Milliampere-level hydrovoltaic power generation through the asymmetric electric double layer of water-graphite interface

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Article

Keywords:

Posted Date: May 11th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2884520/v1

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Abstract

Hydrovoltaic technology is a promising approach for clean and renewable energy generation, owing to its unique ability to generate electricity from the interactions between nanomaterials and abundant water. However, the output current of hydroelectric generators needs improvement, which is usually below 1 mA. Here, we demonstrate a large-scale integration of water-graphite hydroelectric generators that can produce an output current of up to 58 mA, surpassing the performance of existing hydroelectric generators, and capable of powering commercial electronics, such as electric fans and full-color liquid crystal display screens. The high current is achieved by utilizing the asymmetric electric double layer formed at the water-graphite interface when immersed in water. Our results show that this low-cost and scalable hydroelectric generator has the potential to significantly expand the application domain and facilitate the development of clean and renewable energy sources.

Introduction

Water is not just an essential element for life, but it also serves as the largest energy carrier on our planet. With water covering 71% of the Earth's surface, it absorbs roughly 35% of the solar energy received by our planet, resulting in a staggering 60 petawatts ($10^{15}$W) of energy. Despite its tremendous energy potential, utilizing water energy remains a challenging task. While one can harness water energy through driving electromagnetic generators in water dams for clean electricity production, the heavy and complex facilities required to harness flowing water may limit their applications in small and flexible working conditions. The hydrovoltaic effect has opened up novel and readily applicable approaches for generating clean electricity by using nanomaterials that interact with a variety of water sources, including moisture, raindrops, waves, and evaporation. For instance, inserting a piece of graphene into ionic solutions can induce a waving potential of up to 0.1 V as a result of charge transfer driven by an electric double layer (EDL) at a moving boundary. However, the output voltage and current of hydroelectric generators (HEG) are typically insufficient for practical applications, particularly in terms of output current, which is usually below 1 mA. Remarkably, significant progress has been made in polyelectrolyte thin-film devices, which have demonstrated large-scale integration capabilities for high voltage outputs exceeding 1,000 V. However, high-current output has not yet been achieved because of challenges, including insufficient current output of individual HEG, difficulties in large-scale integration, and asynchronous response among HEG units.

In addition to the challenge of optimizing the output performance of HEG, there remain questions regarding the fabrication of HEG including the development of effective design strategies and the selection of suitable materials for electricity generation and electrode construction. Many efforts have been invested in creating a persistent water flow in moisture environment to drive the directional movement of ions, such as maintaining moisture gradients in protein wires from electrogenic bacteria or integrating moisture adsorption with water evaporation using desiccants. However, further investigation is required to determine the feasibility of fabricating HEG with a design strategy that
can spontaneously and continuously generate water flow and output electrical energy under constant environmental conditions. The extensive utilization of mixed electron-ion conductive materials, such as graphene oxide\textsuperscript{8,13,44}, in the fabrication of HEG presents a considerable challenge due to internal short circuiting, which is caused by the compensation and polarization of ions and electronic charges\textsuperscript{45}. In addition, the selection of electrode materials represents a notable obstacle in the fabrication of HEG. Expensive noble metals like gold and platinum are impractical for large-scale integration, while other metals such as copper, iron, aluminum, and zinc are prone to corrosion in the presence of water. Furthermore, it is essential to note that numerous hydroelectric materials, such as oxalic acid and polystyrene sulfonic acid, exhibit acidity, which significantly raises the risk of corrosion in metals when they are exposed to water (Supplementary Table 1). Carbon materials are a promising alternative due to their low cost, high conductivity, and stability. However, further investigation is required to better understand the inherently weak interaction between water and carbon at the liquid–solid interface, as it may have a significant impact on the electrical output.

Here, we report a high-current output water-graphite hydroelectric generator (WG-HEG) based on graphite foils prepared using a simple and scalable impregnation method. When immersed in water, a single WG-HEG unit with an area of 0.25 cm\textsuperscript{2} can produce an impressive voltage of 0.6 V and a current of 150 μA. This output is achieved due to the unique device configurations and conversion mechanism of the WG-HEG. The integration of WG-HEG units can be easily accomplished to offer a device with a current up to 58 mA, surpassing the performance of existing hydroelectric generators. Furthermore, the integration of WG-HEG is capable of powering commercial electronics, including electric fans and full-color liquid crystal displays (LCD) screens. Additionally, we find the underlying mechanism of electricity generation to be the asymmetric electric double layer at the water–graphite interface, as demonstrated by both comparative experiments and calculations of the plane wave density functional theory. Our results provide valuable insights for designing next-generation hydroelectric devices and facilitate the widespread applications of hydrovoltaic technology.

**Results**

**Fabrication and characterization of graphite materials.**

As depicted in Fig. 1a, a WG-HEG module was constructed by a P-type graphite foil and an N-type graphite foil, both of which were prepared using a straightforward and scalable impregnation method (see experimental section for details). Scanning electron microscopy (SEM) images indicate that the graphite foil, with a thickness of 50 μm, is composed of small graphite flakes (Supplementary Fig. 1, 2). The X-ray diffraction (XRD) pattern (Supplementary Fig. 3) reveals two prominent peaks, located at approximately 26.5° and 54.6°. These peaks correspond to the (002) and (004) planes, respectively, of the hexagonal graphite crystal structure, with the (002) peak is sharper and more intense than the (004) peak. The Seebeck coefficient is a measure of the voltage difference generated when a temperature gradient is applied, and its sign changes from negative to positive when the majority carrier switches from electrons to holes\textsuperscript{46}. The schematic of the Seebeck coefficient measurement setup is described in Supplementary...
Fig. 3a. Measurements were conducted using gold electrodes and in nitrogen atmospheres to prevent electrochemical reactions between the graphite foil and the electrode, and minimize the impact of moisture on Seebeck coefficient measurement. The Seebeck coefficient of P-type graphite is measured as positive at room temperature (290 K), approximately +7.8±0.3 μV/K, while pristine and N-type graphite exhibit negative values, around -2.9±0.6 μV/K and -5.9±0.4 μV/K, respectively (see Supplementary Figs. 4b and 5). This result indicates that adsorption-induced chemical doping is an effective approach for tailoring the electrical properties of graphite.

Electricity generation of a WG-HEG unit.

Figure 1b illustrates the step-by-step working principle of the WG-HEG, which can be attributed to the difference in the EDLs formed when the P-type and N-type graphite are in contact with water. When a WG-HEG device is immersed into water, a stronger EDL is formed on the P-type graphite, causing the electrons in the N-type graphite to be driven towards the P-type graphite through an external load. During this process, the electron flow continues until the EDLs on both the P-type and N-type graphite reach an equilibrium state (Fig. 1(ii)). Subsequently, the WG-HEG device is removed from the water and heated at 100°C for 5 minutes to remove transferred charges and residual water molecules on the graphite surface. The electric characteristics of the WG-HEG are measured at 25°C in tap water using a graphite sheet with a 0.25 cm² area and a 5 mm inter-electrode distance. The measured results of the open-circuit voltage and short-circuit current are displayed in Figure. 1c and d. It can be observed that a single WG-HEG unit can repeatedly generate a voltage of about 0.6 V and an impressive current of about 150 μA when immersed in and removed from water. Furthermore, the output voltage is measured with various load resistances, and the optimal output power of 23 μW (92 μWcm⁻²) is achieved at a resistance of 5.1 kΩ (Fig. 2a and Supplementary Fig. 6), which can be calculated using the formula P=V²/R_L, where P represents the power output, V represents the output voltage, and R_L represents the load resistance. In addition, the WG-HEG exerts stable performance after multiple immersions into water and even after being exposed to the ambient environment for 30 days, implying its outstanding stability in both operational and natural environments (Supplementary Fig. 7, 8).

The impact of graphite area, distance between two graphite foils, temperature, and water source on the performance of the WG-HEG were further investigated. The induced voltage exhibited slight variations with changes in all the tested parameters, whereas the output current showed significant changes (Fig. 2b-e). The variation in output current can be attributed to the influence of the tested parameters on the internal resistance of the device. Specifically, increasing the graphite area, reducing the distance between the graphite electrodes, raising the solution temperature, or using a 0.6M NaCl solution can effectively decrease the internal resistance of the device, resulting in a significant increase in output current. Impressively, the output current showed a linear increase with an increase in the graphite area, indicating the excellent scaling properties of the WG-HEG (Fig. 2b). In addition, The WG-HEG exhibits excellent performance even in 0.6M NaCl solution, which is similar to the average ocean salinity, and can be applied across a broad temperature range from 0 to 50°C. This wide temperature range and choice of solutions make it possible to utilize WG-HEGs in most regions of the earth.
Verification for electricity-generating mechanism.

The above-mentioned working mechanism was investigated using both comparative experiments and calculations based on the plane wave density functional theory. Firstly, the interfacial potential between water and the graphite surface was measured at 25°C using an Ag/AgCl reference electrode (Fig. 3a). The results showed that P-type graphite displayed a higher potential of approximately 340 mV, while N-type graphite exhibited a lower potential of around 200 mV relative to the Ag/AgCl reference electrode (Fig. 3b). We further observed a similar difference in P-type and N-type graphite treated with lithium chloride and sodium carbonate, suggesting the universality of this phenomenon (Supplementary Fig. 9, 10). Moreover, the higher zeta potential and smaller contact angle observed on P-type graphite indicate a stronger electric double layer formation at the interface between P-type graphite and water (Fig. 3c and Supplementary Fig. 11). These results reveal the formation of an asymmetric electric double layer at the water-graphite interface when P-type and N-type graphite are immersed in water.

The presence of a charged surface is a necessary condition for the formation of an electric double layer at the solid-liquid interface. The observation of similar induced voltages after removing possible pre-existing charges on the graphite surfaces by grounding or using an ionizing air blower rules out the possibility that these pre-existing charges were the source of the charged graphite surface (Supplementary Fig. 12). The dissolution of metal ions from the active metal electrode results in a negatively charged and low potential metal electrode (Supplementary Fig. 13). However, the mechanism underlying the formation of a charged graphite surface differs from that of the active metal electrode, owing to the stability of graphite in neutral water at ambient temperatures. Additionally, similar voltages were generated in dark environment (Supplementary Fig.14), providing evidence that the photovoltaic effect was not contributing to the charged graphite surface. Remarkably, it has been reported that when the atoms of a substrate like graphite come in contact with a polar solvent like water, the molecules constituting the polar solvent exert a finite electric field on the atoms of the substrate. The influence of solvent polarity on the performance of WG-HEG was investigated by employing solvents with varying polarities. As depicted in Figure 3(d), the voltage outputs generated by solvents such as water, dimethyl sulfoxide, ethylene glycol, dichloromethane, and hexane were approximately 564, 387, 262, 5, and 0 mV, respectively, and exhibited a positive correlation with solvent polarity. These results confirm that solvent polarity is a crucial factor affecting the electricity output of WG-HEG. To provide a further understanding of the observed experimental phenomena, density functional theory (DFT) simulations were conducted to investigate the interaction between graphene and a polar water molecule (see the details of the first principles calculations in Supporting Information). The simulation results indicate that the oxygen atoms in water molecules were found to be located closer to the P-type graphite surface due to the cumulative effects of Coulomb interactions and van der Waals forces. Additionally, the orientation of water molecules on the N-type graphite surface differed from that on the P-type graphite surface. Specifically, the hydrogen atoms in water molecules were observed to be situated closer to the N-type graphite surface (Fig. 3e).
Based on the analysis of contrasting experiments and simulations presented above, we propose a possible mechanism for the formation of the asymmetric electric double layer, as illustrated in Figure 3f. The arrangement of polar water molecules on the surface of pristine graphite induces positive charges on the graphite surface and attracts negative ions in the solution due to electrostatic interactions, resulting in the formation of an electric double layer. The arrangement of water molecules is strengthened and weakened on the surfaces of P-type and N-type graphite, respectively, resulting in corresponding changes to the electric double layer strength on these surfaces. While we propose a possible mechanism for the formation of the asymmetric electric double layer based on initial findings, the underlying mechanism still needs to be further understood in future studies due to the complex interactions between imperfect experimental materials. Specifically, the rough graphite surface could adsorb airborne hydrocarbons spontaneously when contact with air and ions are often present in solution, such as H\(^+\) and OH\(^-\) in water. Moreover, the interaction between water molecules, ions, and the surface of graphite involves not only simple adsorption and desorption phenomena but also possible charge transfer between water molecules and graphite.

**Applications of WG-HEG.**

The scalable integration of electric generators is crucial for increasing the energy output of devices. The utilization of inexpensive experimental materials and a simple fabrication process facilitates the large-scale connection of devices in either series or parallel, thereby increasing the output voltage or current. By connecting 20 units in series, the generated voltage can reach up to 7.3 V (Fig. 4a), and connecting 120 units in parallel results in a linearly boosted current output of about 58 mA (Fig. 4b), demonstrating the outstanding scaling properties of the WG-HEG. Notably, the integrated WG-HEGs have a favorable trade-off between output voltage and current, superior to previously reported integrated devices (Fig. 4c, Supplementary Table 1), indicating their potential as practical power sources. The electric power supplied by the WG-HEG can be stored in commercial capacitors without the need for extra rectifiers. Benefiting from the high current output of the integrated WG-HEG, capacitors with capacitances of 100, 470, and 1000 \(\mu\)F can be charged to 4, 3, and 2 V within 10 seconds, respectively, and maintain a fully charged state (Fig. 4d). To further demonstrate the practical applications of WG-HEGs, capacitors were charged by the WG-HEG integration to power commercial electronics such as an electric fan (Fig. 4e and Supplementary Video 1) and a full-color LCD screen (Fig. 4f and Supplementary Video 2).

**Discussion**

In summary, we have developed a WG-HEG based on a pair of P-type and N-type graphite foils prepared using a simple and scalable impregnation method. By exploiting the asymmetric electric double layer formed at the water-graphite interface, a single WG-HEG unit with an area of 0.25 cm\(^2\) can produce an impressive voltage of 0.6 V and a current of 150 \(\mu\)A. Furthermore, WG-HEG units can be rapidly integrated on a large scale and the high-current output of this integrated device approaches record-high current among similar devices reported to date. The electricity generated by WG-HEG is sufficient to power commercial electronics, such as electric fan and full-color LCD screen. With this level of performance, we
envisage that the unique WG-HEG provide valuable insights for designing next-generation hydroelectric devices and facilitate the widespread applications of hydrovoltaic technology for clean and sustainable energy production.

**Methods**

**Materials.**

Potassium carbonate ($\text{K}_2\text{CO}_3; 99\%$), Sodium carbonate anhydrous ($\text{Na}_2\text{CO}_3; 99.8\%$), Calcium chloride anhydrous ($\text{CaCl}_2; 96\%$) and Lithium chloride ($\text{LiCl}; 99\%$) were purchased from Aladdin (China). Graphite foil (99.99\%) was purchased from Hebei King Carbon Technology Co., Ltd. Ag/AgCl reference electrode filled with saturated KCl solution (218-type) were purchased from Leici Precision Scientific Instrument Co., Ltd.

**Preparation of P-type and N-type graphite foils.**

The P-type graphite was prepared by a straightforward impregnation method. Firstly, the commercial graphite foil was immersed into saturated $\text{CaCl}_2$ solution at room temperature for 12 h. The commercial graphite foil was then taken out and washed with copious DI-water to remove the excessive $\text{CaCl}_2$ on the surface of commercial graphite foil. Finally, the as-prepared graphite foil was dried in oven at 100°C for 12h to remove the residual water. To prepare the N-type graphite, the commercial graphite foil was immersed into saturated $\text{K}_2\text{CO}_3$ solution and prepared in the same impregnating and drying protocol as P-type graphite.

**Electric measurement.**

Electric measurements were performed using B2901A Precision Source/Measure Unit purchased from Keysight Technologies. In order to measure open-circuit voltage and short-circuit current, the voltage output test was set current into 0 nA and the current output test was set voltage into 0 mV, while the range of output and measurement was set to AUTO.

**Characterizations.**

The surface and cross-section morphology were measured by the Scanning Electron Microscope (SEM, JEOL, JSM-6330F). X-ray diffraction (XRD) was performed using a PANalytical Empyrean diffractometer using Cu Ka-radiation. X-ray photoelectron spectroscopy (XPS) was investigated using a Thermo Scientific K-Alpha XPS system. Water contact angles (WCAs) data were recorded using a contact angle measurement system (POWEREACH, JC2000D). The zeta potential measurements of graphite surfaces were conducted using the SurPASS™ 3 instrument manufactured by Anton Paar GmbH in Austria.

**Declarations**
Acknowledgements

This study was conducted under support from the National Natural Science Foundation of China (Grant NO.61704053, 62105098), the Changsha Municipal Natural Science Foundation (No. kq2014059), and Postgraduate Scientific Research Innovation Project of Hunan Province (QL20220102).

Author contributions

H.H. and D.H. designed the experiments and accomplished the original draft. W.N. gave advice on experiments. All authors discussed the results and reviewed the manuscript. H.H. supervised the entire project.

Competing interests

The authors declare no competing interests.

References


Figures

Figure 1

Schematic of electricity generation in the water-graphite-based hydroelectric generator. (a) Three-dimensional diagram of the device configuration of the WG-HEG. (b) Step-by-step illustration showing the working principle of the WG-HEG. Measurement results of (c) voltage generation and (d) current generation of the WG-HEG.
Figure 2

Electric output performance of the WG-HEG and the corresponding influence factors. (a) Output voltage and power of the WG-HEG under variable load resistances. Electric performance as a function of (b) the area of graphite foils and (c) the distance between two graphite foils. The electric output performance in response to different (d) temperature and (e) liquid water. The error bars in this work represent the standard deviation of the statistical means from multiple measurements (n is 5 or more).
Figure 3

Mechanism analysis of the WG-HEG. (a) Schematic illustration of the apparatus for measuring (b) the open-circuit voltage between different graphite foils electrode and an Ag/AgCl reference electrode at room temperature. (c) Output voltage of the WG-HEG under (d) solvents including water, dimethyl sulfoxide (DMSO), ethylene glycol (EG), dichloromethane and hexyl hydride. (e) The orientation of a water molecule adsorbed on suspended P-type graphene and N-type graphene (graphene cell doped by one hole or electron, respectively). (f) Schematic diagram illustrating the arrangement of polar water molecules on the surfaces of pristine graphite, P-type graphite, and N-type graphite.
Figure 4

Demonstration of the WG-HEG as a practical power source. (a) Plot of voltage output with incremental WG-HEG units in series. The inset is the serial circuit model. (b) Relationship between current output and parallel number of WG-HEG units. The inset is the parallel circuit model. (c) Systematic electric performance comparison of various integrated HEG devices including evaporation-induced, moisture-induced and liquid-induced electricity (Supplementary Table 1). (d) Voltage–time curves of commercial capacitors (100, 470 and 1000 μF) charged by an integrated WG-HEG device. (e) Photograph of driving an electric fan via four 1000 μF capacitors in parallel charged by an integrated WG-HEG device. (f) Schematic of the circuit design and photograph of the lighting up of a full-color LCD screen via two 1000 μF capacitors in series charged by an integrated WG-HEG device. The circuit primarily consists of three elements: commercial capacitors charged by the integrated WG-HEGs, a full-color LCD screen and a single-chip computer (Arduino ESP-32F) to input the display message.

Supplementary Files
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- Supplementaryvideo2.mp4