increasing charging curve indicated the contribution of the NG.

After 3 min quick charging, the voltage of the capacitor reached approximately 0.35 V, which was near the output voltage of the DSSC. Then, by switching the connection of the eight charged capacitors from parallel to series by adjusting the switches to position '2' (see Figure 4b), the total output voltage reached $V_{tot} = 0.35 \times 8 = 2.8$ V. This was high enough to drive a commercial LED with a turn-on voltage of around 1.5 V, provided the output power was sufficient at the discharge. By using this voltage amplification technique, we successfully powered a commercial

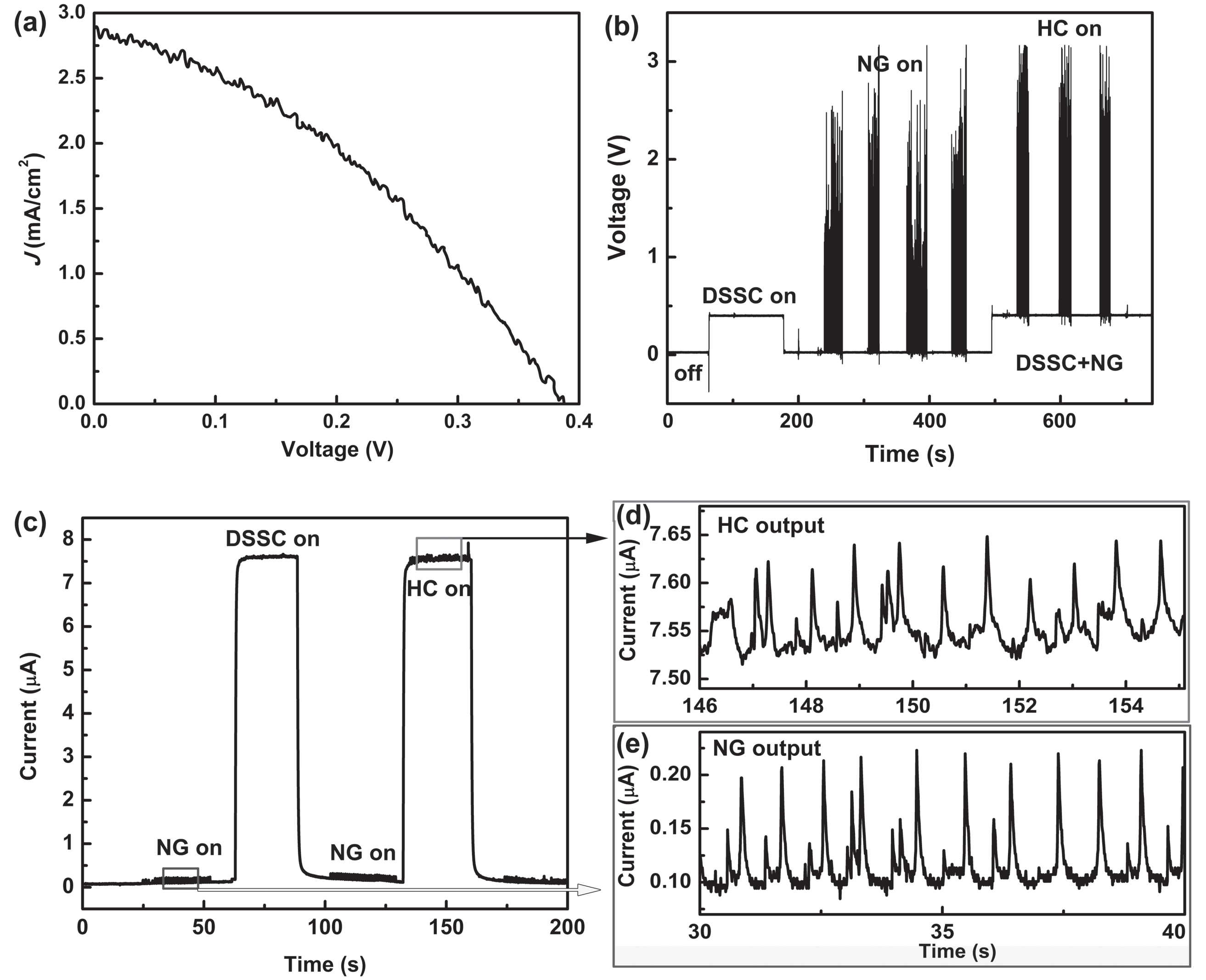

Figure 3. The performance of an optical fiber-based hybrid cell: a) Plot of current density against voltage (*J*–*V* curve) of the DSSC, irradiated via the cross-section of the optical-fiber using a 1.5 AM solar simulator; b) Open-circuit voltage (V_{oc}) of the HC when the NG and the DSSC are connected in series, where $V_{oc(HC)} = V_{oc(DSSC)} + V_{oc(NG)}$; c) Short-circuit current (I_{sc}) of the HC when the NG and the DSSC are connected in parallel; and,d and e) Enlarged view of the $I_{sc(HC)}$ and $I_{sc(NG)}$, clearly showing that the $I_{sc(NG)}$ is 0.13 μA, the $I_{sc(DSSC)}$ is 7.52 μA, and the $I_{sc(HC)}$ is about 7.65 μA, nearly the sum of the output of DSSC and NG.

LED (Figure 4c, Avago Technologies US Inc., HLMP-1700), by a fast discharge of the stored charges. A commercial LED, with an emission spectrum centered at 635 nm, 1.7 V turn-on voltage and 450 Ω, was used in this work. The LED was lit up as soon as the discharging process was triggered. The emitted light lasted for 0.1–0.2 s and was clearly captured against a dim background (Figure 4c). During the whole charging–discharging process, no other power sources were involved in the circuit. The entire circuit is essentially a complete self-powered system, which consists of three components: an energy harvester (the HC), storage units (capacitors), and a functional device (the LED).

In some other applications, only a turn-on voltage is required and the turn-on current can be low; one example is a liquid crystal display (LCD), which is a nonpolar device that can be driven directly by AC power as long as its output potential exceeds a threshold value. **Figure 5**a shows a series of snapshots taken for a full cycle driving of an LCD by the HC at an average frequency of 0.86 Hz, showing the LCD blinking corresponding to each output peak of the HC. The LCD screen used in this work was taken from a calculator that displayed an output of "6" on the screen. The LCD screen was directly powered by a HC without involvement of any external sources, capacitors, or measurement meters. It is obviously that the LCD was lit up at the peak output of the HC (3.0 V), owning to the high voltage contributed by the NG; and the output of the DSSC (0.45 V) was too low to power the LCD (Figures 5b). Thus, the LCD screen blinked when a periodical straining was applied to the HC.

Such an optical fiber-based 3D HC is not simply a combination of a DSSC and an NG, it is a complementary integration of the DSSC and the NG as a solid structure around a single fiber. The cathode of the DSSC is one of the electrodes of the NG as well; the two parts cannot be separated. First, the DSSC

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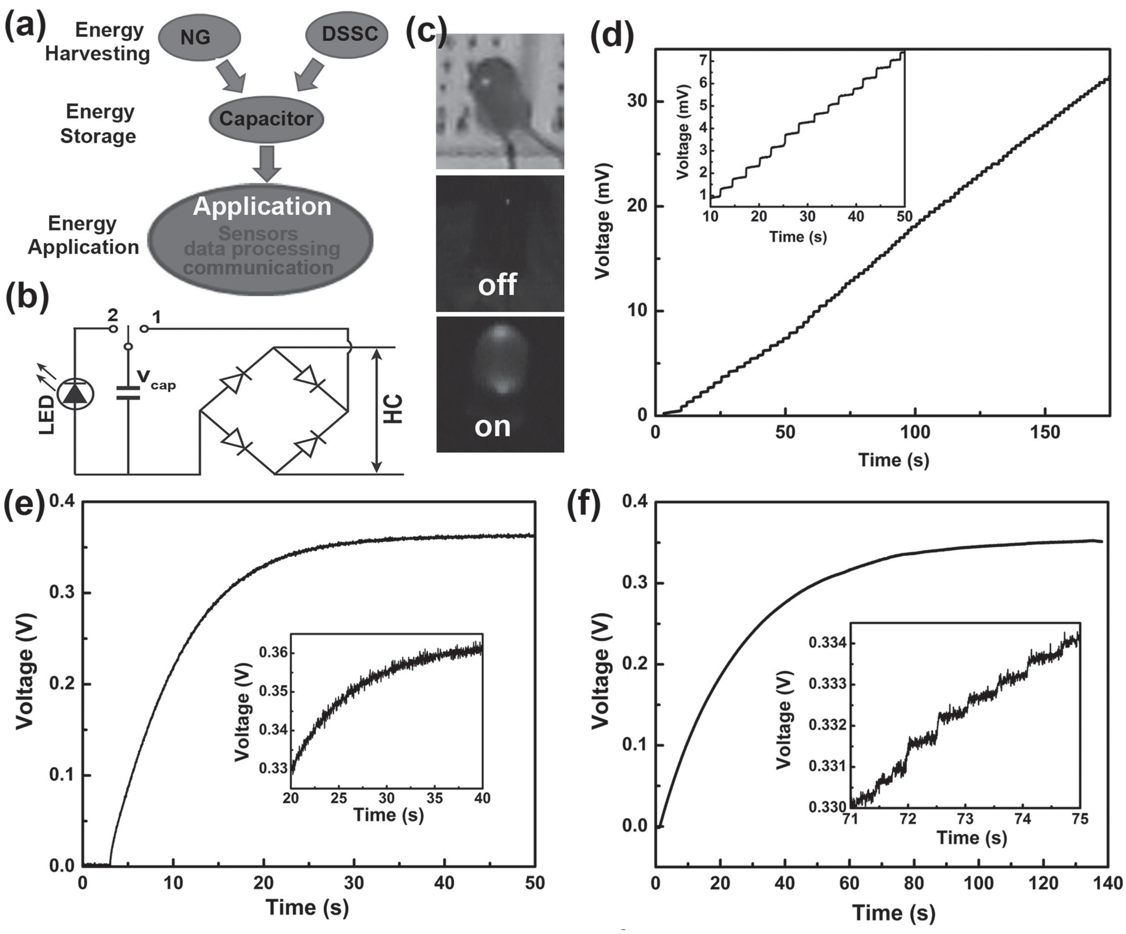

Figure 4. Application of the electric energy generated by the HC to drive a commercial light emitting diode (LED). a) Schematic diagram of the integrated self-powered system, consisting of multi-energy harvesting components, an energy storage component and an energy consuming (application) component. b) Schematic of the charging–discharging circuit for storing and releasing the energy generated by the HC. c) Image of a commercial LED, which is incorporated into the circuit (top), and image of the LED in dim background before (middle) and when (bottom) it was lit up by the energy generated from the HC. d–f) Storage of electrical pulses into capacitors for further application: voltage across a storage capacitor when being charged by an individual NG (d), an individual DSSC (e), and the HC (f). The inserts are enlarged plots corresponding to each charging process. The step in capacitor voltage shown in (d) and (f) occurred when the NG and HC are compressed and released.

cannot work all the time over a full day, even with the help of the optical fiber for light transmission, but the NG can work all of the time, because the widely available mechanical energy in our living environment will let the NG continuously output the power when the DSSC is not available, such as at night and on rainy days. Second, the output of the DSSC and the NG is complementary. The DSSC has a relative high output in current (at μA to mA scale), but the output in voltage is low, only 0.4–0.6 V, lower than the operation voltages required for most personal electronics. For an NG, its output in voltage is as high as several volts, but the output in current is low (only at nA scale). As a result, a hybridization of the two can utilize the high current of the DSSC and the high output voltage of the NG. Third, the HC can serve as a self-powered system as well, in which the NG part can serve as a force/pressure/strain sensor, while the DSSC can serve as a power source.[4] Such self-powered system can be used to monitor smart structures, such as bridges and houses.

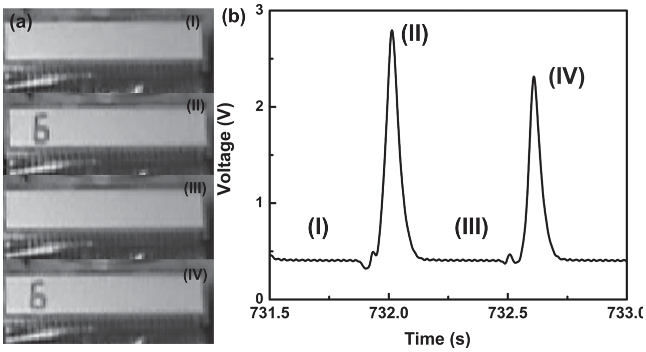

Figure 5. Driving a commercial LCD by a hybrid cell. a) Four snapshots taken from a full cycle driving of a LCD by the HC. The DSSC remains on during this process, and the LCD could only be lit up when the output of the NG reaches a value which is over the threshold of the LCD light-up voltage. b) An enlarged single cycle of the HC output.

In summary, we have demonstrated an optical fiber-based 3D compact hybrid cell, consisting of a DSSC and a nangenerator, to harvest solar and mechanical energy simultaneously or independently, for self-powering nanosystems especially in concealed places. The HC has the advantages of both high current, contributed by the DSSC, and high output voltage, contributed by the NG. The output of the HC with a diameter of 500 μm and a length of 2 cm is about 7.65 μA current and 3.3 V voltage, which is strong enough to power nanodevices and even personal electronics. Our optical fiber-based HC has great potential as a power source for nanosystems in the biological sciences, environmental monitoring, defense technology, and even personal electronics, especially for continually powered devices at remote/concealed locations.

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