

Chemical-to-Electricity Carbon: Water Device

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The ability to release, as electrical energy, potential energy stored at the water:carbon interface is attractive, since water is abundant and available. However, many previous reports of such energy converters rely on either flowing water or specially designed ionic aqueous solutions. These requirements restrict practical application, particularly in environments with quiescent water. Here, a carbon-based chemical-to-electricity device that transfers the chemical energy to electrical form when coming into contact with quiescent deionized water is reported. The device is built using carbon nanotube yarns, oxygen content of which is modulated using oxygen plasma-treatment. When immersed in water, the device discharges electricity with a power density that exceeds 700 mW m^{-2} , one order of magnitude higher than the best previously published result. X-ray absorption and density functional theory studies support a mechanism of operation that relies on the polarization of sp^2 hybridized carbon atoms. The devices are incorporated into a flexible fabric for powering personal electronic devices.

Converting potential energy stored at the water:material interface to electrical energy has become more and more important since water is abundant and widely available.^[1–3] Recently it has been shown that the interaction between nanomaterials (such as carbon nanotubes (CNTs) or graphene) and liquids (such as water, acid solution or salt solution) can convert mechanical energy into electrical form. This enables the development of lightweight, portable, and cost-effective power sources using carbon materials and water sources.^[4–6] Researchers have observed that liquid flowing through single-walled CNTs induces electric current and voltage.^[7] The phenomenon was

explained by the movement of the free charge carriers in the CNTs, which is appealing but resulted in an output voltage of only a few millivolts. Since then, various experiments have been designed to harvest energy from nanomaterials under liquid flow. Several mechanisms have also been proposed: for example, electricity generated by liquids driven along the surface of nanomaterials has been explained by the fluidic-electric effect,^[8–10] while ionic solution flowing along graphene has been attributed to the electrokinetic phenomenon.^[11,12]

Graphene oxide and porous carbon exposed to moisture have been shown to lead to electricity via the proton-transfer effect,^[13,14] but these technologies were applied under water vapor which limited their range of application. Furthermore, surface charging is shown to occur when

water travels past polymer nanowires.^[15] However, the output of these water-based devices has not yet been improved to meet the real applications.

In summary, previously reported approaches required either carefully tuned concentrations of ionic aqueous solutions, or water to flow and interact with the nanomaterials in order to be functional.^[16]

Reliance on such requirements limits electricity production from water sources widely available in nature, including remote settings and daily life. Technology that can utilize a wide range of water sources with improved output can greatly expand the

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scope and portability of water-based electricity devices. Here, we report a carbon-based chemical-to-electricity device that transfers the chemical energy to electrical form when coming into contact with quiescent deionized water. When immersed in water, the device discharges electricity with a power density that exceeds 700 mW m^{-2} , one order of magnitude higher than the best previously published result.

We first pursued the design of a system in which electrical power would be produced by the discharge of chemical energy in the nanotube yarn when it becomes in contact with still, pure water. We chose CNTs as a model material because sp^2 hybridized carbon systems such as CNTs and graphene are common electrode materials used in electricity generation. A single water molecule has a dipole moment, but in liquid form the water molecules are randomly aligned, so the averaged bulk charge is electroneutral. However, if the water dipole can be directionally aligned at the surface of an electrode, positive and negative charges may be separated, potentially leading to charge transfer. Because oxygen modulated sp^2 hybridized carbon systems show strong polarization, which can affect the alignment of water molecules, we proposed that oxygen-induced-polarization electrodes could enable charge transfer with an arbitrary water source (irrespective of its pH or ionicity, flowing or still).

We began with computational studies to investigate the charge-transfer interaction between water molecules and CNTs with local-polarization properties. Here, we assumed that the radii of the CNTs are large enough such that the curvature will not substantially affect the adsorption properties of the sp^2 network; thus, we simplified the computational studies by unrolling the CNTs into graphene sheets. Our density functional theory (DFT) calculations examined the average charge transfer between water and pristine CNT (PCNT), and between water and oxygen-modulated CNT (OCNT). On average 0.005 and 0.280 electrons were transferred from a single water molecule to pristine and oxygen-modulated materials, respectively, as determined by Bader charge analysis.^[17] 3D plots that allow us to visualize charge transfer (Figure 1a) reveal that stronger charge transfer between water and oxygen-modulated materials arises from the interaction between the charge-polarized oxygen-modulated surface and polar water molecules. The higher binding energy for water molecules (0.772 eV) on oxygen-modulated material compared to pristine (0.129 eV) material suggests stronger interaction in the polarized system. Due to the different charge-transfer interactions between these two classes of materials with water, electric current is expected to flow between the two electrodes once they are connected by a water bridge. This suggests that a system

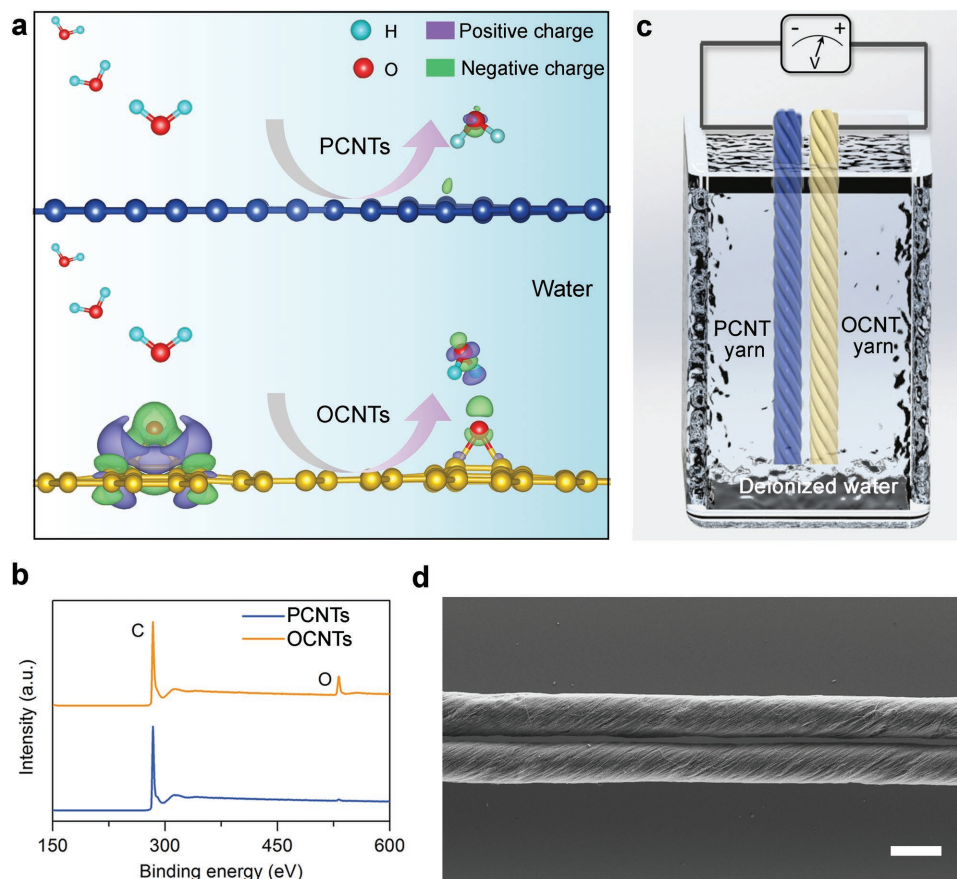


Figure 1. Illustration of the carbon:water device. a) Charge density difference for the interface of water molecules with OCNT and PCNT with an isovalue of $0.002 \text{ e} \text{ \AA}^{-3}$ from DFT calculation. Purple and green isosurfaces represent positive and negative charge in the space, respectively. b) XPS spectra of PCNT and OCNT yarns. c) Schematic illustration of the experimental setup of the fiber-shaped device (FSD). d) SEM image of the PCNT (upper) and OCNT (lower) yarns. Scale bars: $20 \mu\text{m}$ for (d).

comprised of differently polarized carbon-based electrodes may generate electricity in quiescent water.

Using two distinct classes of CNT yarns with different degrees of surface polarization, we designed a carbon:water system to generate electricity in quiescent and deionized water. The CNT yarns exhibited important practical advantages for this wider concept of charge movement due to their high electrical conductivity and physical flexibility.^[18–20] We used oxygen microwave plasma as the oxidation treatment to alter the surface polarization (see Figure S1 and synthesis details in the Supporting Information).^[21–23] Oxygen content was found to increase from 1.3 atomic percent (at%) in PCNT yarn to 8.3 at% in OCNT yarn (Figure 1b).

Next, we fabricated a double-yarn model device and investigated its electrical performance in water. We assembled two aligned CNT yarns in parallel configurations; they were separated by a defined distance and formed a fiber-shaped device (FSD) (Figure 1c,d). With the PCNT and OCNT yarns connected as negative and positive electrodes to a digital source-meter, respectively, an open-circuit voltage of ≈ 0.30 V was obtained and remained almost constant for up to 5000 s (see Figure S2 in the Supporting Information) when the yarns were immersed in water (Figure 2a); a short-circuit current was detected only when the system was immersed in water and connected (Figure S3, Supporting Information). The system generated

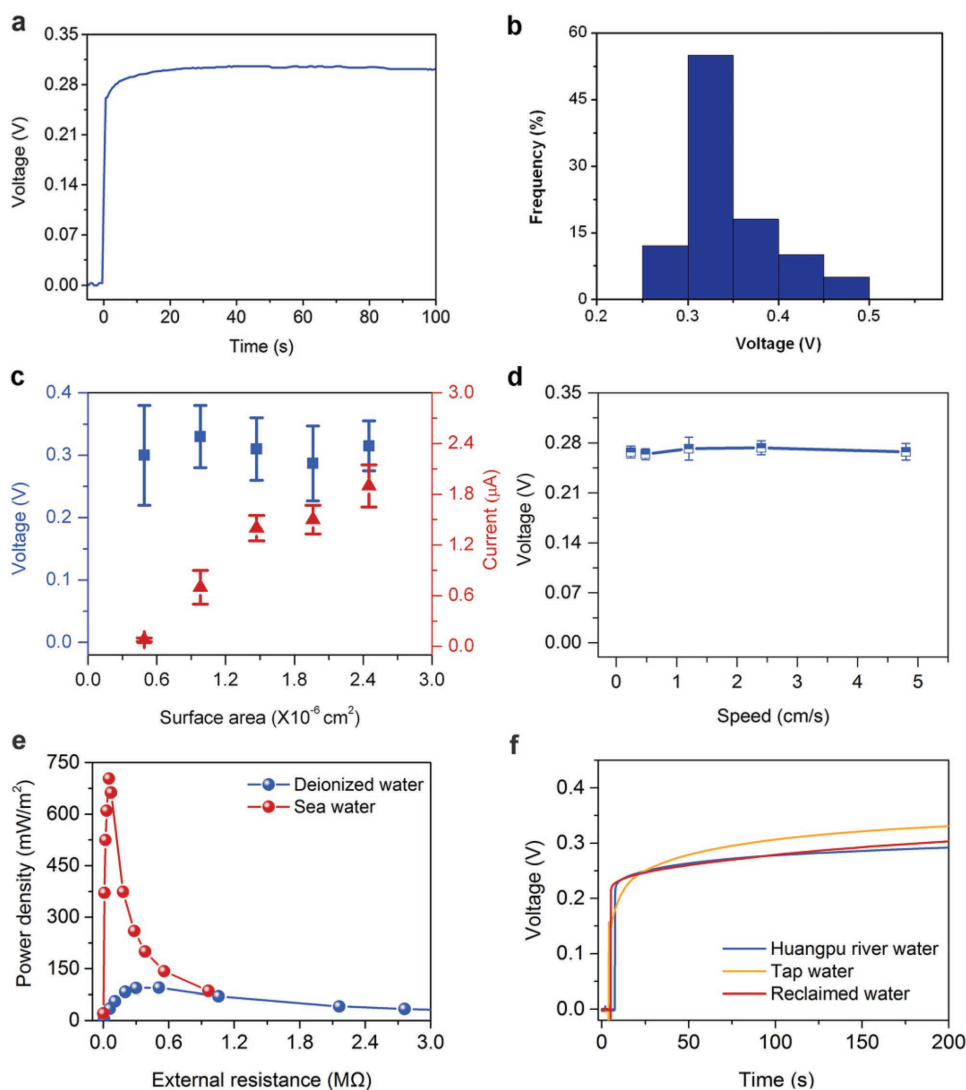


Figure 2. Electricity output of the carbon:water device in deionized water. a) When immersed in deionized water, open-circuit voltage of the device remained constant at around 0.30 V. b) Voltage distributions of carbon:water device. c) Dependence of the open-circuit voltage and short-circuit current on yarn surface area in deionized water. d) Dependence of the open-circuit voltage on immersed speed in deionized water. Increasing the speed at which the device is immersed in deionized water does not alter the open-circuit voltage, suggesting the working mechanism is distinct from previous fluidic devices. e) Dependence of the power density on the electrical resistance of the external circuit in deionized water and sea water. In highly conductive sea water, power density reached 700 mW m^{-2} . f) The open-circuit voltage of carbon:water device in water of Huangpu river (in Shanghai, China), tap water, and reclaimed water from the eastern wastewater plant (in Shanghai, China). The two PCNT and OCNT yarns in (a) and (b) and (d)–(f) contained 1.3 and 8.3 at% oxygen, respectively. The yarn length and diameter were 24 mm and $13.5 \mu\text{m}$, respectively. At least four carbon:water devices were measured for the statistical analysis at (c) and (d).

output voltages within a window of about 0.28 V (Figure 2b). There was no voltage or current when two CNT yarns with the same oxygen content were used (Figure S4, Supporting Information). In addition, when the carbon:water device was totally immersed in the deionized water (Figure S5, Supporting Information), the value of the generated voltage was almost the same as that partly immersed. In this case, evaporation has negligible influence on the generated electricity.

To gain further insight into the device's function, we studied electricity generation as a function of the yarn immersion surface area and immersion speeds. Interestingly, the short-circuit current increased as the immersion length increased, whereas the open-circuit voltage remained nearly unchanged (Figure 2c), suggesting a dependence of the current on the active surface area. The device was also found to be independent of the increase in immersion speed (Figure 2d), indicating that the working mechanism of the device is distinct from previously reported fluidic devices. Moreover, we found that the device was independent of the helical angle of the CNT yarn (Figures S6 and S7, Supporting Information). The output power was investigated by connecting the device to an external load with increasing electrical resistance (Figure S8, Supporting Information). The peak power density of 95 mW m⁻² was observed at a load resistance of 0.5 MΩ in deionized water (conductivity of 7.6 μS cm⁻¹). Due to the high conductivity of sea water (conductivity of 70 mS cm⁻¹), the power density reached 700 mW m⁻² (Figure 2e), far above those of previously reported devices that rely on flowing water or ionic aqueous solutions (Table S1, Supporting Information). In addition to deionized water, the devices also worked effectively in river water, tap water, and reclaimed water, showcasing its wide applicability in a varied range of water sources (Figure 2f).

To understand the underlying mechanism of operation of the carbon:water device, we investigated the changes in the local atomic and electronic structure of the PCNTs and OCNTs after discharging electricity. We studied the near-surface electronic and atomic structure (below 5 nm) via C1s K-edge X-ray absorption spectroscopy (XAS) in total electron yield (TEY) mode (Figure 3a,b). The main features at 285.2 eV correspond to the transition toward unoccupied π₀ states C–C, and the features in the range 286–291 eV correspond to C–X chemistry where X denotes a specifically adsorbed element or functional group.^[24] The peaks that appear at 286.5, 287.2, and 288.2 eV are attributed to hydroxyl (C–OH), epoxy (C–O–C) and carboxyl (COOH) groups, respectively.^[25,26] The original carbon states of PCNTs and OCNTs were found to be significantly different, with evident peaks in the range 286–291 eV, indicating more adsorbed oxygen-functional states in OCNTs compared with PCNTs, especially in terms of C–O–C. We ascribe this to the incorporation of defects during oxygen plasma treatment; supported by transmission electron microscopy images and Raman spectra results (Figures S9 and S10, Supporting Information). The PCNTs were appreciably oxidized after discharging. Spectral features at 286–291 eV indicate that unoccupied π₀ states C–C were oxidized to C–OH and COOH. In the case of OCNTs, while the C–OH feature, which was negligible in the initial state, became prominent, the C–O–C feature almost disappeared after discharging. To investigate the specific variations of these oxygen-functional groups, we examined

the carbon and oxygen atomic structures of these samples via X-ray photoelectron spectroscopy (XPS) (Figure 3c,d).^[27] Peak deconvolution was carried out for C 1s and O 1s spectra. These OCNT and PCNT yarns were also found to have more carbon-oxygen groups present after discharging: specifically, a higher C–OH content was found, consistent with the XAS results.

To elucidate the working mechanism of the carbon:water system, we carried out DFT calculations to determine how OCNT and PCNT interact with water and the limiting potentials for their interactions. According to research on metastability of graphene oxides,^[28] the polarization caused by O atoms on sp² hybridized carbon of OCNTs can lead to absorption of water molecule caused by charge transfer, and finally change the atomic structure of OCNT itself. Based on this observation, we assume that the charge transfer between the water and OCNT may cause the dissociation of the water molecule. Here, we propose two half reactions occurring on OCNT and PCNT during the discharge process. Briefly, OCNT reacts with water to form C–OH on the cathode: OCNT+H₂O+e⁻ = (CNT–OH)+OH⁻_(aq), and PCNT reacts with hydroxide to form C–OH on the anode: CNT+ OH⁻_(aq) = (CNT–OH) +e⁻. We calculated the Gibbs free energies for both half reactions (Figures S11 and S12, Supporting Information). The Gibbs free energy was -0.284 eV for the half reaction with C–O–C group of OCNTs as reactant, suggesting the formation of CNT–OH is favorable. In contrast, the Gibbs free energy for the half-reaction of C=O and COOH groups interacting water were 0.468 and 0.209 eV, respectively. The negative Gibbs free energy suggests that the proposed reactions between OCNT and PCNT with water are possible. We illustrate this reaction mechanism in Figure 3e,f (see reaction paths in the Supporting Information for details on computational methodology). At the water/OCNT interface when OCNT is immersed in water, the highly reactive epoxy group (C–O–C) on OCNT undergoes a nucleophilic attack by water, causing the ring to open and alcohol (C–OH) to form, and this process also produces excess OH⁻ ions. Meanwhile, at the water/PCNT interface, PCNT reacts with OH⁻ ions (Figure 3f). We confirmed the formation of CNT–OH in both OCNT and PCNT experimentally via XAS and XPS. Furthermore, the calculated limiting potential is 0.284 V, which closely matches the experimentally observed potential of 0.3 V (please see reaction paths in the Supporting Information). We term this new process as polarization-induced-dissociation effect, which enables the OCNT and PCNT to electrochemically react with water to generate electrical current.

Inspired by our mechanism, the electricity device has also been fabricated by many other kinds of material, including carbon fiber and graphene oxide (Figure S13, Supporting Information). For practical applications with low costs, the oxygen modification can be replaced by the other methods such as acid treatment. We also sought to improve the performance further by doping metal on the surface of the PCNT yarn to increase conductivity and ability of providing electrons. The device can also be flexible fiber or film with tensile strengths of 10²–10³ MPa, which were higher than most chemical fibers and satisfy real applications. The voltage and current of devices increased with increasing units in series and in parallel. Through the readily combined in series and parallel

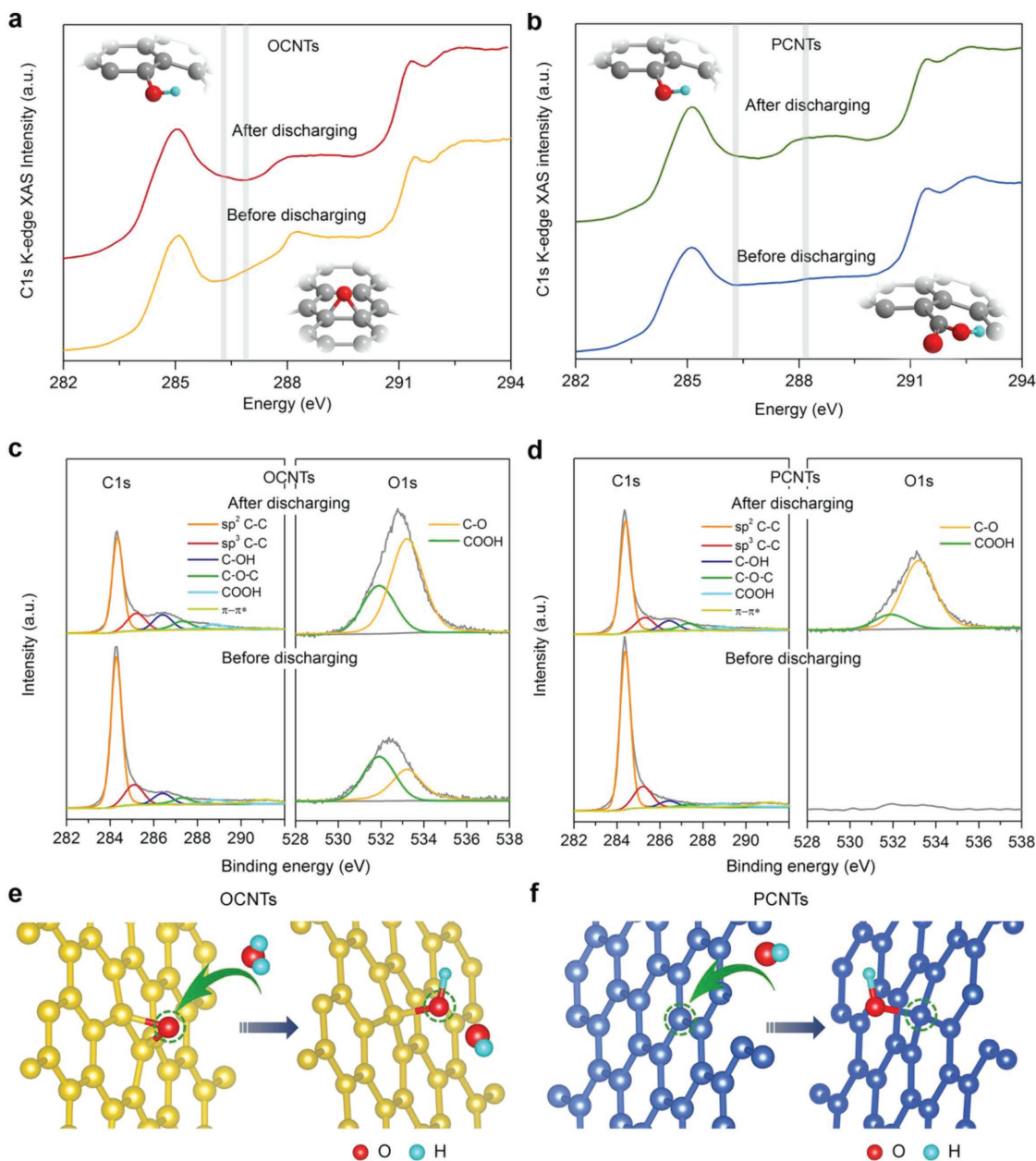


Figure 3. Electricity generation mechanism of the carbon:water device. a,b) Surface-sensitive TEY XAS scans at the C K-edge of OCNT (a) and PCNT (b) yarn before and after discharging. Left and right gray vertical bars indicate the binding energy of C–OH (inset, the top-left image) and C–O–C (inset, the bottom-right image) bond, respectively. c,d) C1s and O1s XPS spectra of the OCNT (c) and PCNT (d) yarn before and after discharging. Left and right gray vertical bars indicate the binding energy of C–OH (inset, the top-left image) and COOH (inset, the bottom-right image) bond, respectively. Schematic illustrations of the electricity generation process of the device. e,f) Half reactions occur on the water/OCNT surface (e) and water/PCNT surface (f).

arrangements, this circuit was able to power a liquid crystal display system, including the panel and corresponding control chip (Figures 4a,b; Figure S14, Supporting Information). We demonstrated the weaving of continuous CNT yarns to form flexible CNT fabrics (Figures S15 and S16, Supporting Information). The CNT fabric was light due to the low density of CNT fiber (0.54 g cm^{-3}) (Figure 4c). By sandwiching PCNT and OCNT fabrics face to face with an insulating separator in the middle, we assembled a fabric carbon:water device. The resulting device was flexible (Figure 4d). The output current

improved from $6.7 \mu\text{A}$ for a 24 mm fiber-shaped device to 2.5 mA for a 40 mm^2 fabric (Figure S16, Supporting Information). We fabricated an “FSD” T-shirt (Figure 4e) that when wet, could power a pedometer wristwatch system (Figure 4f,g and Figure S17, Supporting Information).

In conclusion, we have shown that a carbon:water device based on oxygen-treated CNT yarns can generate electricity from quiescent, deionized water. Experimental and theoretical studies have shown that electricity generation results from the polarization-induced-dissociation effect, whereby

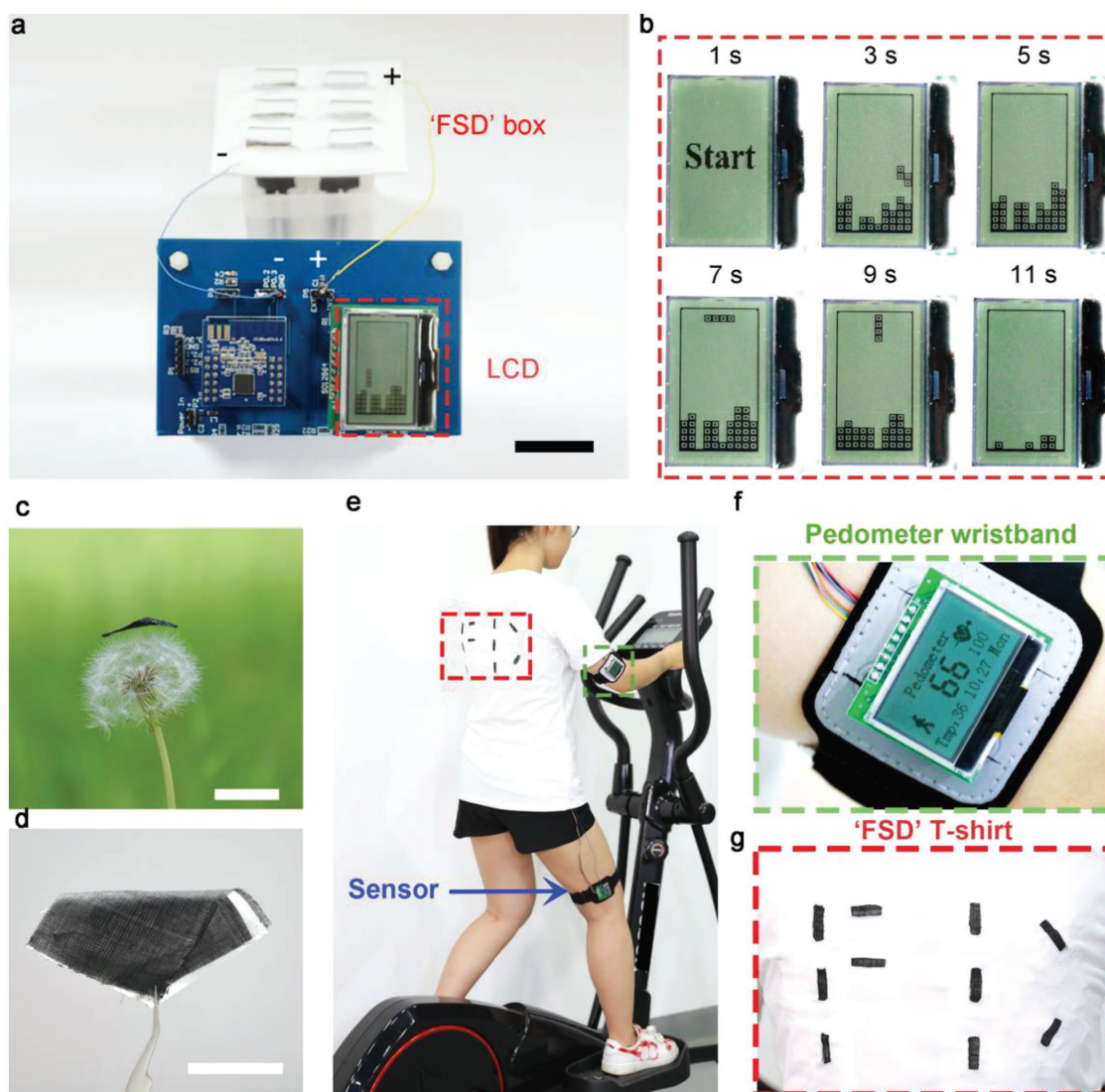


Figure 4. Energy supply application of the carbon:water device. a,b) Photographs of the liquid crystal display with movable sliding blocks powered by an “FSD” box. c) Lightweight CNT fabric on a dandelion. d) Flexible and bendable carbon:water device fabric. e) Photographs of a subject wearing an “FSD” T-shirt and a self-designed pedometer wristband during exercise on an elliptical machine. f,g) Enlarged photographs of the self-designed pedometer wristband and “FSD” T-shirt. Scale bars: 2 cm for (a), 1 cm for (c), and 2 cm for (d).

electric charge is transferred via an electrochemical reaction between CNTs and water induced by the local-polarization of OCNTs. Because our device functions in a variety of water sources and does not require flowing water or ionic solutions, it offers a new water-based electricity generation technology. Furthermore, because it is small, lightweight and flexible, the device can be made wearable and foldable in large scale. We foresee various potential applications in consumer electronics and remote emergency situations where power generation is scarce.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon nanotubes, chemical, electricity, energy, water

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