Supporting Information

Sustainable Electricity from Gravity-driven Nanofluidic Flow of Water through Modified Bio-channels of Coir Fiber

Barsha Rani Bora,^a Monotosh Mondal,^a Nabamallika Nath,^a K.K.R. Datta,^b and Kalyan Raidongia,^{a,c*} ^aDepartment of Chemistry, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India. E-mail: k.raidongia@iitg.ac.in ^bDepartment of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur 603203, Tamil Nadu, India ^cCentre for Nanotechnology, Indian Institute of Technology-Guwahati, Kamrup, Assam 781039, India

Contents

1	Experimental Section2						
	1.1	Fabrication of nanofluidic/energy device	2				
	1.2	Measurement of porosity and tortuosity:	2				
	1.3	Infiltration of GO into the channels of CF (d-CF-G)	3				
	1.4	Functionalization of d-CF-G with pPDA (d-CF-G-P):	4				
	1.5	Surface charge governed ionic transport:	4				
	1.6	Fabrication of bulk device:	4				
	2 0	Characterization	5				
3	Output power comparison by varying electrode separation:						
4	Output power comparison by varying number of fiber:						
5	Calculation of voltage and current using MHS equation:						

1 Experimental Section

Methods

- 1.1 Fabrication of nanofluidic/energy device: Typically, energy harvesting devices were fabricated using 12 CFs of length ~ 2.5 cm. The vertical alignment of the fibers were attained by using polydimethylsiloxane (PDMS) elastomer as the supporting matrix. Two Ag electrodes were connected to the top and bottom portion of the device using Ag conducting paste. The distance between both top and bottom electrode was maintained at 1.5 cm.
- 1.2 Measurement of porosity and tortuosity: Porosity, the percentage of void space

present inside a material was calculated using the equation, $Porosity = \frac{V_V}{V_T}$; To find the total volume of a fiber (VT), diameters of each fiber were recorded using screw gauge and the total volume was determined using the equation, Volume = π x (radius)2 x length of fiber. Again, the volume of the void space (VV) can be replaced by the volume of water that the void can accommodate. DI water was capillary raised inside the fiber for 10 hours and weighted. To measure the weight of the absorbed water, the initial weight (before capillary rise) of the fiber was subtracted from the final weight (after capillary rise). Using the density of water (1000 kg/m³) the volume of the water confined in void was determined.

Tortuosity, the ratio of the distance actually travelled by a tracer through the pore space, L_e , to the straight-line distance between the two points, was calculated using the equation

$$D_{m}^{'} = \frac{\frac{D_{m}}{L_{e}}}{L}$$
, where ratio L_e/L is called tortuosity factor and

 L , where ratio L_e/L is called tortuosity factor and is represented by τ . A device was prepared using RF samples and PDMS as the matrix, similar to our energy harvesting device, but with a larger number of fibers. The device was kept vertically and solution of

KCl electrolyte was poured (V_p) at the top part of the device which was allowed to pass through the RF sample for a particular amount of time t. A conductivity meter was used, whose probe was dipped in the KCl volume, to measure the conductivity value at initial and at different time interval t.

 D_m To get D_m ratio ($D_m = 1.844 \ge 10^{-9} \text{m}^2 \text{ S}^{-1}$), which is equal to the tortuosity value, we need to find D_m^{\dagger} value which can be calculated from the following equation:

$$\frac{M_t}{M_{\alpha}} = (1+\alpha) \left[1 - exp \left(\frac{D_m t}{L^2 \alpha^2} \right) \right]$$
(1)

Where, M_t and M_α are the amount of tracer in the inert bed at time t and amount of tracer after a sufficiently long time of equilibrium, respectively.

$$\frac{M_t}{M_{\alpha}} \approx \frac{(V_p + V)(C_{p^0} - C_p)}{VC_{p^0}}$$
(2)

In equation 2, C_{p^o} and C_p are conductivity values at initial condition and after time t.

Rearranging equation 1 and plotting $ln\left(1-\frac{M_t}{M_{\alpha}\alpha}\right)$ versus t, slope $=\frac{D_m}{L^2\alpha^2}$ can be obtained.

L = length of the RF sample, and $\alpha = \frac{v_p}{v}$; (V_p and V are the volume of electrolyte in the pool and in the packed bed, respectively). Putting these values, we will get D'm. Finally,

 D_{m}

from the ratio D_m we got the tortuosity value τ . Applying the same procedure, the tortuosity value for d-CF, d-CF-G and d-CF-G-P was also calculated.

- **1.3** Infiltration of GO into the channels of CF (d-CF-G): For avoiding deposition of Graphene Oxide flakes on the outer surface of the coir fiber, a vacuum-assisted capillary-driven deposition method was opted. Typically, the bottom parts of 50 number of d-CF were placed on an aqueous GO solution (1mg/ml) to infiltrate GO flakes along with the capillary raised DI water. To expedite the infiltration process of GO dispersion, the coating process was performed inside a vacuum chamber for nearly ~ 26 hours.
- 1.4 Functionalization of d-CF-G with pPDA (d-CF-G-P): The d-CF-G sample was modified with polyphenylenediamine by treating them with an aqueous solution of pPDA (0.5 mg/mL) followed by heating at 80 °C for 3 hours. The obtained sample was then washed with DI water to get the final sample.
- 1.5 Surface charge governed ionic transport: The conductivity of the biofluidic channels present in coir fiber was evaluated using a digital sourcemeter instrument. Figure 1b shows the *I*–*V* curves recorded through a coir fiber device with different concentrations of KCl. The linearity in the *I*–*V* curve confirms the presence of a continuous network of hydrated channels throughout the coir fiber. Conductivity versus concentration plot (Figure 3a) confirms that the biochannels in coir fiber shows the characteristics of surface-charged-governed ionic conductivity. At the high concentration regime (10⁻² M to 1 M), the conductivity values increase linearly with that of the salt concentration, but at the low concentration regime (10⁻³ M to 10⁻⁶ M) it did not change even for orders of magnitude change in the salt concentration. On the contrary, in the bulk water, conductivity decreases linearly with decreasing salt concentration
- 1.6 Fabrication of bulk device: Large scale nanofluidic devices were prepared by encapsulating a bundle of fiber samples of diameter ~ 4.9 cm in freshly prepared PDMS elastomer. After curing, the d-CF bundle in PDMS was cut in circular blocks of height around 1.5 cm. Aqueous dispersion of GO was infiltrated through the fibers using vacuum filtration method, which was

followed by treating with pPDA at 60 °C for 1 hours. Finally, the prepared device was dipped in DI water for 24 hours before using for the application. Copper mesh of diameter 4.4 cm wasused as the top and bottom electrodes.

2 Characterization

All the electrochemical measurements were carried out using a Keithley Source meter (model: 2450). The morphology of the samples was characterized using field emission scanning electron microscope (FESEM) (Zeiss, model: Sigma). Graphitic nature of the P-GO inserted fiber was confirmed by using Raman Spectroscopy (make: Horiba Jobin Vyon, model: LabRam HR). X-ray diffraction patterns were recorded by using Bruker D-205505 Cu-K α radiation ($\lambda = 1.5406$ Å) instrument. Delignified coir fiber was characterized by Fourier transform infrared spectroscopy (PerkinElmer IR spectrometer). The ζ potential of the samples was measured by a Zetasizer instrument (Malvern, Nano-ZS90). The samples were sonicated using Labmam Probe Sonicator.

Infrared spectra (S1) shows characteristic lignin peaks of the fiber, which is absent in the delignified sample, supporting that the delignification has occurred in the sample.

The mechanical property study of individual fiber was carried out using a 5kN Universal Testing Machine. The d-CF-G-P sample shows highest improvement in the breaking stress with corresponding young's modulus value of 4590 MPa.



Figure S1: IR spectra of the sample before and after delignification process.



Figure S2: Stress vs Strain curve of CF



Figure S3: Wetting behaviour of coir nanochannel (1.5 cm long) was monitored by measuring the ionic conductance as a function of time after exposing to DI water. It took around 5 hours to observe the onset of ionic conductance, which gradually increased and reached steady state after 24 hours.



Figure S4: Porosity and tortuosity values for comparison for Raw, d-CF, d-CF-G and d-CF-G-P sample.



Figure S5: Comparison of (a) IR spectra, and (b) output voltage of device made from fiber sample reduced by treating with hydrazine with that of raw CF sample.



Figure S6: Raman spectra of raw fiber and d-CF-G after heating the samples at 120 °C for 1.5 hours in Ar atmosphere.



Figure S7: (a) N1s spectrum (b) EDX spectrum of d-CF-G-P sample, and (c) EDX spectrum recorded on d-CF-G sample.



Figure S8: Cross-sectional FESEM image of a 4 cm long d-CF-G-P sample cut at an interval of 1 cm.



Figure S9: Zeta potential values compared with the effective channel diameter for Raw, d-CF, d-CF-G and d-CF-G-P sample.



Figure S10: Current Vs time plot of d-CF-G-P fluidic device.



Figure S11: Power density of the CF sample as a function of KCl electrolyte concentration.

3 Output power as a function of separation between the electrodes:

Different energy harvesting devices of d-CF-G-P sample were made by varying the separation between the electrodes. With increasing the electrode separation from 1.5 to 2.5 cm we observed a decrease in the output voltage from 234.58 to 45 mV, which was further decreased to 18.33 mV upon increasing the electrode separation to 3.5 cm. Similarly, the power density value was calculated by varying the separation between the electrodes. The highest power density of 97.47 mW/m² was obtained with a separation 1.5 cm (Figure S8).



Electrode separation	Output Voltage (mV)	Output Current (nA)	Power density (mW/m²)	
0.5	143	66.25	36.55	
1.5	234.59	107.7	97.47	
2.5	45	1.89	0.327	
3.5	18.33	7.40	0.520	

Figure S12: Comparison of current, voltage and power density by varying the electrode separation.

4 Output power as a function of number of fibers:

A systematic study was carried out about the effect of changing the number of d-CF-G-P in a single device. For one single fiber output voltage of around 82 mV was obtained, which increases to 109 and 234.58 mV for 6 and 12 number of coir fibers respectively (Figure S9). This indicates how with increasing the number of coir channels the output voltage increases. Similar trend was observed for the output current values.



Output Voltage (mV)	Output Current (nA)	Power density (mW/m2)	
82	1.49	5.656	
109	42	35.32	
234.58	107.7	97.47	
	Output Voltage (mV) 82 109 234.58	Output Voltage (mV)Output Current (nA)821.4910942234.58107.7	

Figure S13: Voltage, current and power density as a function of number of d-CF-G-P fibers inside the energy harvesting device.



Figure S14: Comparison of the output voltage by keeping the water volume at top of the d-CF-G-P device and then at bottom of the same device.



Figure S15: TEM image of raw CF sample. The sample was prepared by breaking CF through vigorous sonication.

5 Calculation of voltage and current using modified Helmholtz and von Smoluchowski (MHS) equation: The output voltage (ΔV) and current (ΔI) values were calculated by using the equations below.

$$\Delta V = \frac{\varepsilon_{rs}\varepsilon_0\zeta}{\eta F} \frac{1}{\sigma_r \Delta P}$$
(1)
$$\Delta I = \frac{\varepsilon_{rs}\varepsilon_0\zeta A}{\eta F} L_{\Delta P}$$
(2)

where, ε_{rs} is the relative permittivity of water (80.1), ε_0 is the electrical permittivity of vacuum (8.85 × 10⁻¹² F m⁻¹), η is the dynamic viscosity of water (1.002 × 10⁻³ kg m⁻¹ s⁻¹), ζ is the zeta potential of the fiber sample (measured for the aqueous dispersion of repeatedly sonicated fiber samples), and F

τ

 $=\overline{\phi}$, is formation factor where τ is tortuosity and Φ is the porosity of the sample.

Sample name	Zeta potential (mV)	Tortuosity (τ)	Porosity% (Φ)	F factor (τ/Φ)	Area (m²)	Conductivity (S m ⁻¹)	Effective channel dimension (nm)
CF	25.1	1.54	64.45	2.38	4.60 x 10 ⁻⁷	2.93 x 10 ⁻³	7.0118
d-CF	42	1.37	76.81	1.78	4.75 x 10 ⁻⁷	2.07 x 10 ⁻³	10.14
d-CF-G	28.8	1.70	58.58	2.90	3.97 x 10 ⁻⁷	1.14 x 10 ⁻³	6.18
d-CF-G-P	30.1	1.83	56.94	3.21	3.01 x 10 ⁻⁷	1.50 x 10 ⁻³	3.642

 Table 1. Table showing the average zeta potential, tortuosity, porosity, F factor, effective pore

 area, and conductivity of CF, d-CF, d-CF-G and d-CF-G-P.

Sample name	Effective pore size h _{eff} (nm)	Calculated voltage (V)	Experiment al voltage (V)	Calculated current (nA)	Experiment al current (nA)	Effective channel dimension (nm)
CF	7.01	3.56 x 10 ⁻³	27.70 x 10 ⁻³	0.32	37.57	7.0118
d-CF	10.14	11.2 x 10 ⁻³	14.24 x 10 ⁻³	0.74	1.77	10.14
d-CF-G	6.18	8.62 x 10 ⁻³	139.43 x 10 ⁻³	0.26	64.30	6.18
d-CF-G-P	3.64	6.19 x 10 ⁻³	272.12 x 10 ⁻³	0.18	107.78	3.642

 Table 2. Table showing comparison of experimental voltage and current from with that

 calculated values (of output current and voltage) obtained from MHS equation.

Unfortunately, large deviation was observed between the MHS equation predicted output potential and current values with that of experimental observed values, indicating incompatibility of the MHS equation in our system. One of the primary hypotheses of the MHS equation is channels with non-overlapping Debye lengths, and therefore, this deviation is attributed to channels with overlapping Debye lengths. Interestingly the deviations increases with the decreasing effective channels dimensions.