Journal Name

COMMUNICATION

Electronic supplementary information for

Electric Power Generation *via* Asymmetric Moisturizing of Graphene Oxide for Flexible, Printable and Portable Electronics

Yuan Liang,[a] Fei Zhao,[b] Zhihua Cheng,[a] Yaxi Deng,[a] Yukun Xiao,[a] Huhu Cheng,[c] Panpan Zhang,[c] Yaxin Huang[c], Huibo Shao[a,*] and Liangti Qu[a,c,*]

[a] Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Key Laboratory of Cluster Science, Ministry of Education, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China.
E-mail: lqu@bit.edu.cn(L.Qu), hbs@bit.edu.cn (H. Shao)

[b] Materials Science and Engineering Program and Department of Mechanical Engineering, The University of Texas at Austin, TX, 78712, USA.

[c] Key Laboratory for Advanced Materials Processing Technology, Ministry of Education of China; State Key Laboratory of Tribology, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, PR China.

Experimental Section

Preparation of GO film.

GO was prepared by oxidation of natural graphite powder according to the modified Hummers' method.[S1,S2] A GO film with 6 cm in diameter and 10 μm in thickness was obtained by drying 3 mL 11.9 mg/mL GO solution in a dish with the diameter of 6 cm in a constant temperature oven of 50 ^{o}C for 6 h. Once the drying temperature is above 50 ^{o}C in the drying process, the GO will gradually be reduced. And the decrease of oxygen content will hurt the voltage output. The thickness of the film depends on the mass of GO. A GO film with the diameter of about 1 mm was fabricated by a puncher.

Screen printing device arrays.

Two types (I and round shape) of screen printing plates were designed. First step, bottom I shape electrode were screen printed on the typing paper by using commercial silver paste. Second step, the GO layers were screen printed on bottom electrode by 14.9 mg/mL GO solution. Third step, top I shape silver electrode were printed on GO. The model of this used high precision screen printing platform is ZB3040H. The mesh number of the screen printing plates is 200.

GO films were integrated on ITO/PET which was treated by oxygen plasma to improve the hydrophilicity. 14.9 mg/mL GO solution were screen printed on ITO/PET and dry in the air to form the GO arrays. The adjacent devices are separated by removing the ITO layer through laser (LAJAMIN LASER (LM-YLP-20F-III) ablation process.

Material characterizations.

The morphology and energy dispersive spectroscopy (EDS) data of the samples were investigated by scanning electron microscope (SEM, JSM-7001F) and energy dispersive analysis of X-rays (EDAX, Peaguas XM2). X-ray photolectron spectroscopy (XPS) data were obtained on an ESCALAB 250 photoelectron spectrometer (ThemoFisher Scientific) with Al Kα (1486.6 eV).

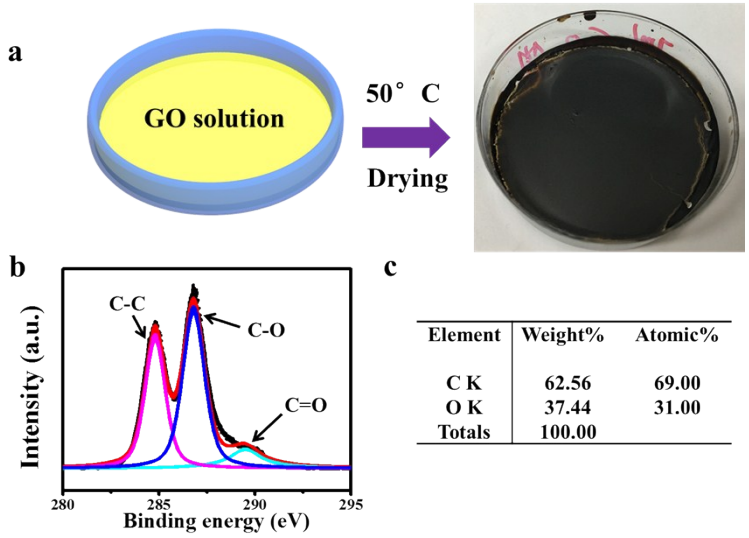
Device characterizations.

Experimental temperature was maintained at 23 ^{o}C. Compressed N_2 gas flows through the deionized water as the sources of moisture, namely wet N_2. The dry N_2 gas serves as dehumidification source. The values of the ΔRH were adjusted by the flow amount of N_2. The environmental temperature and humidity were recorded by Humidity Temperature Meter (SMART SENSOR AR847+). The current and voltage the device was measured by Keithley 2612. The fluctuations of V_{oc} or I_{sc} about the peak values and respond time could be ascribed to the fluctuating of temperature or humidity in laboratory during the measurement.

Electrical test

Since the exchange of the electrodes connecting with the source meter (the top electrode connects the positive pole) led to the reversal of the voltage to the electronegativity (bottom curve), which once again demonstrates the effective movement of the positive charges from the high moisture content to the low. After reaching the peak forward voltage stimulated by wet N_2 under the environmental RH of 60%, a dry N_2 gas stimulating the sample from the top will induce the voltage to quickly decrease and reverse to -0.62 V. This result indicates that **t**he positive charges move from the bottom to top electrode under the stimulation of dry N_2.

Supplementary Figures



Element	Weight%	Atomic%
C K	62.56	69.00
O K	37.44	31.00
Totals	100.00	

Fig. S1 Fabrication and characterization of GO film (a) Schematic illustration of the fabrication of GO film by a facile large-scale drying process. (b) High-resolution C1s X-ray photoelectron spectroscopy (XPS) spectrum of GO. (c) The energy dispersive spectroscopy (EDS) spectra of GO film.

From the XPS spectrum of C1s and EDS spectra, the GO film is rich in oxygen functional groups (C-O, C=O) and the weight proportion of oxygen component is as high as 37.4%, which can hardly be improved by the external auxiliary method such as oxygen plasma. Since the intrinsic O-group content of GO thin film is high, oxygen plasma treatment can rarely make it even higher. And the oxygen content plays a critical role in the energy generation process.

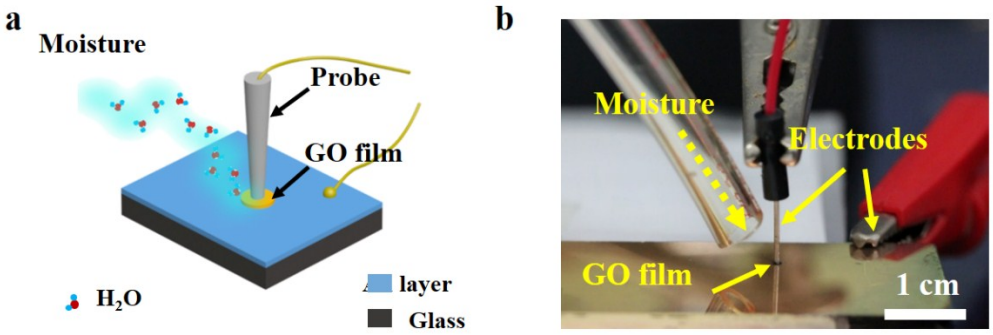


Fig. S2 (a) Scheme of experimental set-up for collecting the electric signal of GO/MIS under moisture. The system consists of GO with diameter of 1 mm and two electrodes: the top probe and the bottom plane electrodes coated with gold. (b) Digital photos of the test mode.

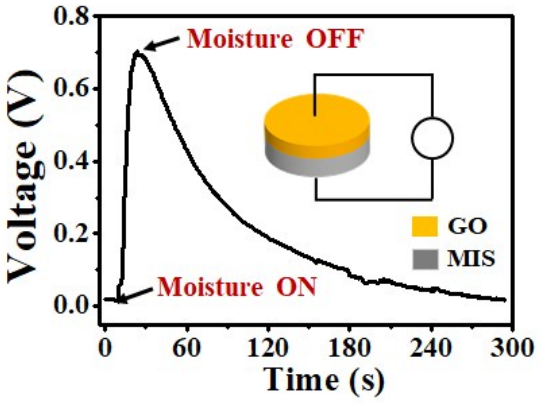


Fig. S3 Voltage output of GO/MIS cell. Inset is the scheme of test connection.

To check the power-generating performance, a GO film with a diameter of 1 mm and a thickness of 10 μm was measured. GO was located between the top probe electrode and bottom glass serving as MIL (also electrode) (Fig. S2a and 2b). The GO/MIS can produce a peak open-circuit voltage (V_{oc}) of 0.72 V under a stimulation of moisture. After the wet N_2 was removed, the V_{oc} gradually decreased to zero (Fig. S3).

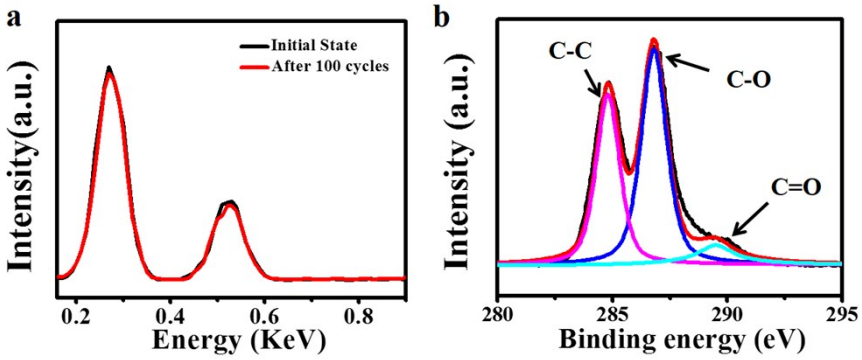


Fig. S4 (a) The energy dispersive spectroscopy (EDS) spectra of the initial GO and after 100 voltage output cycles. (b) High-resolution C1s X-ray photoelectron spectroscopy (XPS) spectrum of GO after 100 voltage output cycles.

The oxygen containing functional groups (denoted as O-groups) on GO have been demonstrated to be stable under ambient environments, while they could be partially removed by active reductants, high applied voltage or strong light irradiation. Such feature indeed hindered further improvement of graphene-based devices that consist GO and functional chemicals, e.g. electrolytes. Our design proposed here actually utilizes the activity of these O-group to enable hygroscopicity and avoids the reactive addictive which will potentially decrease the stability.

Generally, these O-groups are stable during moisture-based hydration-dehydration cycles. The stability evaluation of our device with over 100 cycles has been presented in Fig. 1f, indicating the device is reliable. Extended characterizations of oxygen content and the O-group, including energy dispersive spectroscopy (EDS) and XPS analysis (Comparing with Fig. S1b), reveal that the O-groups are retained after 100 cycles (Fig. S4).

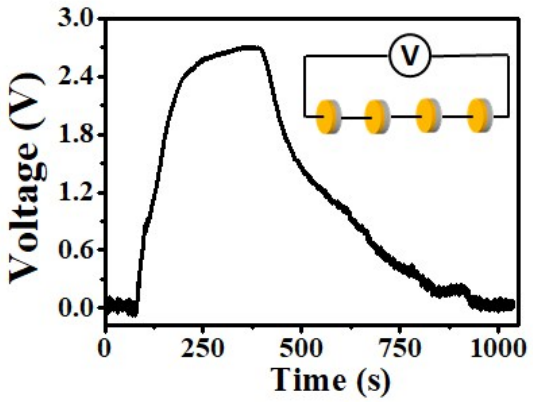


Fig. S5 The voltage outputs of four power-generating GO devices connected in series. Inset is the corresponding diagram of circuit connection.

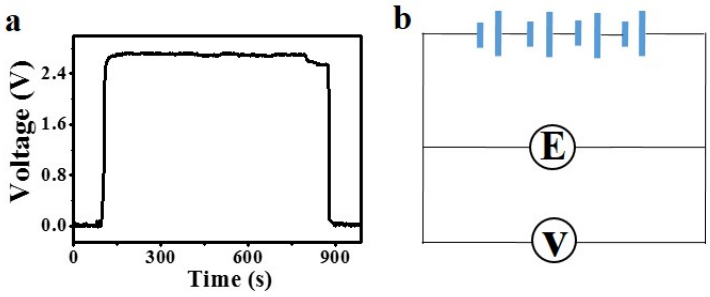


Fig. S6 (a) The voltage outputs of four devices connected in series. (b) Equivalent circuit diagram of the series circuit. "E" stands for electronic watch.

One cycle of energy output density can be calculated as follows. The voltage outputs of four devices (U_s) connected in series can be up to 2.7 V (Fig. S6a). The voltage and current output of the device unit are 0.7 V and 0.3 μA, respectively. The resistance calculation formula:

$R=U/I$

From this formula, the resistance of GO/MIS ($R_{GO/MIS}$) is 2.3 MΩ. It is known that the resistance of the electronic watch (R_E) is 16 MΩ. According to equivalent circuit diagram in Fig. S6a, the current of series circuit (I_s):

$I_s= U_s / (4R_{GO/MIS}+ R_E)$

The energy density calculation formula:

$E=UIt/C$

Where the U, I and t are voltage, current, discharge time, respectively. C could stand for area, volume or mass.

The energy density of this series circuit:

$E=UIt/C=28.4\ J/cm^3$

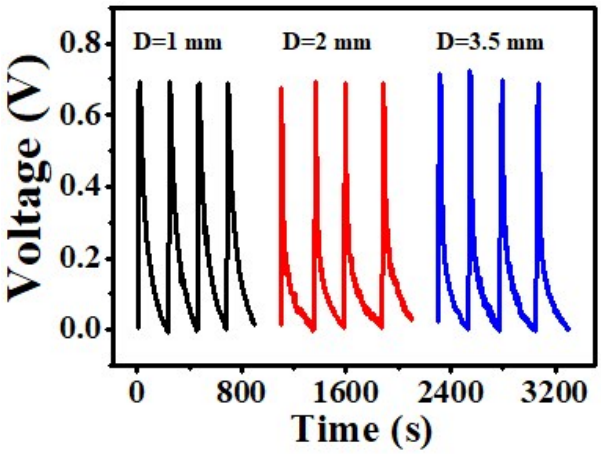


Fig. S7 The voltage responses of the GO/MIS samples with different diameters.

According to the experimental result from our previous works, larger are of GO film results in non-uniform hydration across the GO film. Nevertheless, the voltage outputs of GO/MIS cell with different sizes are almost identical. Indicating that the uniformity are not concerned any more due to advanced strategy demonstrated in our work.

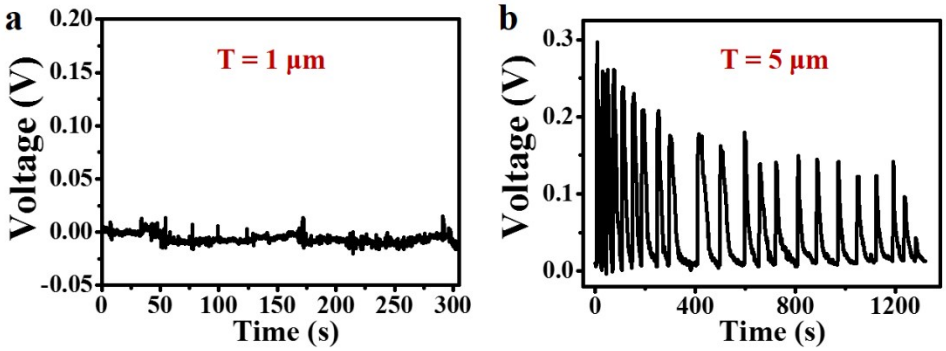


Fig. S8 The voltage responses of the GO/MIS samples with different thickness T = 1 μm (a), T = 5 μm (b).

As shown in Fig. S6, when the thickness of the film is 1 μm, there is no voltage output. With the increase of the thickness T = 5 μm, the induced voltage can be up to 0.3 V. However, the potential decays to 40 mV after 22 cycles. While the induced voltage can stably reach 0.72 V at the T = 10 μm (Fig. 1f). It can ascribed to the difference in water diffusion velocity crossing in different thicknesses of GO films.

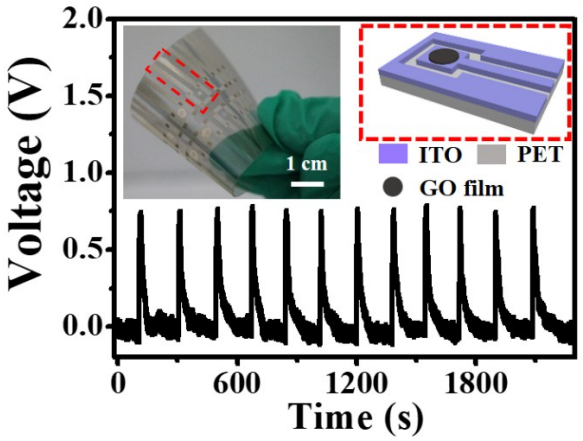


Fig. S9 The V_{oc} of GO integrated on ITO/PET. Inset is the photo of the device array and a scheme showing the single GO film on ITO/PET.

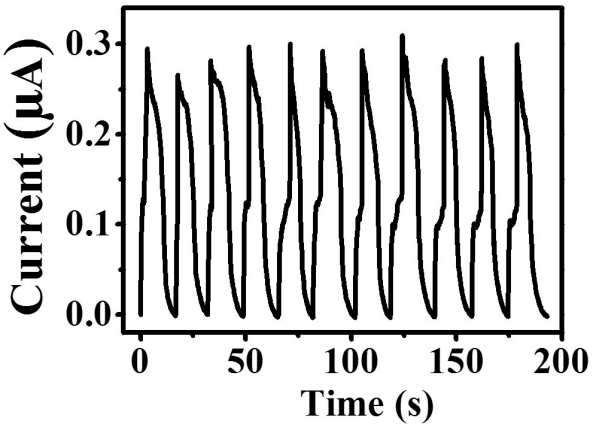


Fig. S10 Current output of GO/MIS cell.

Power generation based on moisturizing hygroscopic materials with asymmetric structure, such as graphene oxide (GO) with a gradient of oxygen-containing groups (O-groups), is first proposed by original structural and material design from our group. The previously reported power generations were mainly focused on the two strategies: (1) establishing gradient of O-groups in GO assemblies to enable moisturizing triggered charge separation and (2) retaining relatively large amount of O-groups to grantee the uniform hydration of GO. All the reports so far considered the moisturizing as an undiversified and homogeneous hydration process over GO assemblies (e.g. Ref. 12 and Ref. 14). Although such a prevalent point of view has been demonstrated by many subsequent research works on moisturizing of GO assemblies, (Ref. S3 and Ref. S4), the influence of gradual water molecular diffusion among the stacked GO nanosheets (in dense thin films) and corresponding inhomogeneous moisturizing of GO film is almost completely unknown. It is exactly our rational design concept of enabling GO-based double layer structure that can asymmetrically absorb moisture, while the O-group uniformly distributed in GO films. The proposed GO-based asymmetric structure opens a new strategy to generate electric power under humidity stimulus without any complicated

treatment (e.g. regulating O-group distribution by electrochemical treatment as shown in Ref. 12 and 14), hence significantly widen potential application scope of such moisturizing based power generation.

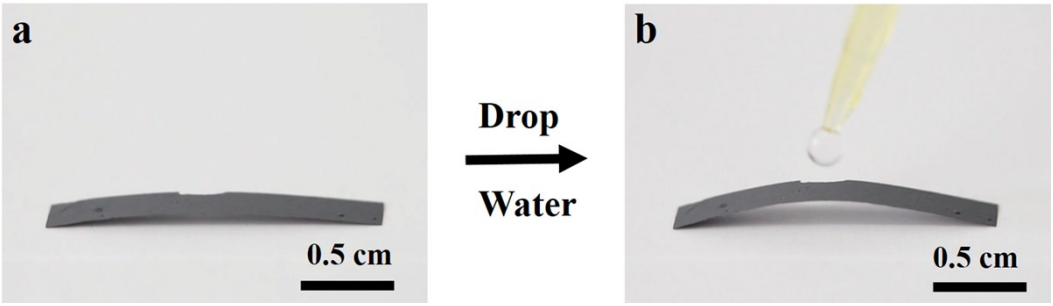


Fig. S11 The water vapor absorption process of GO film.

A moisture is located above the GO film. Due to the asymmetric humidity absorption of the two sides, the film has deformed.

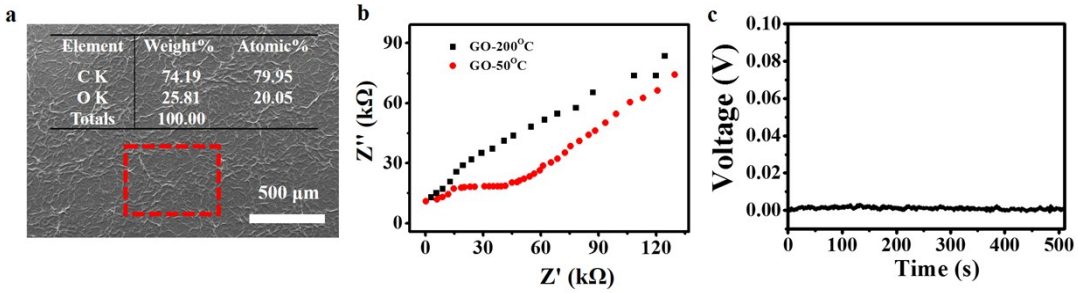


Fig. S12 (a) The carbon and oxygen content spectra of GO dried at 200 °C. (b) Impedance spectroscopies of GO at wet nitrogen (RH = 100%). (c) Voltage output of GO/MIS under ΔRH of 70% after GO dried at 200 °C.

The oxygen content and the kind of oxygen containing functional group on the graphene oxide are related to the output voltage. In the fabrication, GO was dried at 200 °C (GO-200 °C) and the oxygen content decreased to 25.8% (Fig. S12a). According to the impedance spectroscopies of GO, in wet nitrogen (RH = 100%) there is almost no ion to participate in conducting and ionic resistance is high with the increase of the preparing temperatures (Fig. S12b). The result indicates that the number of functional groups that can ionize ions are reduced and GO-200 °C has no voltage output (Fig. S12c).

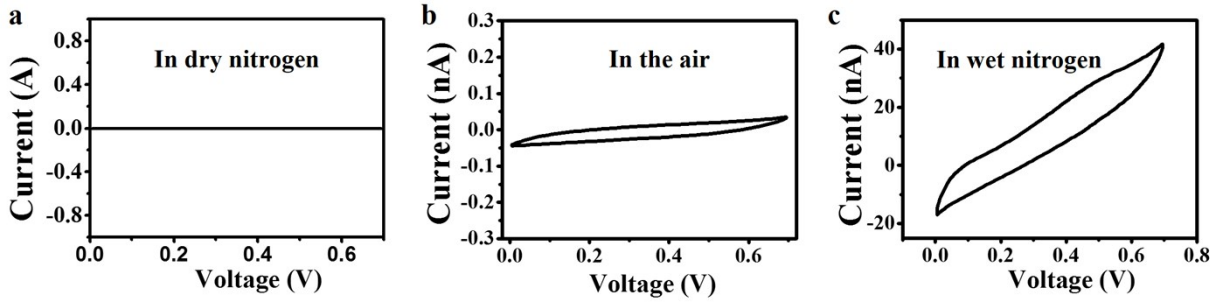


Fig. S13 CV of GO/MIS at (a) dry nitrogen (RH = 5%) (b) air (RH = 30%) (c) wet nitrogen (RH = 100%).

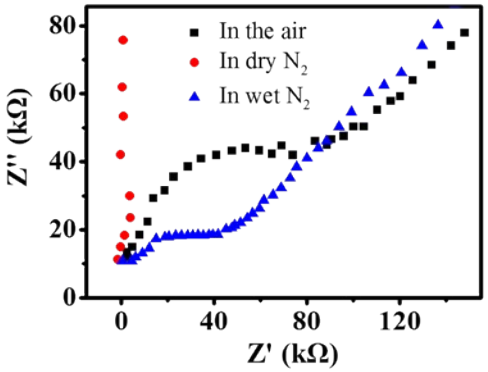


Fig. S14 Impedance spectroscopies of GO/MIS at dry nitrogen (RH = 5%), air (RH = 30%) and wet nitrogen (RH = 100%).

The cyclic voltagramms (CV) and impedance spectroscopies of GO/MIS are characterized respectively under dry nitrogen (RH = 5%), air (RH = 30%), wet nitrogen (RH = 100%) without any electrolytes. In dry nitrogen, the CV of GO/MIS shows a straight line, exhibiting resistance property (Fig. S13). In the air and wet nitrogen, the CV of GO/MIS present spindles, which means that free ions are ionized from the oxygen-containing functional group under the stimulation of water to participate in the electrochemical process. As the relative humidity gets larger the area gets bigger, which indicates that more ions are ionized from the functional group to participate in transport. According to the impedance spectroscopies of GO/MIS (Fig. 14), in dry nitrogen (almost no water) there is almost no ion to participate in conducting and ionic resistance is high. With the increasing of relative humidity (RH = 30%, RH = 100%), the depressed semicircles in the impedance spectroscopy decrease, indicating the ionic resistances reduce. These analysis results are helpful to understand the working mechanism of the generator GO/MIS. Under the stimulation of humidity, free ions are ionized from the oxygen-containing functional group and move directly for the different degrees of hydration from the exposed and the closed side of GO. The conclusion of the greater the humidity the more ions from the CV and impedance spectroscopies, is helpful to understand the experimental result that the voltage became higher with the increase RH in Figure 2i.

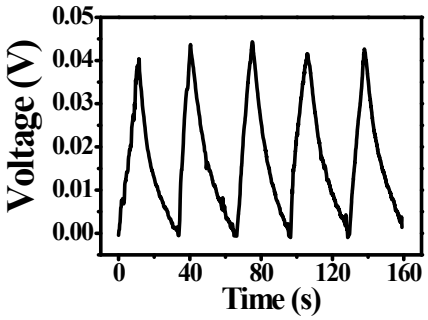


Fig. S15 The voltage outputs of GO foam at ΔRH of 70%.

When the graphene oxide film was characterized by BET to estimate its specific surface area, the nitrogen can hardly be absorbed in it, resulting from the stacked layer structure of GO film as shown in the Fig. 1d. There is no available signal from the BET test, indicating a low specific surface area of our GO film. In fact, such result further demonstrates the proposed mechanism. In GO-based assemblies, high specific area should be realized by porous micro-structure. However, such porous structure will somehow facilitate the diffusion of moisture in GO-based assemblies, reducing the asymmetry of moisturizing, and thus decrease the power output (Fig. S15). The densely stacked GO sheets in the film benefit to the power generation.

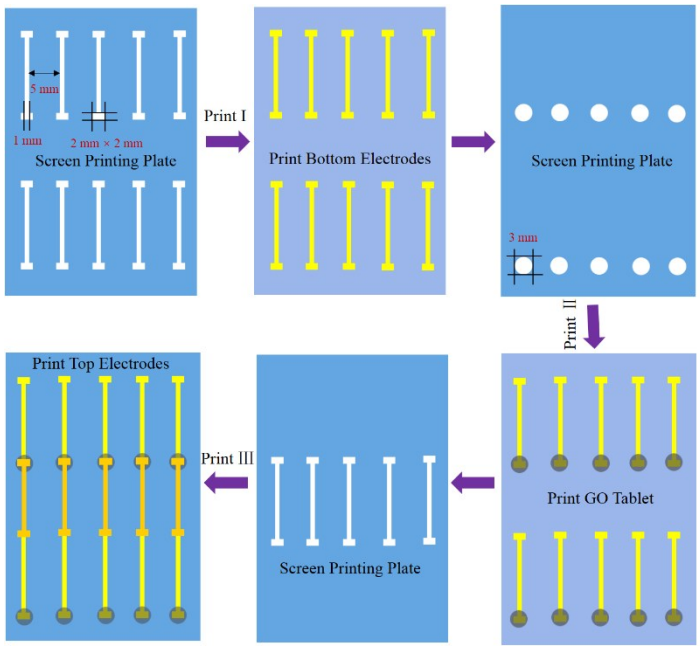


Fig. S16 Screen print process. Step 1: printing bottom electrodes. Step2: printing GO layers. Step 3: printing top electrodes.

References

S1. Y. Liang, Z. Wang, J. Huang, H. Cheng, F. Zhao, Y. Hu, L. Jiang and L. Qu, *J. Mater. Chem. A*, 2015, **3**, 2547.

S2. H. Cheng, F. Zhao, J. Xue, G. Shi, L. Jiang, L. Qu, *ACS Nano*, 2016, **10**, 9529.

S3. D. W. Boukhvalov, M. I. Katsnelson, and Y.-W. Son, *Nano Lett.*, 2013, **13**, 3930.

S4. S. Jiao and Z. Xu, *ACS Nano*, 2017, **11**, 11152.