Nanofluidic Transport through Humic acid modified Graphene Oxide Nanochannels

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Figure S1. (a) FE-TEM image (b) FTIR-spectrum (c) UV-Vis spectrum and (d) Fluorescene spectrum of humic acid, extracted following standard alkaline-acid treatment method.

FTIR spectrum of purified humic acid, peaks around 3440 cm⁻¹ and 1657 cm⁻¹ corresponds to O-H vibrational and aromatic C=C stretching band, respectively. The small shoulder peaks around 2850 cm⁻¹ and 1731 cm⁻¹ can be assigned to stretching of aliphatic C-H and C=O of COOH groups. The UV–vis spectrum of humic acid is broad, and monotonously decreases with increasing wavelength with a minor shoulder at around 265 nm. Humic acid exhibit emmision bands around 470 nm due to the presence of aromatic fluorophores with electron donating functional groups. Fulvic acid shows an stronger emission band at 360 nm, absence of the same reveals succesful extraction of humic acid from soil.



Figure S2. (a), (b) and (c) XPS analysis of humic acid sample which shows that the approximate O/C ratio ~ 0.3 . (d) EDX elemental quantification of humic acid sample carried out under an electron microscope.

The sample for EDX analysis was first prepared by dropcasting humic acid dispersion on a

silicon substrate and was gold coated prior to analysis.



Figure S3. (a) AFM image with corresponding height profile and (b) FESEM images of GO sheets prepared by following modified Hummers method. (c) Cross-sectional FESEM image and (d) IR-spectrum of GO membrane.



Figure S4. (a) Zeta potential of GO-HA composite systems are compared with that of neat GO. (b) Agglomeration behaviour of HA, GO and compositie (15% GO-HA) dispersion upon decreasing polarity of the medium.



Figure S5. Quenching of fluorescence intensity of humic acid dispersion upon addition of GO.



Figure S6. FTIR spectra for HA, GO and 15 % GO-HA composite membrane and comparison of stretching frequencies of different functional groups.



Figure S7. Tensile strength of the membranes: (a) Schematic illustration of the set-up used for measuring tensile strength of the membranes. (b) Bar diagram representation of tensile strength of different GO-HA composite membranes.

Stripes of dimension 20 mm \times 3 mm \times 0.0027 mm were anchored on a support in one end and dragged by putting weights at the other end. The weight lifted by each stripe just before tearing apart was taken as the Maximum load (N). Tensile strength values were calculated from equation (*S1*).

 $Tensile \ Strength \ (MPa) = \frac{Maximum \ load \ (N)}{Cross \ sectional \ area \ (mm^2)} \dots S1$



Figure S8. Bending stiffness of the membranes: (a) Schematic representation of bending stiffness measurement. (b) Bar diagram comparing of tensile strength of different membranes with thickness (20 μ m).

Bending stiffness of the composite membranes were calculated employing Lorentzen & Wetre 2-point method.^{1,2} A known load was placed to one end of the strip, by keeping the other end fixed to a glass slide. Equation S2 was used to calculate the bending stiffness values (S_b).

$$S_b = \frac{60 \times F \times l^2}{\pi \times \theta \times b} \quad \dots \qquad S2$$

Where, F is defined as bending force (F= weight × gravitational constant), l is the distance between the clamp and the load, θ is the angle of deflection under the influence of load, b is the width of the strip.



Figure S9. Molecular selectivity and permeability (a) Weight of the dye molecules separated, and (b) time consumed by different membranes to complete the filtration process.

3 ml Methylene blue dye solutions (200 ppm) were passed through each membrane by vacuum assisted filtration method. The concentration of the dye in the solution before and after filtration were determined by recording its UV-Vis spectra.



Figure S10. Evaporation rate of water from a glass vial covered by different membranes with thickness of ~ 20 microns.

For gravimetric determination of gas phase water permeability glass vials filled with water are covered with membranes ($\sim 20 \ \mu m$), vacuum grease was employed to ensure the sealing. Solvents evaporation rate through each membrane was analysed by measuring the weight loss of the sealed vials at regular time intervals



Figure S11. Current response plot of in-plane water diffusivity measurement.



Figure S12. Ionic conductivity of different nanofluidic devices as function of electrolyte concentration showing the point of transition concentration (C_t). C_t of different membranes were determined from intersection of the lines laid over two distinct *viz*. bulk and surface charge governed conductivity regimes.



Figure S13. TEM examinations of the dispersions of (a) 10 %, (b) 15 % and (c) 20 % GO-HA mixtures.

Equilibrium Molecular Dynamics Simulation



Figure S14. (a)-(c) simulated nanoflakes of humic acid. Simulated GO nano sheet of size (d) 100×100 Å². (e)-(f) 70×100 Å².

We also investigated the performance GO-Humic acid composite membrane with different humic acid composition through equilibrium molecular dynamics (MD) simulations. For this we first constructed humic acid nanoflakes and GO nanosheets of various sizes as shown in Fig. S14 where the hydroxyl and epoxy functional groups are located on the basal plane while the carboxyl functional groups are located at the edges³ with an elementary composition of $C_{10}O_1(OH)_1(COOH)_{0.5}$.^{4,5} These GO nano sheets and the humic acid nanoflakes are then arranged in space to get the GO-Humic acid composite membrane of desired proportion. Fig. S15a depicts layered GO membrane without humic acid. Fig. S15b, S15c, S15d represent layered GO membrane with humic acid composition of 10%, 15% and 20% respectively. The value of the geometric parameters of the membranes are as follows: H = 8 Å, W = 5 Å and D = 10 Å. After the construction of the layered GO membrane each of the membrane is hydrated with a water box of size 147 × 102 × 64 Å³. The water molecules within 2 Å of the GO nano

sheet are removed, after which the number of water molecules in the hydrated box are 19894. Then a methylene blue (MB) solution box (4 MB molecules and 7745 water molecules in a box of size $147 \times 102 \times 32$ Å³) is placed above and below the hydrated membrane to construct the



simulation system as shown in Fig. S16.

Figure S15. MD simulated structure of (a) Pure GO membrane (b) 10 % GO-HA membrane (c) 15 % GO-HA membrabe and (d) 20 % GO-HA membrane. Red color is for oxygen atoms, green color is for carbon atoms and cyan color is for hydrogen atoms.

Figure S16. Simulation system with 15% GO-HA membrane. In the GO-HA membrane red color is for oxygen atoms, green color is for hydrogen atoms, cyan color is for carbon atoms. Water molecules are shown with red and green dots with red color for oxygen atoms and green color for hydrogen atoms. The MB⁺ ions are shown with blue color and Cl⁻ ions are shown with black color.

Simulation Methodology



The equilibrium MD simulation was carried out using NAMD 2.11⁶ with optimized potentials for liquid simulations-all atom (OPLS-AA)⁷ force field. We used TIP3P⁸ water model for the water molecules. The bond length of the water molecules is held constant using SETTLE algorithm.⁹ We computed the van der Waals interaction through Lennard-Jones potential with a cut off distance of $r_c = 12$ Å. Particle mesh Ewald method (PME)¹⁰ is used for the long range electrostatic interactions. The equation of motions is integrated through velocity Verlet integration method with a time step of 1 *fs*. The simulation system is then energy minimized and equilibrated for 1 *ns* at a constant pressure of 1 *atm* and temperature of 300 *K*. After equilibration the production run is carried out for each of the system for 8 *ns*. During the simulation the pressure was kept constant with modified Nosé-Hoover method where the barostat oscillation time and damping factors both were set to 0.3 *ps*. Similarly, temperature was kept constant using Langevin dynamics with a damping factor of 5 *ps*⁻¹. In most of the existing literature in membrane simulation membrane are constraint during the simulations. However, in the present work no constraint was applied in the membrane to have a better resemblance with the experiment.



Figure S17. Schematic diagram of the device employed for nanofluidic energy harvesting from concentration gradient.

An nanofluidic device consisting of two chambers, separated by a cation selective GO-HA composite membrane is fabricated by using PDMS elastomers. KCl solution of different concentration were introduced in both the chambers (1 M in the higher concentration chamber, and 10⁻³ M in the lower concentration chamber). A sourcemeter (Keithley 2450) instrument was used record trans-membrane potential and diffusion current across the membranes.



Figure S18. No measurable open circuit voltages were observed when perm-selective GO-HA membrane were replaced with (a) PTFE membrane of pore dimension $1\mu m$ and (b) non-permeable plastic barrier (c) Open circuit voltage harvested from concentration gradient across the different GO-HA membranes through agar-agar salt bridges.

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