Sustainable generation of electricity using carbonized lignin/thermoplastic polyurethane composite films in water

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Harvesting energy from water/carbon interfaces represents an eco-friendly approach to addressing the global energy crisis. Unlike conventional nanogenerators utilizing carbon nanomaterials, which typically require integration into specific systems with external pumps for liquid flow, this study presents the fabrication of a novel water-driven energy generator (WEG) utilizing composite films that integrate carbonized lignin, with varying oxygen-containing groups, and thermoplastic polyurethane in an aqueous environment. Upon optimization, the WEG demonstrates remarkable performance, achieving stable output voltage and current of 210 mV and 1.04 μ A, respectively. The WEG's output voltage demonstrated remarkable stability and reproducibility during numerous cyclic bending tests. Furthermore, by simply connecting eight WEGs in series, an elevated voltage of 1.63 V can be achieved, and these scalable units have the capability to directly power commercial electronics, such as light-emitting diodes. This energy conversion technology may provide new insights into the design of WEGs capable of harvesting water energy.

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1. Introduction

Currently, the burgeoning field of clean and renewable energy has enormous potential to delay the depletion of fossil fuels and solve the urgent energy crisis. Given that water is one of the most abundant natural resources, water energy has garnered considerable attention over the past few decades. The collection and transformation of large water energy from natural resources have been extensively investigated [1,2]. Hydropower is a popular method for utilizing water resources; however, to achieve efficient operation, these facilities typically require enormous turbines, high-tech equipment, and specific locations with significant changes in the water level. Recently, the capacity of water-carbon interactions to unlock the potential energy harbored within water has garnered growing attention [3–6]. With the use of carbon nanomaterials, including graphene, carbon

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nanotubes, and carbon nanoparticles, several studies have attempted to convert water droplet energy, water wave energy, and water-moving energy into electrical energy [7–9]. This useful energy conversion method has a lot of potential for directly powering small electronic devices or creating self-powered systems.

Numerous studies have established the ability of water/carbon interfaces to convert water energy into electrical energy [10,11]. However, these water-carbon systems encounter two major hurdles. Firstly, the electricity generation process is intricate due to the necessity of an external pump to propel the liquid flow [12,13]. Secondly, the electrical output of these devices remains modest, with most previously reported voltage values falling within the millivolt or microvolt range [14–16]. Therefore, it is highly desirable to develop high-performance, simple, and more compact WEGs suitable for practical applications.

Here, building upon the aforementioned water-enabled power devices, we present a novel design for an enhanced electricity generator that harnesses the charge-transfer interaction at the water-carbon interfaces. It comprises two distinct composite films, crafted from thermoplastic polyurethane (TPU) and carbonized lignin (CL), separated by a spacer. TPU was selected as the matrix owing to its remarkable adaptability and flexibility, whereas CL, modified with various oxygen-containing groups, was incorporated into the generator to influence the arrangement of water molecules, thereby conferring local polarization properties. Upon submersion in water, the novel water-enabled electricity generator (WEG) exhibited a stable output voltage of 210 mV and a current of 1.04 μ A. The WEG demonstrated exceptional stability and reproducibility during numerous cyclic bending tests. In addition to water, the WEG is capable of generating electricity in NaCl solutions and other natural aquatic resources. Furthermore, the electrical output of the WEG can be increased by linking multiple generators in series. The materials and methodologies reported herein establish the foundation for the development of economically viable and adaptable WEGs that can harness water energy.

2. Materials and methods

2.1. Materials

Polyester-based thermoplastic polyurethane (TPU, Elastollan 1185 A) was supplied by BASF, while dimethylformamide (DMF, 99.5% AR) and *p*-toluenesulfonic acid (98.5% AR) were purchased from Aladdin. Enzymatic lignin was commercially obtained from Shandong Longli Biotechnology Co., Ltd. (China). Additional chemical reagents, including sodium chloride (NaCl), potassium hydroxide (KOH), and hydrochloric acid (HCl), were acquired from Shanghai Macklin Biochemical Technology Co., Ltd. (China).

2.2. Preparation of carbonized lignin with different oxygen-containing groups

Prior to carbonization, the enzymatic lignin underwent purification. The lignin was initially soaked in a *p*-toluenesulfonic acid solution and then heated to 50°C. Subsequently, 20 g of enzymatic lignin powder was added to the aforementioned *p*-toluenesulfonic acid solution. The resultant mixture was stirred at 50°C for 10 min (at a speed of 200-300 r min⁻¹) to guarantee complete dissolution of the lignin. Deionized water was then added to reduce the concentration of *p*-toluenesulfonic acid to 35%, followed by vacuum filtration to collect the filtrate and remove any

filter residue. An appropriate amount of water was added to the filtrate to adjust the concentration of *p*-toluenesulfonic acid to 10%, and the solution was allowed to stand until lignin precipitation occurred. After stratification, the upper liquid was filtered out, and the filter residue was collected. The filter residue was subsequently washed with deionized water until it was neutral and then dried in an oven at 105°C to complete the purification process. After being dried, the enzymatic lignin underwent carbonization in a tubular furnace (NHA5614, Nanbei Instruments Co. Ltd., China) at a temperature of 1000°C, with a heating rate of 5°C min⁻¹ under continuous nitrogen flow for 4 h. Once cooled to room temperature, the carbonized lignin was extracted from the furnace and subjected to ball-milling at 400 rpm for 6 h, yielding CL powder with a reduced oxygen content (denoted as CL_l). For the synthesis of carbonized lignin with enhanced oxygen content, a modified thermal protocol was implemented, wherein enzymatic lignin was heated to 400°C at the same heating rate of 5°C min⁻¹ under a nitrogen atmosphere, with a reduced dwell time of 1 h. Afterward, the sample was removed and cooled to room temperature. KOH activator was then added to a mortar in a 1:2 ratio, thoroughly ground and mixed, and subsequently heated to 800°C in a nitrogen atmosphere using the tubular furnace for 1 h. Following carbonization, the sample was again cooled to room temperature and reacted with excess hydrochloric acid until all KOH was removed. The sample was then washed with deionized water until the pH of the filtered liquid reached neutrality. Finally, the carbonized sample was dried in an oven at 105 °C for 24 h, removed, and then subjected to ball-milling at 400 rpm for 6 h to obtain CL powder with a higher oxygen content, denoted as CL_h .

2.3. Preparation of the TPU/CL composite film

Initially, a specific quantity of CL_l powder was introduced to 4.6 g of DMF solution and subjected to ultrasonic treatment (YM008-SP, Fangao Microelectronics Co. Ltd., China) for a duration of 30 min at room temperature. Subsequently, 400 mg of TPU were added to the solution and thoroughly stirred for 5 h. Following this, the mixed solution underwent additional ultrasonic treatment for 2 h and was finally stirred for 12 h to achieve a uniform suspension. Various TPU/CL_l mixtures with CL_l weight contents of 40%, 50%, and 60% were prepared and referred to as CL_l40 , CL_l50 , and CL_l60 , respectively. 0.5 mL of the final solution was placed into a 2 cm × 4 cm silica mold and placed in a chamber at 25°C and 80% RH overnight to obtain the cured composite film. Afterward, the composite film was soaked in 1 L of deionized water for 0.5 h to wash off the residual organic solvent and dried at room temperature. Similarly, TPU/CL_h films with CL_h weight contents of 40%, 500 mg of TPU powder were added to 25 mL of DMF and subjected to ultrasonic treatment for a duration of 2 h at room temperature, resulting in the obtainment of a separator solution. Then, a TPU-based separator was obtained via the same method as the TPU/CL composite film.

2.4. Fabrication of the WEG

The two distinct composite films, TPU/CL_l and TPU/CL_h , with dimensions of approximately 0.2 mm in thickness, 40 mm in length, and 20 mm in width, were assembled utilizing a TPU-based separator with dimensions of ~0.05 mm thickness, 40 mm length, and 20 mm width. A thin layer of DMF solution was coated between them to facilitate assembly. The separator served the purpose of preventing short circuits between the two films. Copper wires and conductive copper

paste were utilized to establish a connection between the two composite films. A Keithley 6514 system electrometer was used for all WEG output voltage and current measurements.

2.5. Characterization

A scanning electron microscope was used to study the films' surface morphology (SEM, PHENOM F16502). Utilizing X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Scientific, USA), the chemical composition of the sample surface was examined.

3. Results and discussion

3.1. Design and characterization of WEG

Figure 1a shows a schematic representation of the experimental setup and the WEG device. A simple casting technique that can manufacture films with different CL concentrations was used to create the TPU/CL composite films. The WEG device demonstrates significant elasticity (Fig.1b), allowing it to be bent to any angle. The SEM images of the hybrid material depicted in Fig.1c and 1d reveal that the composite film has a strong interconnectivity and an outstanding 3D porous structure. Its surface roughness is also enhanced by the heavy loading of CL particles. The XPS spectroscopy analysis was conducted to investigate the peak appearance and elemental composition of C and O in the carbonized lignin (Fig.1e and 1f). The results indicate that the peaks for C and O elements are centered at 532 eV and 284 eV, respectively, and the oxygen content in CL_h is 1.62 times higher than that in CL₁. Furthermore, a comparative analysis of the C 1s spectra for CL_h and CL_l was also performed, as shown in Fig.1g and 1h. There were found to be four main peaks with centers at 284.8 eV, 286.1 eV, 286.8 eV, and 288.7 eV, which represent C-C bonds, C-OH bonds, C-O-C bonds, and C=O bonds, respectively. [17]. Through peak area analysis, the percentages of C-OH bonds in CL_l and CL_h were determined to be 7.57% and 5.57%, respectively; the percentages of C-O-C bonds were 5.52% and 15.06%, respectively; and the percentages of C=O bonds were 13.14% and 8.89%, respectively. According to the results, CL_h that has been activated by KOH contains a greater percentage of C-O-C bonds than CL_l.





Fig. 1. (a) Diagrammatic representation of the experimental configuration used to determine the WEG's power generation. (b) Photographs of the curled WEG. Scanning electron microscope image of (c) CL_150 and (d) CL_h50 films. (e) XPS spectra and (f) percent oxygen atoms of CL_1 and CL_h . XPS spectra of C 1s of (g) CL_1 and (h) CL_h at high resolution.

3.2. The working mechanism of WEG

Although a single water molecule possesses a dipole moment, the water molecules are oriented randomly in their state of liquid, which causes the net charge to average zero. Nonetheless, this separation of positive and negative charges may make charge transfer easier if the water dipoles can be oriented in a certain direction at the surface of an electrode [18]. Studies have demonstrated that the interface binding energy between water molecules and high-oxygenated carbon materials is greater than that of low-oxygenated carbon materials in a polarized system [19]. Since these two kinds of materials interact differently with water in terms of charge transfer, it is expected that an electric current will flow between the two electrodes when they are joined by a water bridge. In this case, C-O-C bonds in the CL_h with a greater oxygen content react with water to generate C-OH on the anode, whereas C-C bonds in the CL_l with a lower oxygen content sare connected. The half-reaction equations for these processes are as follows:

On the water/CL_h surface, this half-reaction occurs:

$$CL_h + H_2O + e^- = CL_h - OH + OH^-_{(ac)}$$
(1)

And for water/ CL_l surface, the half-reaction is:

$$CL_l + OH^-_{(aq)} = CL_l - OH + e^-$$
(2)

In order to better understand the mechanics behind the recovery phenomena, we examined how the atomic structure of TPU/CL films changed after an electrical discharge. The discharge procedure involved connecting CL_{150} to the negative electrode and CL_{150} to the positive electrode of a voltmeter, utilizing an external resistor for continuous discharge. Prior to and following discharge, the carbon (C) and oxygen (O) atomic structures of CL_{150} and CL_{150} were measured using XPS. Their C 1s and O 1s spectra were subsequently observed and examined. Figure 2 (a) illustrates the carbon and oxygen functional groups of $CL_{1}50$ prior to and following discharge. Hydroxyl groups (C-OH), C-C bonds, carboxylates (-COOH), and cyanate functional groups (O=C-N) were represented by the peaks in the C1s spectra at 286.5 eV, 284.8 eV, 287.8 eV, and 289.0 eV, respectively; within this range of 286-291 eV, peaks attributed to polyurethane were also identified. Post-discharge analysis revealed a significant increase in the C-OH peak intensity for CL₁50, accompanied by the emergence of a new -COOH peak; conversely, there was a decrease in peak height for C-C bonds due to oxidation processes leading to the formation of C-OH and COOH functionalities. Furthermore, in the O 1s spectra obtained from CL₁50 after discharge, a notable enhancement in intensity at the characteristic peak associated with C-O bonds confirmed that oxidation had occurred post-discharge.

Figure 2 (b) displays the spectra of C1s and O1s for CL_h50 before and after discharge. Upon discharge of CL_h50 , the C1s spectrum reveals a more prominent -COOH peak, which was originally weak, and a significant increase in the characteristic C-OH peak. Meanwhile, the characteristic peak of the C-O-C bond of CL_h50 almost disappears, indicating its involvement in a chemical reaction during the discharge process leading to the formation of C-OH. Additionally, the occurrence of the chemical reaction is further confirmed by the increase in the C-O peak in the O 1s spectra of CL_h50 , as shown in Figure 2(b). XPS investigations have shown that polarization-induced dissociation

effects of water molecules generate electrical output and have validated the formation of C-OH on both CL_150 and CL_150 surfaces.



Fig. 2. XPS C1s and O1s spectra of (a) $CL_{1}50$ and (b) $CL_{h}50$ prior to and following discharge.

3.3. Output performance of WEG

The open-circuit voltage of WEGs with varying CL contents was examined in order to assess the electrical output performance. As shown in Figure 3a, minimal voltage generation was observed when WEGs were fabricated using two identical CL₁50 or CL_h50 films. However, a significant opencircuit voltage of 210 mV was generated when the WEG was constructed with two distinct composite films (CL₁50/CL_h50). Figure 3b highlights that the CL content is a crucial factor influencing the generator's performance. When the CL content reached 50%, the output current reached its maximum value of 1.04 μ A. Under the same experimental conditions, further studies were conducted by maintaining one film as either CL₁50 or CL_h50 and varying the proportion of carbonized lignin in the opposing film. Figure 3c illustrates that the output voltage and current for CL₁50/CL_h40 were approximately 20 mV and 0.14 μ A, respectively, while those for CL₁50/CL_h60 were around 30 mV and 0.37 μ A, respectively, both lower than those of CL₁50/CL_h50. Similarly, CL_h50/CL_i40 and CL_h50/CL_i60 had comparatively low output voltage and current, as shown in Figure 3d. This demonstrates that variations in the CL content within the two films directly impact the electrical output performance.



Fig. 3. (a) Output voltage of the composite films. (b) Dependence of voltage and current on the CL₁/CL₁ type and CL₁/CL_h type WEGs. (c) Output voltage and current of CL₁50 paired with CL_h40, CL_h50, and CL_h60, respectively, and (d) output voltage and current of CL_h50 paired with CL₁40, CL₁50, and CL_h60, respectively.

To evaluate the performance of the WEG under varying conditions, a WEG with $CL_{l}50/CL_{h}50$ films in deionized water was investigated, with an immersion depth fixed at 4 cm during measurements, unless otherwise specified. As the temperature increased, the open-circuit voltage of the generator decreased significantly (Fig. 4a). This may be attributed to the thermoelectric effect occurring between the copper electrode on the films' surface and the carbonized lignin material [20], resulting in a thermoelectric potential opposite to the polarization effect of water. When the water temperature reached 55 °C, the output voltage hit its lowest point, at -135 mV. Additionally, the effect of pH was examined. The greatest response was observed at a pH of 7, while reduced voltage production was observed in acidic and alkaline circumstances (Fig. 4b). The change in output voltage is primarily due to the ionized H⁺ in water neutralizing OH⁻ and preventing charge transfer under acidic conditions, and excess OH⁻ in the solution inhibiting the nucleophilic reaction of the C-O-C bond of CL_h with water and impeding the formation of the current circuit under alkaline conditions.



Fig. 4. (a) Output performance of WEG in deionized water at different temperatures. Three separate experiments provided the error bars. (b) Variation of voltage with pH. (c) Open-circuit voltage of WEG in NaCl solutions with various concentrations. (d) Output voltage and current dependence on the depth of immersion.

To explore the applicability of WEG in salt solutions, the output voltage of WEG was measured in NaCl solutions with concentrations ranging from 0 to 0.4 mol L⁻¹. As shown in Figure 4c, the output voltage gradually increased with an increase in NaCl concentration. At 0.1 mol L⁻¹, the voltage was approximately 282 mV, and it rose to 357 mV at 0.4 mol L⁻¹. The experimental results demonstrate that increasing the NaCl concentration enhances the output voltage. This is because the directional charge movement between the positive and negative electrodes creates an electric field effect on NaCl, and Na⁺ and Cl⁻ are also polarized, leading to directional charge transfer, which synergistically enhances the output electrical properties. Furthermore, the submerged area plays a crucial role in influencing the performance of the WEG. As the submerged depth increases, the output current rises but the output voltage remains relatively constant, as shown in Figure 4d. This indicates that the current is positively correlated with the number of active sites provided by the composite films' surface.

3.4. Application of WEG

Cyclic tests, including repetitive bending at a 7 mm radius, were used to examine the WEG's resistance to bending. As shown in Fig. 5a, the generator's mechanical and electrical dependability is outstanding, as seen by the current varying just 4% over 100 cycles. Figure 5b presents the output performance of WEG from various water sources. It is noteworthy that energy conversion from seawater surpasses that from suspensions with lower ion concentrations.



Fig. 5. (a) Output voltage following a predetermined number of bends. (b) Comparison of various water environments' output voltage and current. (c) The output voltage generated by WEGs connected in series.
(d) Eight WEGs connected in sequence illuminated a single commercial green LED.

Enhanced polarization and directed charge transfer of salt ions, which produce a larger electrical output, are the main causes of this phenomenon. Theoretically, the output electricity generated by the WEG device could be significantly increased through series connections. When three WEG devices were linked in series, the corresponding output voltage increased to 0.61 V, as shown in Figure 5c. Eight WEGs connected in series in a typical application scenario produced an output voltage of 1.63 V (Fig. 5d), which was enough to power devices that emit green light. This shows that WEGs have a great deal of potential as a practical energy source for small electronic devices.

4. Conclusions

On the basis of differentially oxidized carbonized lignin, we have created a novel waterenabled energy generator. A systematic investigation was conducted into the relationship between the WEG's output performance and the water's temperature, pH, NaCl concentration, and CL content. When the $CL_{l}50/CL_{h}50$ WEG is operating at optimal conditions, it may produce voltage and current of up to 210 mV and 1.04 μ A, respectively. In addition, WEG's output voltage demonstrates outstanding stability and repeatability throughout a range of bending cycle tests. Along with deionized water, the WEG may generate electricity from a variety of other water resources. By connecting the generators in series, the electricity generated by the WEG can be multiplied. This WEG shows the potential of carbonized lignin as a cutting-edge material for energy applications and shows promise for capturing energy from water.

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