Supporting Information:

Reconstruction of Soil Components into Multifunctional Freestanding Membranes

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Figure S1. Spectroscopic characterization of humic acids: Photographs showing aqueous dispersion of (a) vermiculite layers, exfoliated from vermiculite crystals as shown in the inset, and (b) purified humic acid, extracted from soil sample shown in the inset (c) XRD pattern of raw vermiculite purchased from Sigma Aldrich, (d) UV-Vis, (e) IR and (f) Fluorescence spectra of humic acids extracted from native soil samples.
Figure S2. (a) FESEM, (b) AFM image along with height profile, (c) TEM and (d) HRTEM images of exfoliated vermiculite layers obtained by employing two-step ion-exchange method.
Figure S3. XRD patterns of pure VM, 30 %, and 50 % HA composite membranes.
Figure S4. Bending stiffness measurement: (a) Schematic diagram describing parameters of the bending stiffness measurement. (b) Photographs showing bending of 20 %, 30 % and 50 % HA strips.

Bending stiffness values of soil membranes were determined by employing Lorentzen & Wettre two-point method.\textsuperscript{1-3} A known load (4.5 mg) was placed to one end of the rectangular strip (typically 25 mm × 4.5 mm × 0.045 mm) keeping the other end fixed to a glass slide. The following equation was used for the calculation:

\[
S_b = \frac{60 \times F \times l^2}{\pi \times \theta \times b} \quad \text{(I)}
\]

Where \(S_b\) is bending stiffness, \(F\) is defined as bending force \((F = \text{weight} \times \text{gravitational constant})\), \(l\) is the distance between the clamp and the load, \(\theta\) is the angle of deflection under the influence of load, \(b\) is the width of the strip.

The strips were then transferred to a chamber containing solvent vapors in order to study the change in bending angle of the strips on exposure to different solvent atmosphere.
Figure S5. Bending stiffness of the soil membranes in (a) different solvent environment, and (b) different humidity.
Figure S6. Force Vs stress plot of composite membranes compared to that of the vermiculite membrane.

The weight required to the break the strip was used as maximum load to calculate tensile strength by using following formula,

\[ \text{Tensile Strength (MPa)} = \frac{\text{Maximum load (N)}}{\text{Cross sectional area (mm}^2)} \]  \hspace{1cm} (2)
Figure S7. FT-IR spectra of 50 % HA membrane is compared with that of purified humic acids, exfoliated vermiculite layers: The diminishing intensity of IR band corresponding to O-H vibrations ($I_{3325\text{ cm}^{-1}}/I_{1030\text{ cm}^{-1}} = 0.25$) for soil membrane ($I_{3325\text{ cm}^{-1}}/I_{1030\text{ cm}^{-1}} = 0.71$) as compared to that of pure humic acids ( $I_{3325\text{ cm}^{-1}}/I_{1030\text{ cm}^{-1}} = 0.88$) support involvement of -OH groups in the crosslinking process.
Figure S8. (a) Schematic representation and (b) photograph of the nanofluidic device used for harvesting green energy from concentration difference. (c) Trans-membrane potential of soil membranes as a function of time, under three fold concentration gradient ($C_H = 1 \text{ M}$, $C_L = 0.001 \text{ M}$). For plotting the bar diagram shown in Figure 3b the potential values were taken at around 35 minutes from each curve (dotted circle in the potential curve).

Nanofluidic devices having two compartments separated by soil membrane were fabricated to test the efficiency of energy harvesting from concentration differences by the soil membranes. Typically, chambers were filled with 2 ml aqueous solutions, 1 M KCl in the high concentration ($C_H$) chamber and $10^{-3}$ M KCl in the low concentration ($C_L$) chamber. Two Ag/AgCl electrodes were inserted into the chambers to measure trans-membrane potential and diffusion current across the membrane as a function of time.
Figure S9. UV-Visible spectra comparing the absorbance of methylene blue (MB) before and after passing through (a) 70 % HA membrane, (b) 50 % HA membrane, (c) 30 % HA membrane and (d) 20 % HA membrane respectively for four consecutive times.

60 ml aqueous solution (100 ppm) of Methylene blue (MB) dye was passed through 10 mg membranes of composition 70 %, 50 %, 30 % and 20 % HA and the filtrate was collected and studied under UV-Visible spectrophotometer.
Figure S10. Photographs of the energy harvesting devices after (a) 12 hours and (b) 7 days of immersing in electrolyte solutions.

The stability of Energy harvesting devices with membranes comprising 50 %, 30 %, 20 % and 0 % humic acids were tested over a long period of time by soaking them with electrolyte solutions. The membrane with 0 % humic acids broke after 12 hours while that of composites were stable for more than 10 days.
Figure S11. Raman spectra of 20%, 30% and 50% HA membranes heated at 550 °C compared to 50% HA membrane before heating treatment.
Figure S12. FT-IR spectra of Humic acid and reduced humic annealed at 500 ºC in nitrogen atmosphere. The conversion of carboxyl functionality is demonstrated by the disappearance of carbonyl peak at 1653 cm⁻¹.
Figure S13. XRD pattern of 50% HA film before and after heating at 550 °C in nitrogen atmosphere.
Figure S14. Characteristic I-V curve of pure humic acids heated at 550 °C in nitrogen atmosphere.
Figure S15. (a) Schematic and (b) equivalent circuit of the device used for the impedance analysis. Where, $R_1 =$ membrane resistance, $C_1 =$ membrane capacitance, $R_2 =$ interface resistance, $C_2 =$ interface capacitance. As both the electrodes are symmetrical, the equivalent circuit is simplified into two $R/C$ circuits in series with a Warburg impedance ($W$) for proton diffusion impedance. (c) A representative impedance data fitted with the equivalent circuit shown in Figure S15b.
Figure S16. Schematic representation of experimental set-up used for NH$_3$ vapor sensing.

The sensing device was fabricated by connecting two Cu wires to silver paste painted on both ends of strips cut from heated 50 % HA membrane (dimension 1.5 cm x 4.5 mm x 0.049 mm). The as prepared device was mounted on an aluminium closed container placed on a hot plate (maintained at 100 °C). The container was connected to a nitrogen inlet and outlet to maintain inert atmosphere inside the system. The inside temperature of the container was recorded as 75°C during the measurements. The electrical resistance of the device was recorded by using a Keithley Source meter instrument (model 2450) as a function of time. Ammonia vapors with desired concentrations were introduced by injecting a calculated amount of ammonium hydroxide into the glass container. The response % was calculated by the equation:

\[
\text{Response} \% = \frac{R_a - R_g}{R_a} \times 100 \quad (3)
\]

Where, \(R_a\) and \(R_g\) are the resistance in the absence and presence of ammonia vapors, respectively.
References

