Supporting Information

S1. Experimental Section

Growth of ZnO NW film on carbon fibers. Carbon fibers are used not only as the flexible soft substrate onto which a ZnO thin film is grown at high temperature but it also acts as an electrode for charge transport. The source materials were ZnO powder (Alfa Aesar, 99.9%, 200 meshes), activated carbon particles (Alfa Aesar, steam activated, acid washed) with equal ratio in mass, which were placed at the center of a tube furnace. The carbon fibers were located at about 10 cm from the source materials, by the carrier gas. The carrier gas was a mixture of oxygen and argon (99.9%, Georgia Tech) at a ratio of 1:4 at a flow rate of 40sccm. The growth temperature was 960 °C.

Fabrication and characterization of the hybrid NG and the self-powered nanosystem. The hybrid generator is designed on carbon fibers, consisting of a fiber nanogenerator and a fiber bio fuel cell. Each hybrid generator can be achieved on an individual carbon fiber. For easily handling and fabrication, and also for improve the performance, we build our hybrid NG on a bundle of carbon fibers which including around 1000 carbon fibers. The FNG is fabricated by etching the ZnO NW film at one end of the carbon fiber, contacting the top surface using the silver paste and tape (or other metal deposition, such as Au electrodes) and leading out two electrodes from the surface and the core part. The entire FNG part was packaged with a thin layer of soft epoxy polymer to ensure the robustness of the device and also isolate possible moisture erosion to the NWs.

Glucose oxidase (GOx, from Aspergillus niger, type X-S) and laccase powder (from Trametes versicolor) were purchased from Sigma-Aldrich, multiwall carbon nanotubes from Hanhwa Nanotech (diameter 39 nm, purity 95%), and phosphate buffer solution (PBS, pH 7.0) from Fluka. All chemicals were used as received. Carbon nanotubes were dissolved in ethanol and untrasonicated for 1 h to form 2 mg/ml dispersion. A 4 mg/ml solution of GOx in PBS solution and a 4 mg/ml solution of laccase in PBS solution was prepared. The FBFC was located at the other part of the same carbon fiber. A layer of PMMA was coated on the carbon fiber as an insulator, two separated gold electrodes were patterned onto PMMA layer and coated with carbon nanotubes (CNTs) (20 μL), followed by immobilization of GO_x (2 μL) and laccase (2 μL) to form the anode and cathode, respectively. The device was then stored under 4 ℃ for at least 4 h before use. Prior to use, the electrodes were rinsed in pure PBS. 0.5 wt% glucose/PBS (pH=7.0) is used as the biofuel in the performance test. The life span is about 2 month with the output decreased by 20%, by storing the device under 4 ℃ after measurement each time.

In our study, the as-fabricated alternating current nanogenerator was measured by the dynamic mechanical stimulation triggered by a linear motor that provided a controllable impact speed, force and frequency. A voltage preamplifier (Stanford Research Systems, Model SR560) and a current preamplifier (Stanford Research Systems, Model SR560) were used to measure voltage and current output of the devices, respectively.

S2. Fabrication Process of the fiber devices

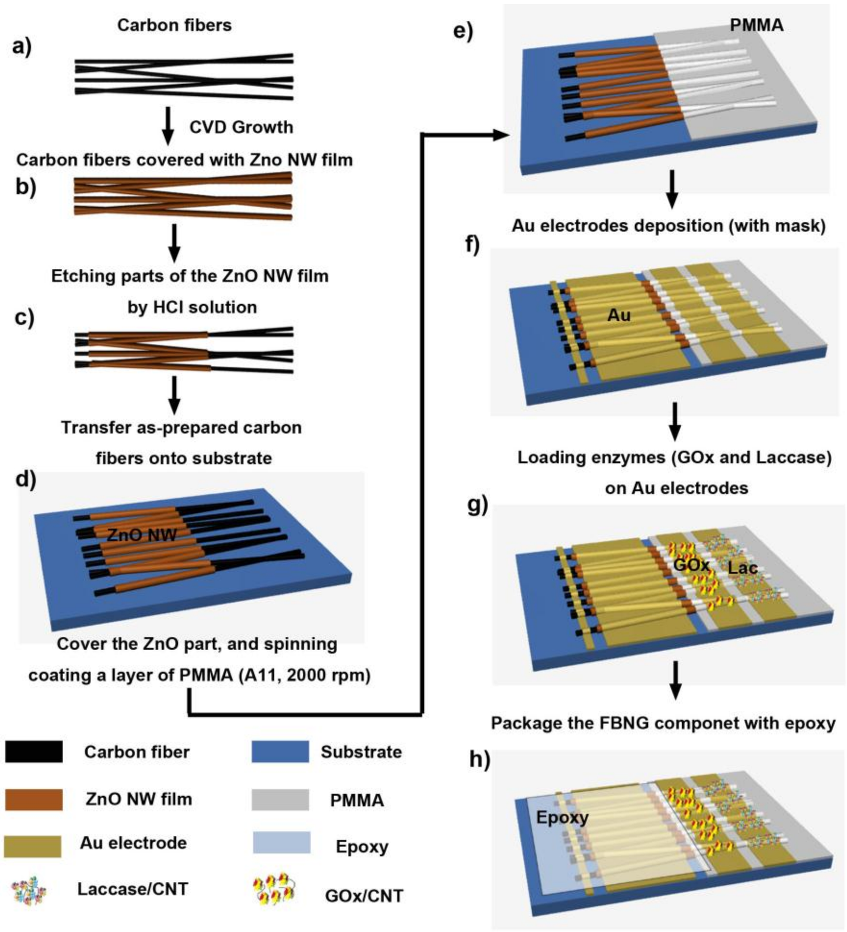


Fig. S1. The fabrication process of the carbon fibers based hybrid nanogenerators

Fiber-based hybrid nanogenerator fabrication process:

(1) Grow ZnO NW film on carbon fibers (Fig. S1a) by VLS method (Fig. S1b)

(2) Etch parts of the ZnO NWs, exposing two ends of the carbon fibers (Fig. S1c)

(3) Transfer as prepared ZnO NW/carbon fiber onto substrate (any kind of insulator substrate) (Fig. S1d)

(4) Spin coating a layer of PMMA (A11, 200rpm) onto the right exposed part of the carbon fibers (Fig. S1e)

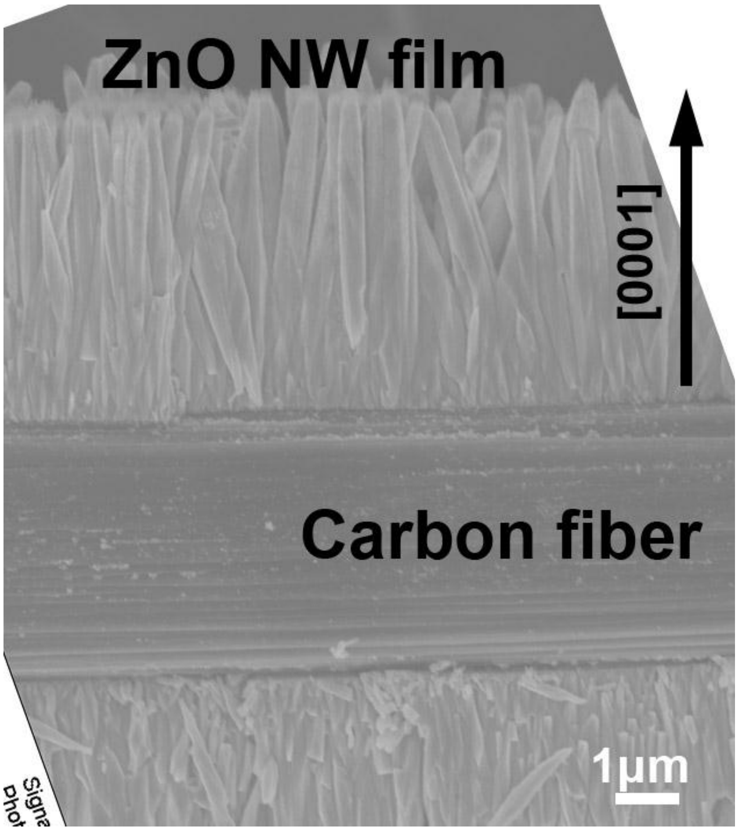
(5) Deposition Au film as top electrodes (Fig. S1f)

(6) Load CNT/enzymes (GOx and laccase) onto electrodes (Fig. S1g)

(7) Package the nanogenerator part by using a thin layer of epoxy, to isolate possible moisture erosion to ZnO NWs (Fig. S1h)

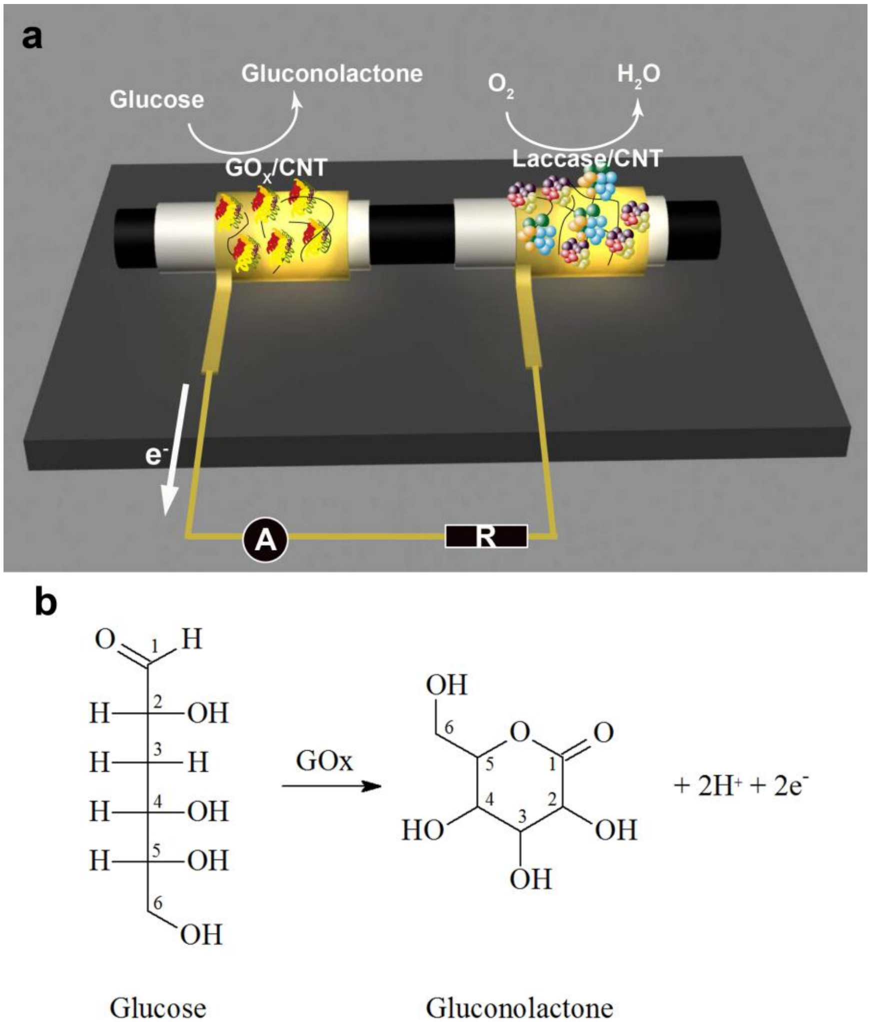
S3. Cross-section view of ZnO NW film

Fig. S2. SEM image shows the cross-section view of a ZnO NW film grown on carbon fiber.



S4. Working Principle of a biofuel cell

Fig. S3. a, Design of a single carbon fiber based biofuel cell. b, the chemical reaction at the anode of a biofuel cell. c, the chemical reaction at the cathode of a biofuel cell.



c

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \xrightarrow{Laccase} H_2O$$

When the FBFC is in contact with a bio-liquid that contains glucose, the corresponding chemical processes occurring at the two electrodes are: glucose is electrooxidized to gluconolactone at the anode (Fig. S2b)[S1] and dissolved O_2 is electroreduced to water at the cathode (Fig.S2c)[S2], creating a corresponding chemical potential drop between the two electrodes, which drives the flow of electrons through the external load.

S5. "Hybrid nanogenerators for self-powered systems" and "hybrid nanogenerators as self-powered systems"

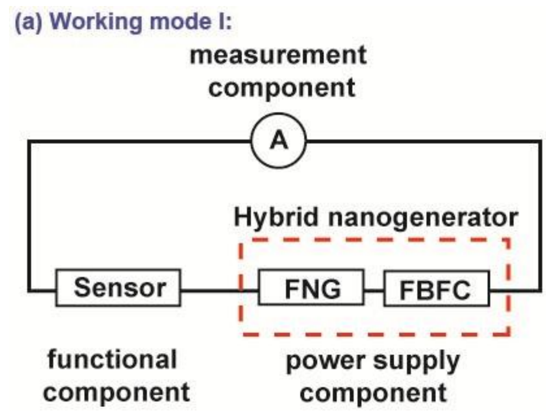


Fig. S4a. Working mode I: "Hybrid nanogenerators for self-powered systems"

The hybrid nanogenerator (both FNG and FBFC) working as a power supply component, they drive the other sensor in the circuit. For example, we demonstrated driving a pH sensor and a UV sensor by using a nanogenerator or a hybrid nanogenerator as a power source. The data in Fig. 2 is obtained in this working mode.

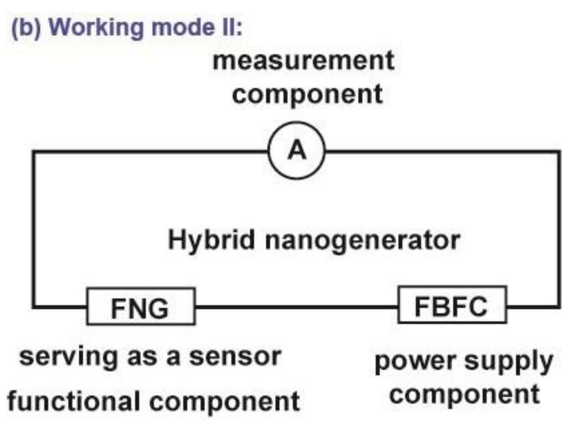


Fig. S4b. Working mode II: "Hybrid nanogenerators as self-powered systems"

In this working mode, no more sensor is needed. The ZnO NW film based FNG can serve as a pressure sensor, while the FBFC serves as a power supply component. Thus, such a hybrid nanogenerator switches to a self-powered nano-system. The data in Fig. 3 and Fig. 4 is obtained in this working mode.

S6. Experimental setup in Fig. 3 and Fig. 4

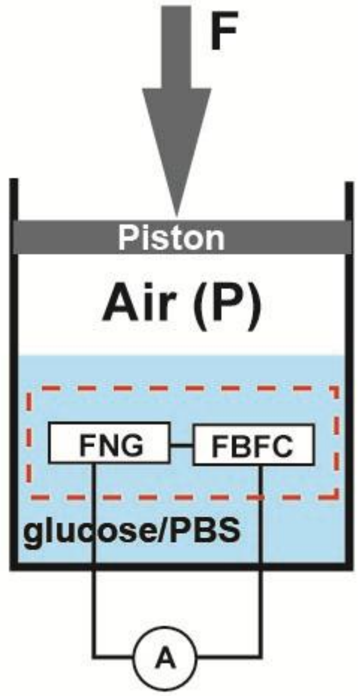
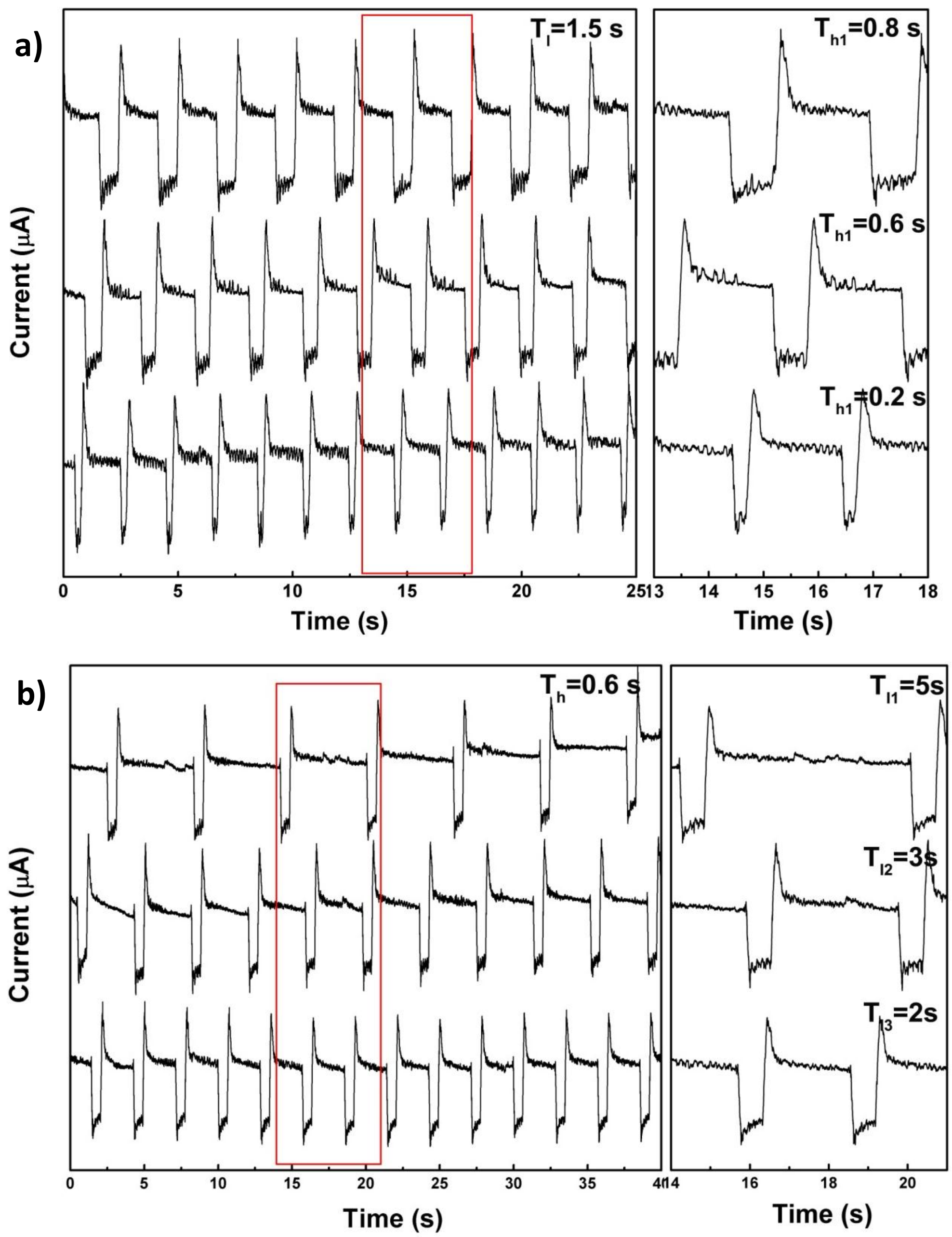


Fig. S5. In the experiment, the hybrid nanogenerator is immersed in glucose/PBS solution inside a closed container, as show in the figure. When a periodic force is applied onto the piston, the air in the closed container is compressed; as a result, the pressure applied on the solution (also on the devices) increases, the current in the circuit increases. When the pressure is released, a rapid and obvious decrease in current is detected, as shown in Fig. 3 and Fig. 4.

S7. Switch-off experiment compared with Figs.4c and 4d

Fig. S6. a, Measured current from the hybrid NG by varying the holding time while keep the interval during which the pressure is off being constant. **b**, Measured current from the hybrid NG by varying the period at which the pressure is applied, while the time interval for holding the pressure is a constant. These switch-off experiments solidly supported that our hybrid nanogeneraters work very well as self-powered nanosystems.



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[S2] a) S. C. Barton, H. H. Kim, G. Binyamin, Y. C. Zhang, A. Heller, *J Am. Chem. Soc.* **2001**, 123, 5802-5803; b) F. Trudeau, F. Daigle, D. Leech, *Anal. Chem.* **1997**, 69, 882-886.