

## Communication

## A self-powered sensor with super-hydrophobic nanostructure surfaces for synchronous detection and electricity generation

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## ABSTRACT

A new kind of self-powered sensor which can synchronously detect the salinity of water solution from 0 mmol/L to 1 mmol/L and generate electricity is developed. The power generation of this self-powered sensor is realized by repeatedly moving water droplets down from hydrophobic PDMS surface to generate negative charges on the surface of PDMS at first and change the capacitance between two electrodes to drive the screen charges (electrons) moving back and forth between two electrodes, subsequently. The ability for droplet to change the capacitance depends on its salinity. So the self-powered sensor can successfully detect the solution's salinity. Furthermore, both the distance between two electrodes and the thickness of PDMS film can influence the change quantity of capacitance when the water droplets are same, which benefits to the improvement of self-powered sensor's detection ability. Finally, the performance of this self-powered sensor can also be optimized by improving its current signal through modulating external load.

## 1. Introduction

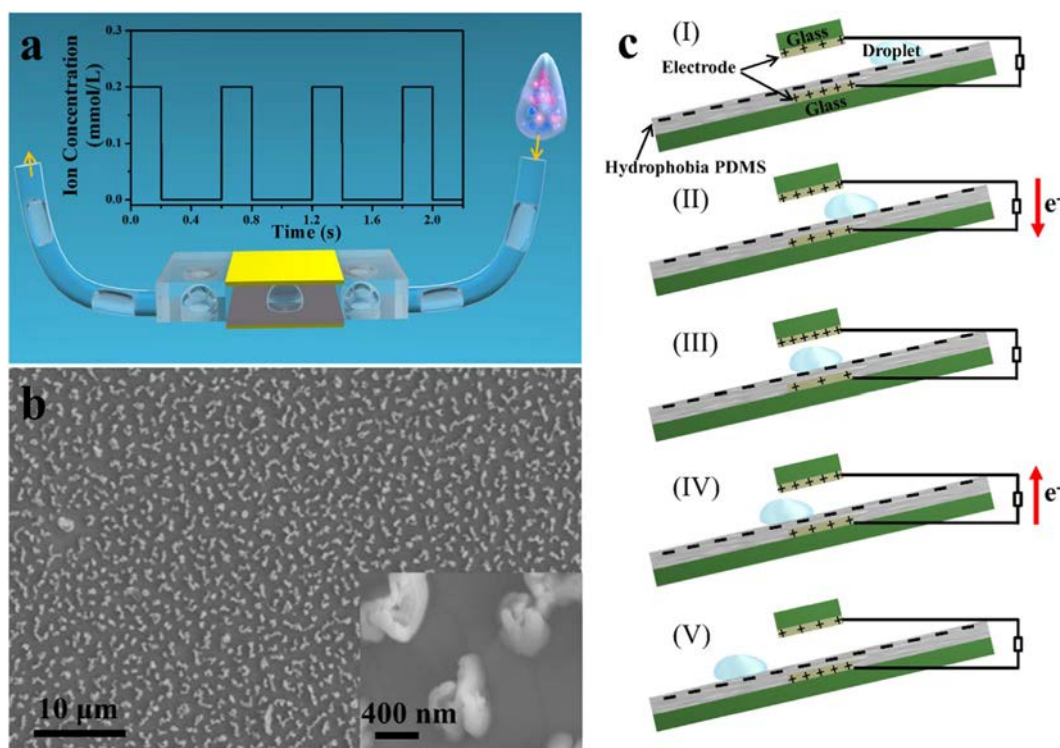
Sensors are widely used in the modern society and help us feel the world by gathering certain information of subjects. By integrating thousands or even more sensors into one network with information processing module, a more comprehensive analysis can be made since a greater variety of information can be gathered and analyzed at the same time. With the fast development of every kinds of sensors, they have paved the way for realizing the internet of things [1] and other sensing networks. But how to power these widely distributed and numerous sensors is still a great challenge. Powering them through cable is obvious impractical because of price and technical difficulty. So currently, in most cases, the numerous sensors are powered by batteries. However, on one hand, not only the life time of the sensor network is constrained by its battery [2], but also sensors of different type consume energy in different rates, which requires additional effort to match batteries and sensors for energy saving [3]. And replacing all these batteries for countless sensors requires huge effort. On the other hand, for the bio-sensors implanted *in vivo*, it is potentially harmful to put batteries inside the body since most batteries contains toxic ions like  $Pb^{2+}$ , the batteries' low capacity because of their small size for implanting greatly limits the sensor's working time [4], and it is hard to replace these batteries since it means another more surgeries. So, both the cable power supply and battery are difficult to satisfy the power

requirement of the widely dispersed and a large amount of sensors or implantable bio-sensors. It is a great challenge to explore a new way to power the sensors in the internet of things or other sensors network.

To conquer the challenge of power supply, self-powered nanosystem, which can harvest energy from the environment to power sensors, is proposed [5]. One way is applying solar cell to harvest solar energy in environment to power sensors [6]. Unfortunately, it has intrinsic limitations because there is no solar light in some environment such as forest and night. Fortunately, mechanical movements exist everywhere in the world, so researchers explored nanogenerators which can convert mechanical energy to electric energy to power the numerous sensors [7,8]. For example, Zhang et al. reported a self-powered glucose sensor by combining a triboelectric nanogenerator (TENG) with a glucose sensor [9]. Zheng et al. reported a self-powered UV sensor by combining TENG with a ZnO nanowire UV sensor. And by using ZnO nanowire, which is sensitive to UV light, as part of nanogenerator, it can be also used as self-powered sensors [10]. Zhang et al. reported a self-powered UV detector whose working mechanism is that the output of the piezoelectric nanogenerator (PENG) can be modulated by using UV light with different intensity [11]. Lin et al. designed Au nanoparticles as part of TENG and showed it can work as a self-powered mercury detector [12]. Actually, all the above self-powered sensors are the integration of power consuming sensor and energy harvesting module. They all need an external power

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**Fig. 1.** (a) Schematic of the self-powered sensor. (b) SEM image of hydrophobic PDMS film. Inset: the enlarged image of nano-pillars. (c) The flow direction and working mechanism of sensor after PDMS film fully charged. From top to bottom: (I) new droplet starts to move down; (II) droplet starts to move into sensor; (III) droplet fully moves into sensor; (IV) droplet starts to move out of sensor; (V) droplet completely moves out of sensor.

source like sun light or mechanical motion which are not stable, so they need to be combined with an energy storage module such as battery to give a stable power supply for sensors [6,9]. It would be simple and effective if the sensor can generate electricity by the sensing material during the sensing process to power itself. In this case, this new kind of self-powered sensor will simultaneously act as a sensor and a power generator, and its operation doesn't rely on the power generator and energy storage module. In that way, the intrinsic implication and application of self-power sensors will be expanded, which will greatly push forward the development of sensors' network and internet of things.

In this paper, we developed the above mentioned new kind of self-powered sensor with super-hydrophobic nanostructure surfaces. It can synchronously detect the salinity of water solution and generate electricity to reflect the salinity through water flowing. During its detection process, no external power module is needed. The self-powered sensor itself outputs the current and voltage related with salinity when water droplets roll down. With the increasing of the salinity of water from 0 to 1 mmol/L, the current signal decreases monotonously from 2.44 nA to 1.00 nA, and the voltage signal shows a similar tendency which decreases from 0.24 V to 0.092 V. The detect limitation is 0.04 mmol/L and the sensitivity is 0.34 per mmol/L.

## 2. Experimental methods

### 2.1. Fabrication of lower electrode with hydrophobic PDMS (lower part)

Firstly, the glass substrate was cleaned with acetone and deionized (DI) water for deposition. Then, a 1.3 cm×1.8 cm thin film of Cr and a thick film of Ag was deposited onto the substrate in sequence by magnetron sputtering method. The Ag film works as the lower electrode and the Cr film is used to enhance the adhesion between Ag film and glass substrate. After that, the mixture of PDMS monomer and curing agent with a volume ratio of 10:1 was spin coated onto the

Ag film and kept horizontal for one night to make PDMS further spread uniformly on the Ag film. Subsequently, the PDMS was cured in an oven at 80 °C. Finally, to obtain super-hydrophobic PDMS surface, it was put into the reactive ion etching (RIE) machine and etched for 80 min at room temperature, and then washed with hydrochloric acid and DI water. The detailed procedure can be found in our previous work [13].

### 2.2. Fabrication of upper electrode (upper part)

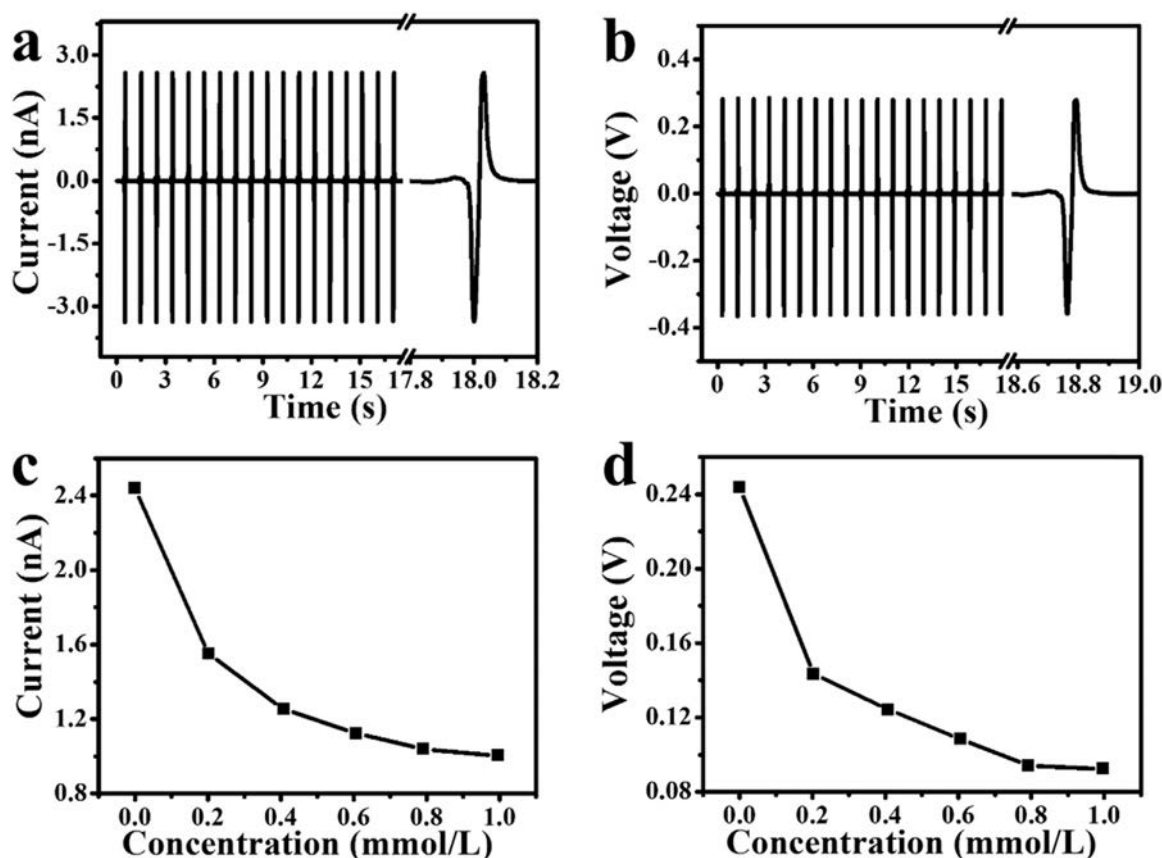
Firstly, the glass substrate was cleaned by the same procedure we used above. Then a thin film of Cr with 1.3 cm×1.8 cm was also deposited on the substrate. Then, the Pd film was deposited onto the same area as the upper electrode of the device.

### 2.3. Assembly of the self-powered sensor

The lower part and upper part were jointed together by a glass spacer. The two electrodes were carefully adjusted to be exactly overlapped. Then the device was put onto a homemade shelf to form an inclined self-powered sensor with super-hydrophobic surfaces for synchronous detection and electricity generation.

### 2.4. The output performance measurement of the self-powered sensor

For the characterization of the sensor, a separatory funnel was placed on the top of the device to generate a steady dropping of water droplet with a fixed frequency. In this way, each droplets generated from the funnel has a fixed volume and same speed when move through the sensor. And the whole experiment was carried out in a faraday cage to shield external noises. NaCl solution with different concentration is poured into the separatory funnel and is used as water source. Then, the separatory funnel began to generate a steady dropping of water droplet with a fixed frequency. The droplets moved into the sensor with same speed and volume. After signal is stable, the data was collected.



**Fig. 2.** (a) The generated pulse of the current output. After the break: one expanded pulse of current for further clear illustration. (b) The corresponding voltage output. After the break: one expanded pulse of voltage for further clear illustration. (c) The dependence of current peaks on NaCl concentration. (d) The dependence of voltage peaks on NaCl concentration.

And all the electrical data was collected by the SR560 and SR570 preamplifiers of Stanford Research Systems.

### 3. Results and discussion

The self-powered sensor's structure is schematically shown in Fig. 1a. This sensor has two parts with a certain distance between them. The lower part consists of an Ag electrode on glass covered by a hydrophobic PDMS film. This hydrophobic PDMS film is crucial for the sensor because it prohibit the water traces (surface wetting) on its surface. To make this sensor function properly, the size and shape of water droplets should be kept same since they all influence the output besides the salinity. By using the super-hydrophobic PDMS, the size and shape of water droplets would be same since no water traces affect the movement of water droplets. And, these water traces can speed the dissipation of tribo-induced surface charges of PDMS. After RIE treatment and acid wash, many micron size pillars are created on the PDMS film's surface as shown in Fig. 1b. These pillars are the key reason for the hydrophobicity of the PDMS. Using this method, a contact angle of  $154.6^\circ$  can be obtained. The upper part is a Pd thin film sputtered on a glass and used as the counter electrode. Two electrodes are carefully adjusted to be fully overlapped in the vertical direction to their surface. A variable spacer is used to adjust the distance between two electrodes. Finally, this sensor is kept tilted for a certain angle to create a slope for water rolling down.

The working mechanism of the self-powered sensor is shown in Fig. 1c. When the droplet rolls down from the hydrophobic channel, the friction between PDMS and water droplet can result in the separation of charges, leaving positive charges on droplet and negative charges on PDMS surface, as well as the positive screen charges on the surface of both electrodes. By letting droplets continuously move down from the hydrophobic surface, electrons from new droplet will also

transfer to the PDMS, resulting more negative charges accumulate on the surface of the PDMS, and thus more screen charges on electrodes. This process continues until the PDMS holds too many negative charges to prevent new electrons from transferring, leaving a nearly neutral water droplet to directly roll down. At this time, the self-powered sensor reaches an equilibrium state. And our sensor's detection function begins to work after this stage.

To generate power, the screen charges (electrons) on two electrodes are driven to move through external circuit. In a traditional TENG [14], the movement of a charged surfaces, like negative charged water droplets surfaces or positively charged metal surfaces push the screen charges moving through the external circuit to generate power. However, in our self-powered sensor, a nearly neutral water is designed to push the screen charges moving through external circuit by changing the capacitance between two electrodes. And its dielectric property would determine the magnitude of capacitance change. As shown in Fig. 1c(I), at the equilibrium state, i.e., the original state of detection, when a new droplet moves down on the PDMS channel, no more tribo-charge is generated because PDMS cannot hold more negative charges. Then, as shown in Fig. 1c(II), when this uncharged droplet moves into this sensor, the capacitance between the surface of PDMS and the upper electrode ( $C_1$ ) starts to increase due to the permittivity of the water is higher than that of the air. The capacitance between the surface of PDMS and the lower electrode ( $C_2$ ) remains unchanged in this process. Thus, the upper electrode possesses a lower electric potential than before and the electrons start to move to the lower electrode through external load to reach a new balance. And when the water droplet fully moves into this sensor (Fig. 1c(III)), the upper electrode possesses the lowest electric potential and the lower electrode obtains most electrons. Then, as the droplet begins to move out of the sensor (Fig. 1c(IV)), the electric potential of the upper electrode starts to decrease. As a result, the electrons flow back to the upper electrode

from the lower electrode through the external load. When the droplet fully gets out of the sensor (Fig. 1c(V)), the potential fully recovers to its original value. When a new droplet moves down, a new cycle begins. Since the ability of a droplet to change the capacitance  $C_1$  is basically due to its higher permittivity, the output current or voltage would change if the permittivity of the droplet changes with its composition. Droplet with higher permittivity can change the capacitance  $C_1$  more effectively and a higher output electrical signal is produced in this way. With the good monotone relationship between the output and the permittivity, the self-powered sensor can be used to detect the composition of droplet. Also, to detect the composition of droplet, the shape of the droplet should be kept same. And this is achieved by using a separatory funnel to generate a steady dropping of water droplet with a fixed frequency, so each droplet has a same volume which only based on the physical shape of separatory funnel. Also, the channel as well as the lower part of self-powered sensor should be hydrophobic to make sure the droplet can move down the channel freely with no water pinned on them.

To test the power generation ability of this self-powered-sensor, DI water droplets were first used to flow through the self-powered sensor. Fig. 2a and b shows the output short circuit current and open circuit voltage of this sensor during the flowing of water droplets. An expanded pulse is shown for both current and voltage. As shown in Fig. 2a, the short-circuit current firstly shows a negative output with peak value of 3.36 nA, corresponding to a current density of  $14.3 \mu\text{A}/\text{m}^2$ , followed by a positive output peak of 2.50 nA. As shown in Fig. 2b, the open-circuit voltage also firstly shows a negative output with peak value of 0.35 V, followed by a positive output peak of 0.28 V. According to the working mechanism of this self-powered sensor, the electrons first moves to the lower electrode when the droplet moves into the sensor, resulting negative current and voltage pulses. And when the droplet moves out of the sensor, the electrons move backward, in this process, the positive current and voltage pulses can be measured. Next, the self-powered sensor was used as a completely self-powered sensor to detect the concentration of NaCl solution without any external power module. Fig. 2c and d show the peak values of short circuit current and open circuit voltage of self-powered sensor when NaCl solution with different concentration flowing through it. The peak values of the voltage and current given in these figures are the statistical average value calculated from ten peaks in original data. The current begins with 2.44 nA when no NaCl is added. And then fast drops to 1.25 nA when the concentration is 0.41 mmol/L and finally slowly drops to 1.00 nA at 1 mmol/L. The output voltage also shows a similar downward trend with NaCl concentration which starts with 0.24 V and fast drops to 0.14 V and finally ends at 0.092 V. A detection limit of 0.04 mmol/L and sensitivity of 0.34/mmol/L are calculated when the concentrations range from 0.2 mmol/L to 0.8 mmol/L (Fig. S1).

As is confirmed by many studies [15–17], when NaCl concentration increases, the permittivity decreases. In this self-powered sensor, it would cause a lower change of capacitance  $C_1$ . As a result, the output electrical signal of the sensor decreases. The monotonous relation (Fig. 2c) between current and NaCl concentration and the monotonous relation (Fig. 2d) between voltage and NaCl concentration both show that this self-powered sensor can detect NaCl concentration from 0 mmol/L to 1 mmol/L without any power consumed.

To optimize the sensing ability of self-powered sensor, its structure should be rationally optimized. Since our self-powered-sensor is based on the competition of two capacitors (capacitance  $C_1$  and capacitance  $C_2$ ). Change the capacitance of two capacitors can modify the output of the self-powered sensor. A bigger capacitor can hold more charges while a smaller one holds less. When the capacitance of one capacitor increase, the screen charges should be redistributed. In this sense, the initial capacitance of both capacitors can effectively influence the current and voltage output of self-powered sensor.

Fig. 3a and b show the relationship of the short-circuit current peak value, calculated electric charge, open-circuit voltage peak value with the distance of two electrodes, respectively. The current, voltage and the charge quantity all show a similar decrease tendency when the height increases. The current peak is 2.97 nA, corresponding to a charge quantity of 0.06 nC when the distance starts at 7.04 mm. And the peak gradually decreases to 0.93 nA, corresponding to a charge quantity of 0.02 nC when the distance increases to 11.39 mm. The voltage also decreases from 0.32 V to 0.10 V. The reason for this behavior can be explained as follow. With a smaller height, the droplet can almost occupy the whole volume between two electrodes, resulting in an enormous change of  $C_1$ . And sufficient electrons can flow to the lower electrode due to a much higher electric potential difference. Thus, a larger output is generated. However, when the height increases, the droplet cannot fully fill the volume between two electrodes, leaving a larger gap of air between two electrodes. Thus, the change of  $C_1$  is much smaller than before. The larger the distance is, the smaller the changing becomes. At the same time, the distance between two electrodes should not be too small that the droplet would contact the upper electrode, otherwise the droplet would rub the upper electrode and cause the charge transfer. To sum up, to realize the best performance of self-powered sensor, the distance of two electrodes should be kept close enough yet leave enough space to let the droplet moves through the sensor. This is systematically studied through the following experiment.

The output current and voltage of self-powered sensor with different relative thickness PDMS film is shown in Fig. 4. The relative thickness is calculated by comparing the mass of the remaining PDMS with the coating area fixed. Since the coating area and the density of PDMS are the same, the mass of the remaining PDMS is proportional

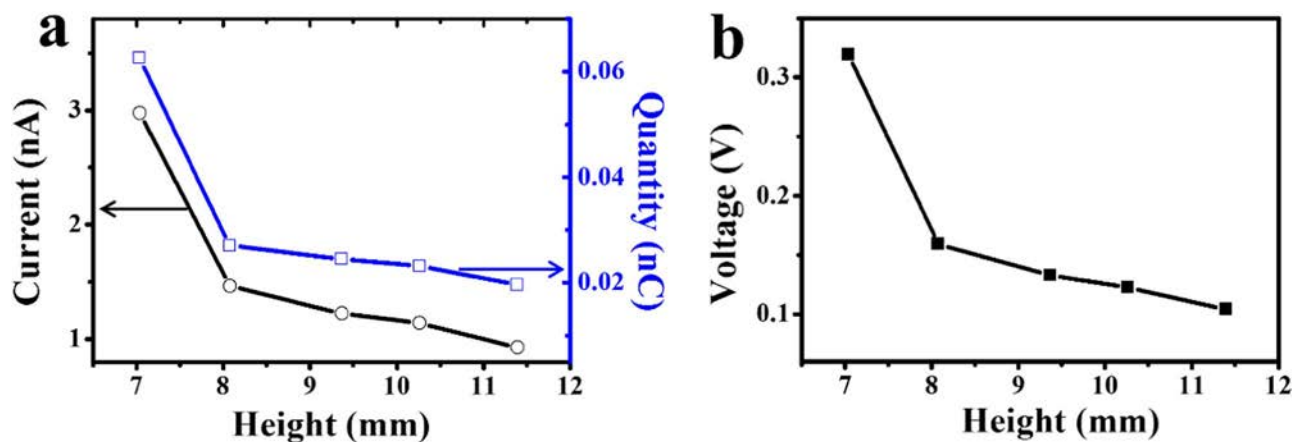


Fig. 3. (a) The influence of the output current peaks (indicated by the arrow pointing left) of sensor by the height between two electrodes, and the correspondingly calculated electric quantity (indicated by the arrow pointing right). (b) The corresponding output voltage.

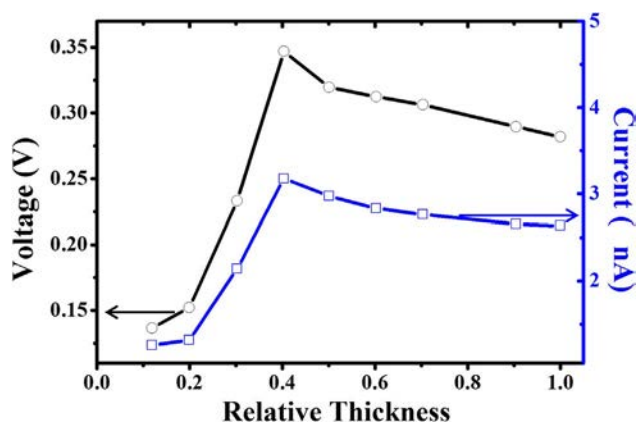


Fig. 4. The influence output voltage (indicated by the arrow pointing left) and current peaks (indicated by the arrow pointing right) of sensor by the relative thickness of the PDMS film.

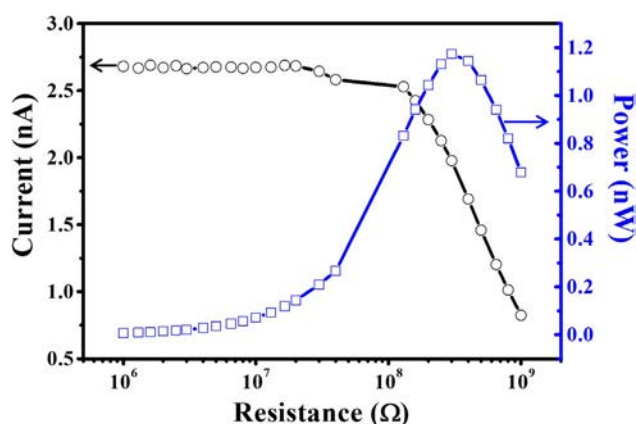


Fig. 5. Dependence of output current peaks (indicated by the arrow pointing left) and corresponding power peaks (indicated by the arrow pointing right) of sensor on the resistance of the external load.

to the thickness. The current peak value and voltage peak value both show an upward trend at first and then followed by mild decline. The maximum value of current and voltage is 3.18 nA and 0.35 V respectively, at a relative thickness of 0.4. This trend can be understood as follows. The capacitance  $C_2$  would be very large if the PDMS film is very thin. And when the droplet moves through sensor, the droplet-induced changing of the capacitance  $C_1$  is relatively too small to push the charges to flow through external load. And when the PDMS film is too thick, the capacitance  $C_2$  becomes very small. Thus, the capacitance  $C_1$  is dominant and the screen charges mostly locate at the upper electrode. When the droplet moves through the sensor, only few charges left at lower electrode are pushed to flow to the upper electrode to be rebalanced. This would also cause a smaller output of the sensor.

As a sensor that can generate power, it is crucial to know the optimal external load for its best performance. So the external load matching for the self-powered sensor is investigated. The current and voltage signal of this self-powered sensor can be simply tuned by external load. In this way, a desired output signal can be obtained just changing the external load. Fig. 5 shows the peak value of the output current and the corresponding output power at different external loads ranging from 1 MΩ to 1 GΩ. The black line stands for the current peaks and the blue line is the corresponding power. The current decreased slightly before the resistance reaches about 0.1 GΩ at first, then drops

sharply. However, the corresponding power increased at first when increasing the loaded resistance, and reaches a maximum value of 1.17 nW at 0.3 GΩ, corresponding to a power density of 5.0 mW/m<sup>2</sup>. Then, it starts to decrease and finally reaches at a value of 0.67 nW at 1 GΩ. This suggests that our sensor works most effectively around a load of 0.3 GΩ.

#### 4. Conclusion

In this paper, a self-powered sensor which can synchronously detect the salinity of water solution and generate electricity is developed. The output voltage and current decreased from 0.24 V and 2.44 nA to 0.092 V and 1.00 nA when increasing the salinity of water solution from 0 mmol/L to 1 mmol/L. With a good liner relationship between short-current change ratio  $((I-I_0)/I_0)$  and the concentration of NaCl ions ranging from 0.2 mmol/L to 0.8 mmol/L, a detection limit of 0.04 mmol/L and a sensitivity of 0.34/mm<sup>2</sup> are calculated. The working mechanism of this sensor is based on the movement of screen charges between two electrodes to generate power. Droplets with larger relate permittivity can push more screen charges move to the upper electrode, thus has a larger output. By changing the distance between two electrodes and the thickness of PDMS film,  $C_1$  and  $C_2$  could be tuned to match each other to achieve higher output. And an optimized current output of 3.36 nA is achieved when the external load's resistance reaches 0.3 GΩ. The concept of self-powered sensor shows that the detection can also be a power generating process, which may further be applied to other detection process.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.01.023.

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