Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

How the Optimal Configuration of Electrodes on a Hydrovoltaic Device Changes with Water Conditions

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Contents:

1. General functionalization of graphite

This section outlines the general acid functionalization of graphite used to produce the FG materials discussed in the main.

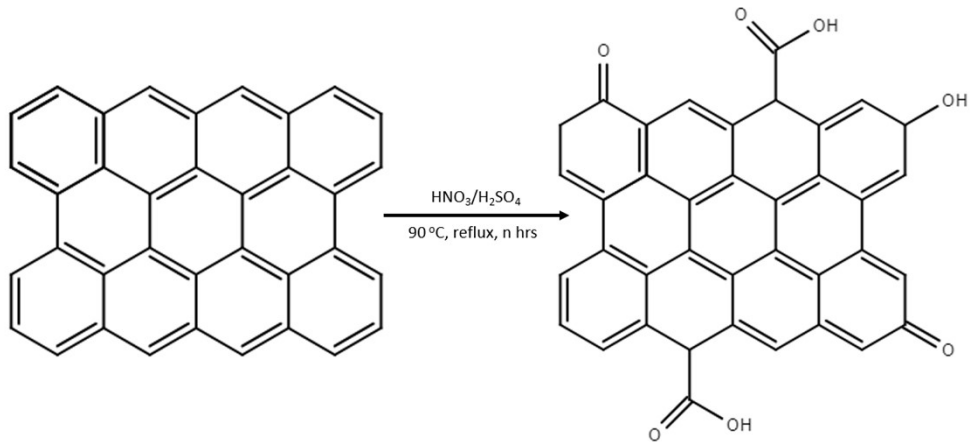

Figure S1. A general schematic demonstrating the acid-functionalization of graphite. Sp^2 bonds in the graphitic structure break and new sp^3 bonds to functional groups such as carboxyl's (-COOH), carbonyl's (-C=O), and hydroxyl's (-OH) are formed.

2. ‘Short-circuiting’ of conductive FG6 devices

This section demonstrates the ‘short-circuiting’ of highly conductive FG6 devices when working and counter-electrodes are directly connected to the active surface in a CE configuration.

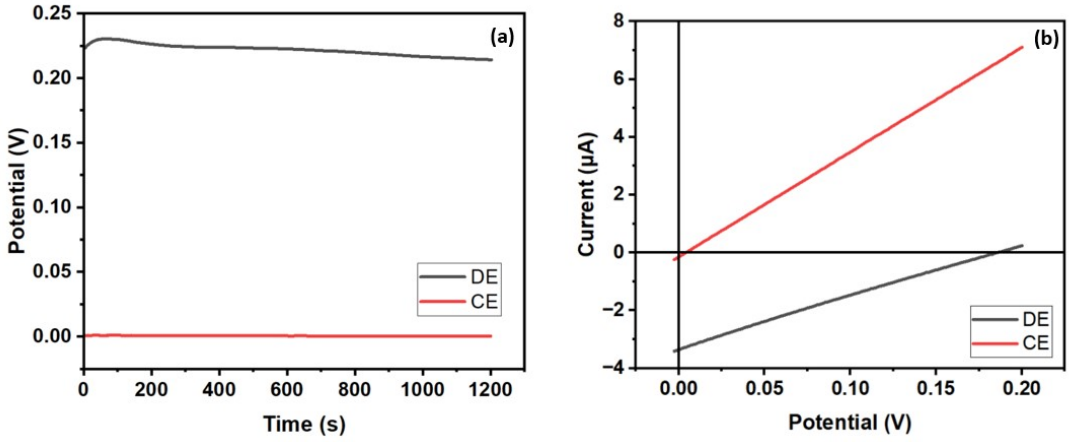

Figure S2. (a) The open-circuit potentials (OCP’s) of the *same* FG6 hydrovoltaic device with connected and disconnected graphene paste electrodes demonstrating that the device ‘short-circuits’ as a result of low resistance in a CE configuration, and (b) the linear sweep voltammetry measurements (LSV’s) associated with the same DE and CE configurations confirming the ‘short-circuiting’ effect.

3. Setup for nitrogen-purged device measurement

This section outlines the experimental setup used to assess the performance of FG hydrovoltaic devices in a nitrogen-purged environment.

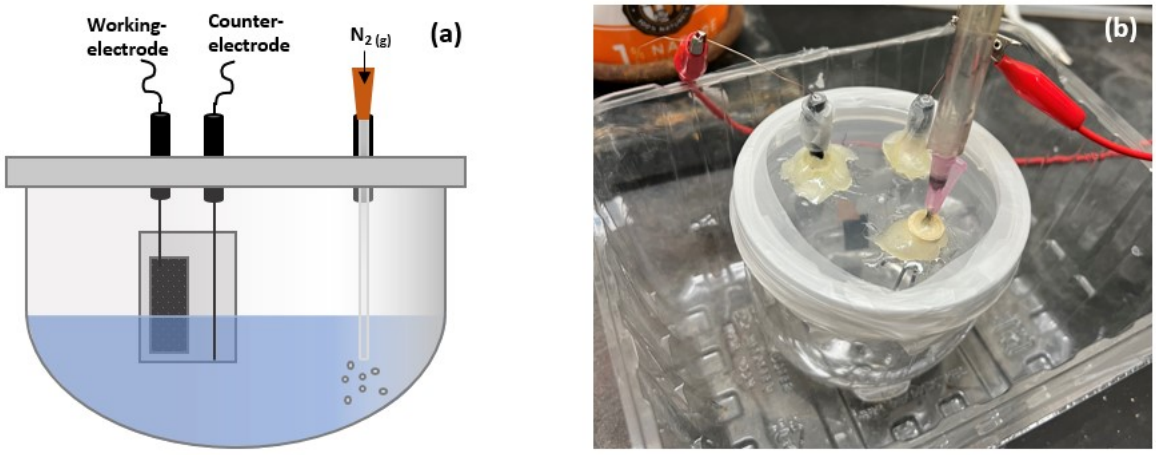

Figure S3. (a) A schematic of the experimental setup used to assess the performance of FG devices, showing copper-wire electrodes fed through semi-sealed plugs in a

container and a needle bubbling N_2 gas into the water, and (b) the physical setup for reference.

4. V_{OC} and I_{SC} values of CE and DE FG24 devices in various ionic solutions

This section provides the OCP and LSV plots associated with values presented in **Table 1**.

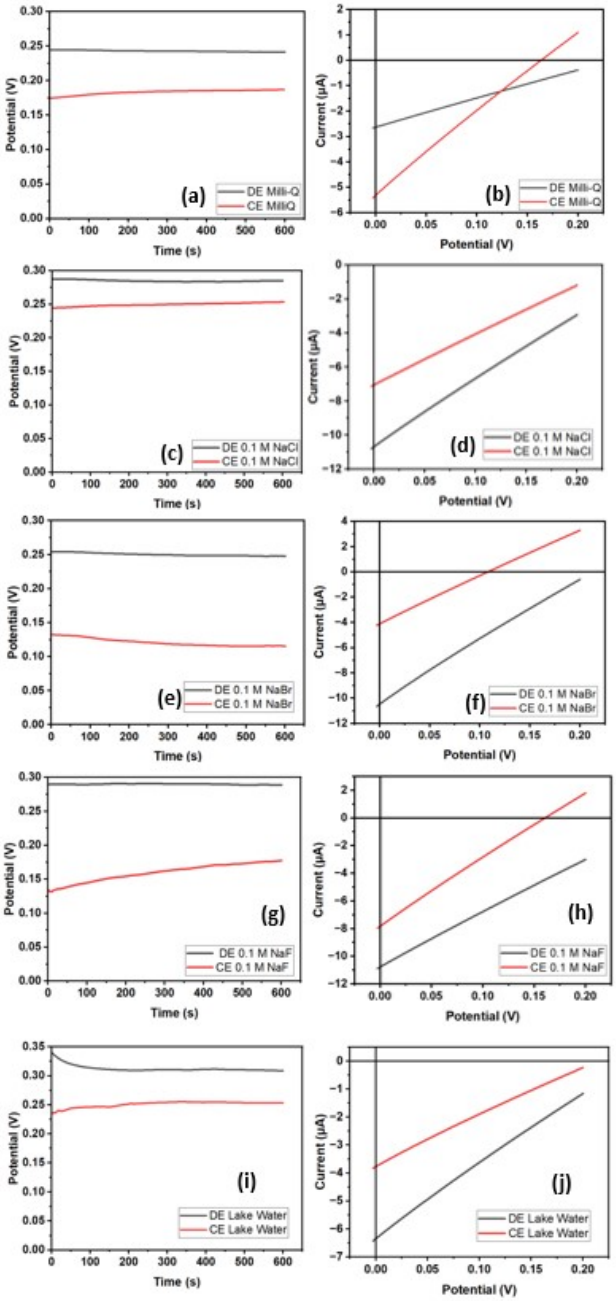

Figure S4. (a) and (b) depict the V_{OC} and I_{SC} plots associated with DE and CE FG24 devices in Milli-Q water, (c) and (d) provide the V_{OC} and I_{SC} plots associated with DE and CE FG24 devices in 0.1 M NaCl solution, (e) and (f) provide the V_{OC} and I_{SC} plots associated with DE and CE FG24 devices in 0.1 M NaBr solution, (g) and (h) provide the V_{OC} and I_{SC} plots

associated with DE and CE FG24 devices in 0.1 M NaF solution, and (i) and (j) provide the V_{OC} and I_{SC} plots associated with DE and CE FG24 devices measured in lake water.

5. Device performance in NaCl solutions of varying concentrations

This section details the performance of CE and DE FG devices in Milli-Q water, 0.1 M NaCl, 0.2 M NaCl, and 0.3 M NaCl. Typical OCP measurements were recorded for devices, then current output was estimated using chronoamperometry. The chronoamperometry measurements mimicked LSV measurements in that sufficient potential was applied to devices to result in zero voltage, then current flow was measured over time. Device performance inevitably drops off as a result of the applied bias, so current decreases over time.

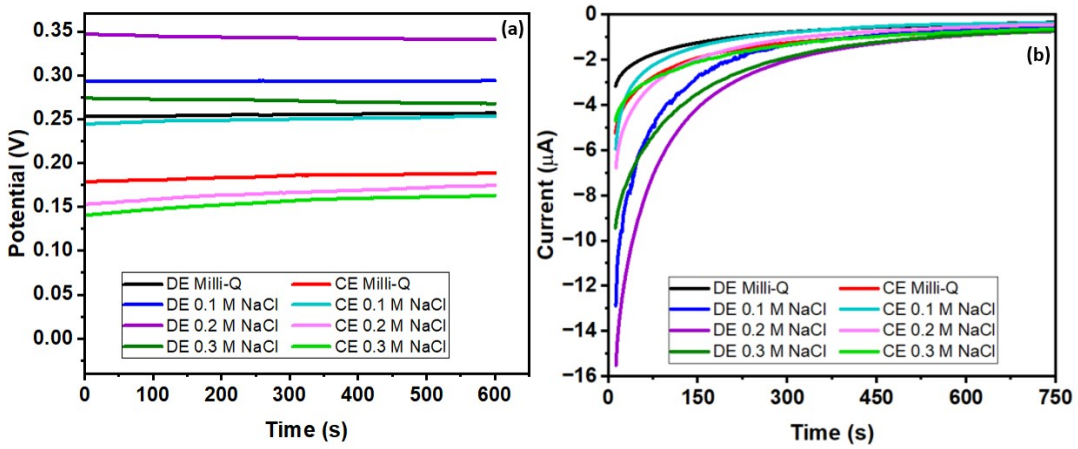

Figure S5. (a) Shows the open-circuit potentials of DE and CE FG24 devices in Milli-Q and NaCl solutions of varying concentrations, and (b) depicts the chronoamperometry curves associated with those devices, demonstrating current output over 750s.

6. Preparation of functionalized graphite

This section provides details of the functionalization of graphite, including demonstrating the reflux setup, the neutralization step, and the final FG material before and after grinding.

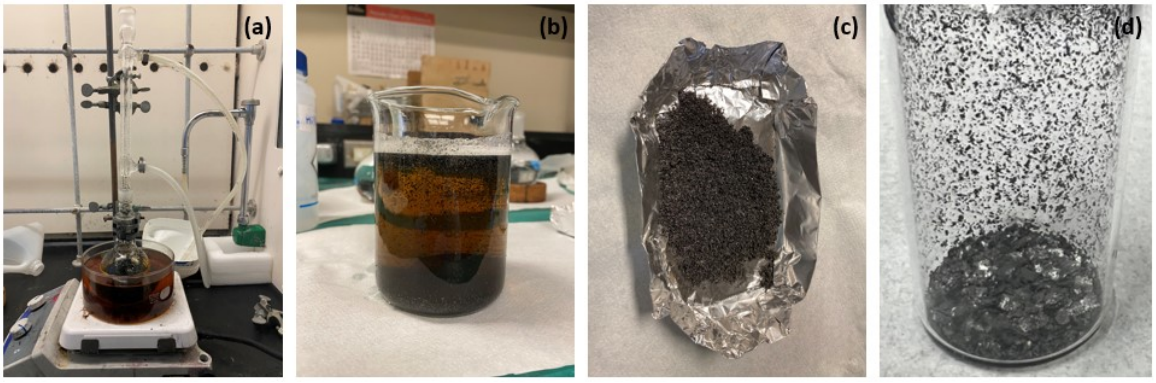

Figure S6. (a) shows the reflux setup for graphite functionalization in which 1 g of graphite is stirred (700 rpm) for 6, 12, or 24 hours with 65 mL H_2SO_4 (95%) and 22.5 mL HNO_3 (95%) in a 300 mL round-bottom flask partially immersed in oil (90 ^oC) and connected to a condenser tube above, (b) shows the mixture of functionalized graphite (FG) and acid following the functionalization and dilution in 250 mL of Milli-Q water, (c) depicts the FG product after drying overnight in an oven at 60 ^oC, and (d) the finished FG product after grinding in a mortar and pestle.

7. Preparation of FG devices

This section details the steps involved in preparing hydrovoltaic devices using 6, 12, or 24-hour functionalized graphite material.

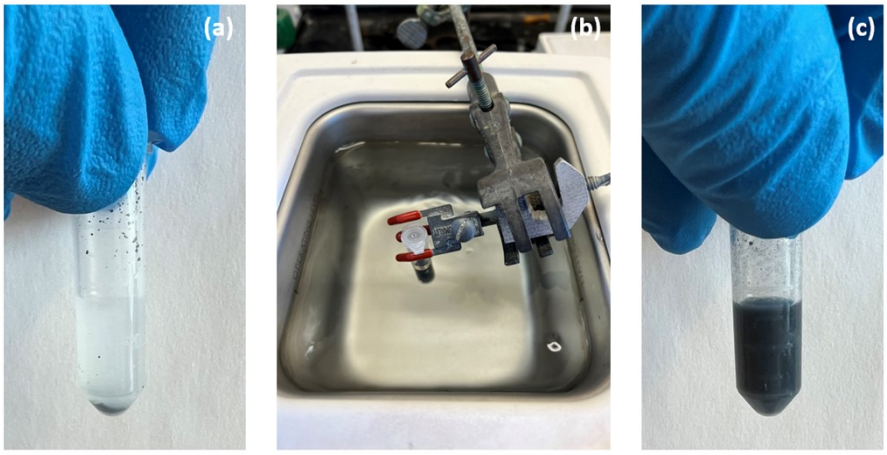

Figure S7. (a) shows a mixture of 4.5 mg SDS, 15.0 mg PVDF, and 9.0 mg of FG24 in 800 µL isopropanol prior to sonication, (b) depicts the sonication setup, and (c) demonstrates the same mixture of after 10 minutes of sonication.

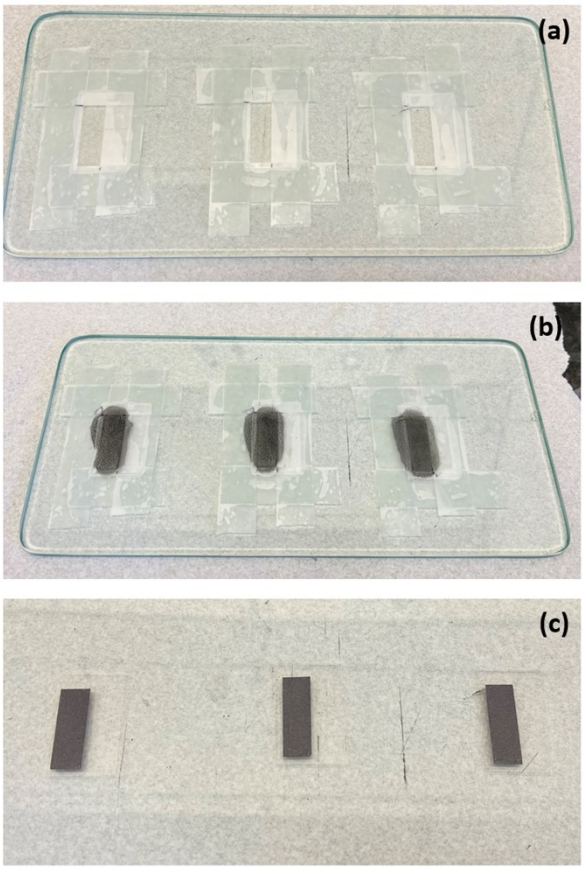

Figure S8. (a) depicts three 1 x 3 cm^2 PET sheets affixed to a glass plate with clear tape, (b) demonstrates FG devices immediately after the first round of drop-casting, and (c) shows finished devices after a second round of drop-casting and overnight drying.

8. Electrode connections and potentiostat measurements

This section demonstrates finished devices with copper wire/tape electrodes (DE) and graphite paste electrodes (DE and CE), as well as the general measurement setup for OCP measurements, LSV measurements, and chromoamperometry measurements.

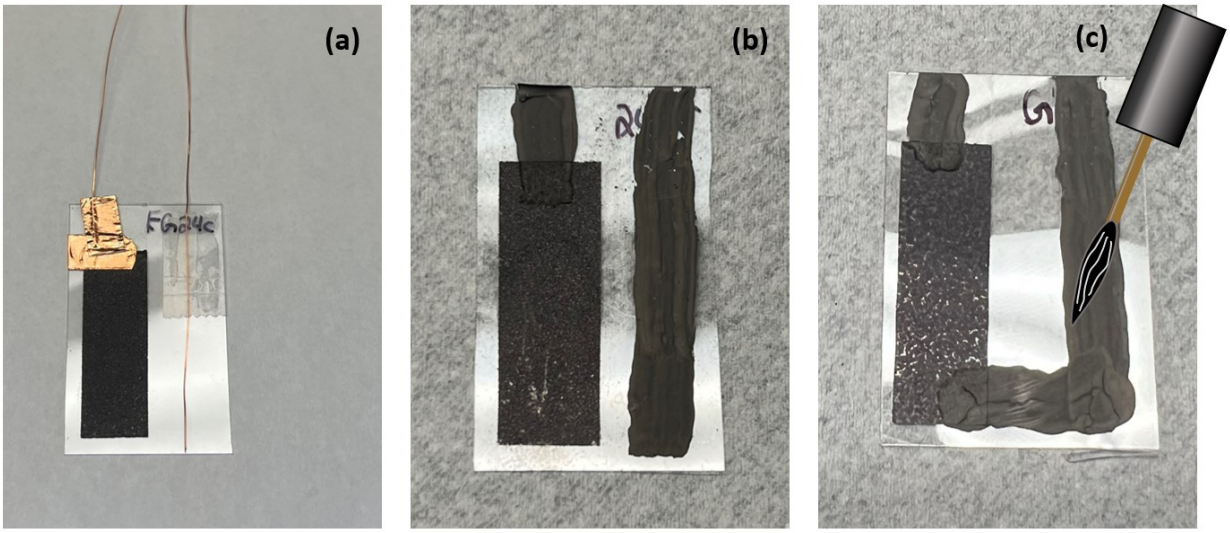

Figure S9. (a) depicts a finished FG24 device with a copper tape/wire working electrode and copper wire counter electrode, (b) depicts a FG24 device with graphite-paste (GP) working and counter-electrodes painted on in a DE configuration, and (c) depicts a FG24 device with GP working and counter-electrodes painted on in a CE configuration.

9. General measurement setup

This section outlines the general setup used to evaluate the power output of the FG hydrovoltaic devices under various conditions.

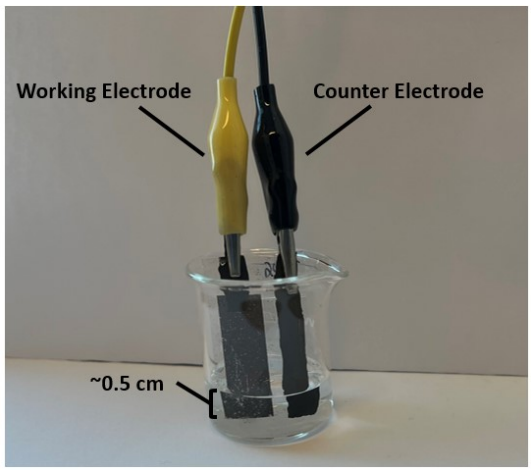

Figure S10. demonstrates the general measurement setup of a device, with working and counter-electrodes connected via wires to a potentiostat.