Geometry Effect on Voltage Generation from Capillary Driven Water Evaporation in Carbon Black Film

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ABSTRACT

The utilization of spontaneous capillary driven water evaporation to generate electricity can be considered as a green and potential approach to the energy and pollution issues in very recent years. Various attempts have been made to harvest this green energy in the previous works, which is from the interactions between water molecules and solid materials of nano-structures. However, few literatures reported the capillary driven evaporation phenomena for the device design, especially the effect of geometry was not considered. Therefore, four porous carbon black films with different geometries are inhouse fabricated and tested in present work. It is found that the generated open-circuit voltages in different geometrical films are different accordingly. Through optimizing the geometry of the film, the generated voltage is increased by up to 200% in present experiment. It should be a promising way to improve the output performance of this kind of electricity generation devices. The principle behind this evaporation-induced electricity generation and the effect of geometry on volume flow inside the porous film are then revealed. The findings in this work can be used to guide the design of green evaporation-induced electricity generators.

Keywords: voltage generation, capillary driven evaporation, geometry effect, nano porous films

NOMENCLATURE

Abbreviations	
SEM	Scanning Electron Microscopy
EDL	Electric Double Layer
Symbols	
λ_D	Debye length
ε	permittivity of liquid
ε_0	permittivity of a vacuum
R	universal gas constant
Т	absolute temperature
n _{bulk}	concentration of solution

Ζ	valence number
F	Faraday's constant
V_s	streaming potential
ΔP	pressure difference
σ	conductivity of solution
ζ	zeta potential
η	viscosity of solution

1. INTRODUCTION

The development of social civilization and the progress of science and technology are fast in recent years. However, the consumption of energy has also shown an explosive growth, followed by an increasing environmental pollution. Nowadays, these two problems have been two serious global issues. Therefore, finding new green energy to replace the traditional fossil one is necessary [1]. Based on the recent research works, it is reported that converting the environmental energy into electrical one should be possible. Several new energyconversion techniques, such as piezoelectric [2, 3], thermoelectric [4, 5], and triboelectric ones [6, 7], have been proposed. However, these techniques normally require external energy inputs, such as mechanical energy or thermal energy, which cannot continuously provide output. Nowadays, a new energy harvest technique has been proposed, named as "hydrovoltaic effect" [8]. It is demonstrated that the electricity can be generated through the interaction between water molecules and nano materials, including fluid flowing [9, 10], droplet dropping [11, 12], and liquid evaporation [13-24]. Considering the spontaneity and ubiquity of water evaporation on the earth, it is valuable to harvest this energy dissipated to the environment, which occupies 75% of energy received from sun [25].

Zhou et al. [13] demonstrated that the evaporation on an ethanol carbon black film can output a continued open-circuit voltage of 1.0 V under ambient conditions, which was annealed and plasma-treated. The evaporation-driven water flow in the nano carbon pores

generates the electricity. However, the mechanical characteristic of this flame-deposited ethanol carbon black film should be improved. Zhou et al. [14] then continued their fabrication. Methylbenzene soot, ethyl cellulose and terpineol were mixed with ethanol, and a uniform carbon slurry was prepared after stirring and heating process, which was printed on Al₂O₃ substrate. A continued voltage of 1.0 V can also be generated with this robust all-printed porous carbon film. The glass fiber was added into the above slurry [15], and as a result, Zhou et al. achieved a self-supporting porous carbon film. As it needs no extra substrate, the water can evaporate from both sides of the carbon film at the same time, which obviously increase the output power density. To further improve the output capability, Zhou et al. [16] modified the zeta potential of carbon particles through adjusting the functional groups on the surface and fabricated a two-layer carbon film with opposite ion preferences, which can achieve an output of ~5 V.

In addition to carbon materials, there are many other materials can be used for electricity generation based on water evaporation, such as Ni-Al layered double hydroxide [17], porous graphene oxide sponge [18], silicon nanowire arrays (SiNWs) [19], microporous alumina [20], and even nature wood [21]. With freezedrying method, Yao et al. [18] used one porous graphene oxide sponge to convert surrounding environment energy to electricity through water evaporation. The obtained open-circuit voltage was at 0.63 V. The streaming potential was assumed to make this contribution. Sun et al. [19] found that an open-circuit voltage of ~400 mV can be generated via water evaporation in SiNWs. Considering the Debye screening effect and Coulomb interaction, they believed that the electron concentration gradient due to the internal flow was the mechanism behind the electricity generation. Kim et al. [22, 23] realized natural water evaporationinduced electricity generation through porous films of ZnO, MoS₂ and SiO₂, respectively. According to the theoretical analysis and experimental observation, they explained that the continuous ion-electron interactions at an electrolyte-nanoconduit interface is a key to the continuity of electricity generation, which was also verified through the analysis of ion specificity and concentration dependency in the device.

However, few literatures put focus on the capillary driven evaporation process. In addition to the environmental parameters (such as temperature, humidity, wind speed, etc.) affecting it, the geometry of the devices also has an influence on it, since the geometry has a direct impact on the size of the evaporation area, and more importantly, the liquid flow inside the devices. Guo et al. [24] fabricated an isosceles trapezoid-shape porous carbon film, and found that the geometry can have effect on the generated voltage due to the varied flow rates and capillary heights. Therefore, optimizing the geometry of the devices at the stage of fabrication is an efficient and simple way to improve the output power performance of the green evaporationinduced electricity generation devices. In this work, four carbon black films with different geometries are fabricated and tested. The influence due to the geometry on the capillary and evaporation process is studied, which should be a key factor to the electricity generation through spontaneous capillary driven water evaporation.

2. EXPERIMENTAL METHOD

The porous carbon black films are fabricated based on a printed method [14]. 2 g carbon black power is mixed with 4 g ethyl cellulose, 12 g terpineol and 150 mL ethanol. Then it is stirred with a magnetic stirrer at 70 °C. After 300 minutes, around 50 mL of carbon slurry with good uniformity and viscosity can be obtained. The preparation process is shown in Fig. 1 (a).



Fig. 1 (a) The preparation process of carbon slurry and (b) Photo of experimental samples

 Al_2O_3 ceramic sheets are used as the substrates, and are cleaned ultrasonically in acetone, ethanol and deionized water for 20 min each. After drying with nitrogen gas, several clean substrates can be provided.

Carbon nanotube ink is printed on the Al_2O_3 substrates as electrodes. Then, carbon slurry is printed on the substrates in the designed geometry, as shown in Fig. 2. The size of the substrate is 85 mm × 30 mm × 1mm. The width of both electrodes is 5 mm, and the distance between two electrodes is 65 mm. The positive electrode is on the top, and the bottom one is the negative electrode. The width of sample 1 # is 20 mm, and the width of sample 2 # is 10 mm. The geometry of sample 3 # is narrow at the top (10 mm) and wide at the bottom (20 mm), which is opposite to sample 4 #. The length of these two parts is the same, both are 32.5 mm. In addition, the printed slurry of each sample is extended up and down 10 mm in length, which is to overlap two electrodes.



Fig. 2 Schematic diagram of the dimension of experimental samples

The samples are annealed in the Muffle furnace at $350 \,^{\circ}$ C in air for 2.5 hours, then they are naturally cooled. Fig. 1 (b) is the photo of experimental samples. At last, these four samples are wired and the exposed electrodes are sealed with epoxy. The observation with scanning electron microscopy (SEM) is performed to analyze the morphology of the samples.

The samples are put into containers with an appropriate amount of deionized water, which can immerse the bottom electrode. And the samples are connected to a data acquisition system, which collects the value of open-circuit voltage of each sample and uploads it to a computer every 5 seconds.

3. RESULTS AND DISCUSSION

The SEM image (Fig. 3) shows that the porous carbon black film consists of nanoparticles is under a loosely

aggregated status, which form the micro and nano channels for water to flow through.

In previous studies [14, 18, 19, 21], the mechanism of the evaporation-induced electricity generation was discussed with the analytical and experimental methods. It is believed that as the deionized water contacts the carbon surface, an electric double layer (EDL) will be formed at the water-solid interface. Furthermore, if the radius of pore is smaller than the Debye length of deionized water, the EDLs will overlap. The overlapped EDLs will repel ions with the same electrical property as the surface of the solid materials, and only allow ions with the opposite electrical property to pass through the pore, thus forming one way nanochannel for ions [26]. Ions in the deionized water that are electrically opposite to the surface of the carbon film will accumulate in the direction of liquid flow, thereby generating a streaming potential [27].



Fig. 3 SEM image of the porous carbon black film

The Debye-Hückel formula can be adopted to determine the Debye length [28, 29]:

$$\lambda_D = \sqrt{\frac{\varepsilon \varepsilon_0 RT}{2n_{bulk} z^2 F^2}} \tag{1}$$

in which, λ_D is the Debye length, ε is the permittivity of water, ε_0 is the permittivity of a vacuum, R is the universal gas constant, T is the absolute temperature, n_{bulk} is the concentration of solution, z is the valence number and F is the Faraday's constant. According to this formula, the Debye length of deionized water is calculated to be about 900 nm.

As shown in Fig. 3, there exists the pores with radius less than 900 nm, which can generate the streaming potential.

Fig. 4 shows the electricity generation via spontaneous capillary driven water evaporation. The combined effect of capillary force and natural evaporation induces an upward water flow in the film, whose surface is negatively charged, thus the protons (H^+) and hydronium ions (H_3O^+) are carried uphill in the pores with a radius less than 900 nm. Finally, a higher potential is generated at the electrode on the top [14].



Fig. 4 Schematic diagram of the electricity generation via spontaneous capillary driven water evaporation in carbon black films

The generated open-circuit voltages are different in the experimental samples with different geometries, as shown in Fig. 5. However, the trends of this value over time are the same: rise-fall-rise and gradually tend to a stable value. The initial moment is as the bottom electrode is immersed by deionized water. The samples are kept at an inclination of 45°. Under the capillary effect, the deionized water flows upward through the pores in the film. Therefore, the generated voltage also increases to a maximum value rapidly. At this point, the capillary distance has reached the maximum value and the sample is saturated. After that, the capillary action becomes weaker, so the value of the generated voltage gradually decreases. Finally, as the evaporation and capillary gradually become balanced, the voltage also approaches a relatively stable value. After about 7500 seconds, the open-circuit voltage generated by sample 1 # - 3 # stabilized at around 25 mV, 30 mV, and 75 mV, respectively.

The streaming potential can be calculated as [30]:

$$V_S = \frac{\varepsilon}{\sigma \eta} \Delta P \zeta \tag{2}$$

in which, V_s is the streaming potential, ε is the permittivity of water, σ is the conductivity of solution, η is the viscosity of solution, ΔP is the pressure difference over the channel, ζ is the zeta potential, which is the potential at the plane of shear.





Here, only the pressure difference will have influence on the streaming potential, since all other parameters, such as the conductivity of solution, remain the same. And the pressure difference is related to the volume flow of the liquid [27]. Since the carbon black nanoparticles are uniformly distributed in the carbon slurry, and the slurry is evenly printed on the Al₂O₃ substrate, it can be assumed that the number and size of pores in the carbon black film are also uniformly distributed. So, the initial velocity of deionized water is the same at the inlet of all the samples. Under the same condition of the inlet velocity, the larger the crosssectional area, the larger the volume flow. Therefore, the initial volume flow in sample 1 # is larger than that in sample 2 #. However, the carbon black nanoparticles are interconnected, forming the channels in different directions. Since sample 1 # is wider than sample 2 #, the flow distance in sample 1 # is larger than that in sample 2 #, which causes a higher friction loss and a smaller flow velocity. The flow velocity decreases gradually with the height. Although sample 1 # has larger initial volume flow, the loss along the channel is also higher than that of sample 2 #. Therefore, it is hard to directly determine which volume flow of these two samples is larger. According to the experimental data, it can be shown that the open-circuit voltage generated by sample 2 # is slightly higher than that of sample 1 #, so it can be inferred that the volume flow of sample 2 # is larger.

The advantage of sample 1 # is the larger initial volume flow, while the advantage of sample 2 # is the less flow loss along the channel. Under such assumption, sample 3 # is fabricated, which integrates these two advantages. It is narrow at the top and wide at the bottom. One sudden-shrinked geometry is formed at the junction of these two sections. Although it may lead to a large loss, the velocity of the fluid also increases suddenly at the junction. Therefore, the volume flow in sample 3 # is the largest among sample 1 # to 3 #, and the generated open-circuit voltage in sample 3 # is about 3 times that of sample 1 # and 2.5 times that of sample 2 #. In other words, by optimizing the geometry of the sample, the generated voltage can be increased by 200% and 150%, respectively.



Fig. 6 Capillary height in sample 3 # and sample 4 #

In addition, sample 4 # is also fabricated, the geometry of which is opposite to sample 3 #. Therefore, the generated voltage is lowest. In present experiment, only a small part of the pores has a radius less than 900 nm in the carbon black film, and the samples have not undergone any surface modification treatment, so the value of the generated voltage should be very low. Furthermore, although all the exposed electrodes are sealed with epoxy, there still exists one unavoidable electrochemical reaction in present experiment, and the generated voltage is a slightly fluctuating negative value. Therefore, the collected value of open-circuit voltage will be smaller than the real value generated by the evaporation. In this experiment, these two generated voltages of sample 4 # offset each other. Therefore, the

experimentally measured value of voltage generated by sample 4 # is close to zero. It can further confirm the above inference. Fig. 6 shows the observed capillary height of sample 3 # and 4 #, and this also proves that the geometry has a great influence on the capillary driven evaporation process, which should be a key factor to the electricity generation via spontaneous water evaporation.

4. CONCULSION

In conclusion, the geometry has a great effect on the generated electricity through spontaneous capillary driven water evaporation. Samples with different geometry have different capillary height, evaporation area, fluid velocity and volume flow. Through the optimization of the geometry, the generated opencircuit voltage in sample 3 # is about 3 times that of sample 1 # and 2.5 times that of sample 2 #, respectively. Therefore, this work provides a promising way to enhance the output performance of the hydrovoltaic devices.

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REFERENCES

[1] Chu S, Majumdar A. Opportunities and challenges for a sustainable energy future. J Nature 2012;488(7411):294–303.

[2] Katsouras I, Asadi K, Li M, Van Driel TB, Kjaer KS, Zhao D, Lenz T, Gu Y, Blom PW, Damjanovic D, Nielsen MM, De Leeuw DM. The negative piezoelectric effect of the ferroelectric polymer poly (vinylidene fluoride). J Nature Materials 2016;15(1):78–84.

[3] Lee TI, Lee S, Lee E, Sohn S, Lee Y, Lee S, Moon G, Kim D, Kim YS, Myoung JM, Wang ZL. High-power density piezoelectric energy harvesting using radially strained ultrathin trigonal tellurium nanowire assembly. J Advanced Materials 2013;25(21):2920–2925.

[4] Harman TC, Taylor PJ, Walsh MP, LaForge BE. Quantum dot superlattice thermoelectric materials and devices. J Science 2002;297(5590):2229–2232.

[5] Boukai AI, Bunimovich Y, Tahir-Kheli J, Yu JK, Goddard 3rd WA, Heath JR. Silicon nanowires as efficient thermoelectric materials. J Nature 2008;451(7175):168–171.

[6] Fan FR, Tian ZQ, Wang ZL. Flexible triboelectric generator. J Nano Energy 2012;1(2):328–334.

[7] Wang J, Wu C, Dai Y, Zhao Z, Wang A, Zhang T, Wang ZL. Achieving ultrahigh triboelectric charge density for

efficient energy harvesting. J Nature Communications 2017;8(1):88.

[8] Zhang Z, Li X, Yin J, Xu Y, Fei W, Xue M, Wang Q, Zhou J, Guo W. Emerging hydrovoltaic technology. J Nature Nanotechnology 2018;13(12):1109–1119.

[9] Kral P, Shapiro M. Nanotube Electron Drag in Flowing Liquids. J Physical Review Letters 2001;86(1):131–134.

[10] Zhao Y, Song L, Deng K, Liu Z, Zhang Z, Yang Y, Wang C, Yang H, Jin A, Luo Q, Gu C, Xie S, and Sun L. Individual Water-Filled Single-Walled Carbon Nanotubes as Hydroelectric Power Converters. J Advanced Materials 2008;20(9):1772–1776.

[11] Yin J, Li X, Yu J, Zhang Z, Zhou J, Guo W. Generating electricity by moving a droplet of ionic liquid along graphene. J Nature Nanotechnology 2014;9(5):378–383.
[12] Yang S, Su Y, Xu Y, Wu Q, Zhang Y, Raschke MB, Ren M, Chen Y, Wang J, Guo W, Ron Shen Y, Tian C. Mashanism of Electric Dower Congration from Jonic

Mechanism of Electric Power Generation from Ionic Droplet Motion on Polymer Supported Graphene. J Journal of the American Chemical Society 2018; 140(42):13746–13752.

[13] Xue G, Xu Y, Ding T, Li J, Yin J, Fei W, Cao Y, Yu J, Yuan L, Gong L, Chen J, Deng S, Zhou J, Guo W. Waterevaporation-induced electricity with nanostructured carbon materials. J Nature Nanotechnology 2017;12(4):317–321.

[14] Ding T, Liu K, Li J, Xue G, Chen Q, Huang L, Hu B, Zhou J. All-Printed Porous Carbon Film for Electricity Generation from Evaporation-Driven Water Flow. J Advanced Functional Materials 2017;27(22):1700551.

[15] Ding T, Liu K, Zhou J, Xue G, Li J, Chen Q, Yang P. Evaporation induced electricity generation in freestanding and flexible carbon-based hybrid film. J Chinese Science Bulletin 2018;63(27):2846–2852.

[16] Li J, Liu K, Ding T, Yang P, Duan J, Zhou J. Surface functional modification boosts the output of an evaporation-driven water flow nanogenerator. J Nano Energy 2019;58:797–802.

[17] Sun JC, Li PD, Qu JY, Lu X, Xie YQ, Gao F, Li Y, Gang MF, Feng QJ, Liang HW, Xia XC, Li CR, Xu SC, Bian JM. Electricity generation from a Ni-Al layered double hydroxide-based flexible generator driven by natural water evaporation. J Nano Energy 2019;57:269–278.

[18] Zhang G, Duan Z, Qi X, Xu Y, Li L, Ma W, Zhang H, Liu C, Yao W. Harvesting environment energy from waterevaporation over free-standing graphene oxide sponges. J Carbon 2019;148:1–8.

[19] Qin Y, Wang Y, Sun X, Li Y, Xu H, Tan Y, Li Y, Song T, Sun B. Constant Electricity Generation in Nanostructured Silicon by Evaporation-Driven Water Flow. J Angewandte Chemie International Edition 2020;59(26):10619–10625. [20] Kaur M, Ishii S, Nozaki R, Nagao T. Hydropower generation by transpiration from microporous alumina. J Scientific Reports 2021;11(1):10954.

[21] Zhou X, Zhang W, Zhang C, Tan Y, Guo J, Sun Z, Deng X. Harvesting Electricity from Water Evaporation through Microchannels of Natural Wood. J ACS Applied Materials & Interfaces 2020;12(9):11232–11239.

[22] Yoon SG, Yang Y, Yoo J, Jin H, Lee WH, Park J, Kim YS. Natural Evaporation-Driven Ionovoltaic Electricity Generation. J ACS Applied Electronic Materials 2019; 1(9):746–1751.

[23] Yoon SG, Jin H, Lee WH, Han J, Cho YH, Kim YS. Evaporative electrical energy generation via diffusiondriven ion-electron-coupled transport in semiconducting nanoporous channel. J Nano Energy 2021;80:105522.

[24] Zhang S, Fang S, Li L, Guo W. Geometry effect on water-evaporation-induced voltage in porous carbon black film. J Science China Technological Sciences 2021;64(3):629–634.

[25] Stephens GL, Li J, Wild M, Clayson CA, Loeb N, Kato S, L'Ecuyer T, Stackhouse PW, Lebsock M, Andrews T. An update on Earth's energy balance in light of the latest global observations. J Nature Geoscience 2012;5(10):691–696.

[26] Koltonow AR, Huang JX. IONIC TRANSPORT Twodimensional nanofluidics. J Scinence 2016;351(6280):1395–1396.

[27] Van der Heyden FHJ, Bonthuis DJ, Stein D, Meyer C, Dekker C. Power Generation by Pressure-Driven Transport of Ions in Nanofluidic Channels. J Nano Letters 2007; 7(4):1022–1025.

[28] Gray CG, Stiles PJ. Nonlinear electrostatics: the Poisson–Boltzmann equation. J European Journal of Physics 2018;39(5):053002.

[29] Wolkenberg A, Przesławski T. Charge transport diagnosis by: I–V (resistivity), screening and Debye length, mean free path, Mott effect and Bohr radius in InAs, In_{0.53}Ga_{0.47}As and GaAs MBE epitaxial layers. J Applied Surface Science 2008;254(21):6736–6741.

[30] Olthuis W, Schippers B, Eijkel J, Van den Berg A. Energy from streaming current and potential. J Sensors and Actuators B: Chemical 2005;111-112:385–389.