Synthesis of Highly Stable and High Water Retentive Functionalized Biopolymer-Graphene Oxide Modified Cation Exchange Membranes

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S1. Physiochemical and Electrochemical Characterization of Hybrid Membrane:

Water uptake, dimension change

All the prepared membranes were dipped in distilled water for 24h. Wet weight and dimension of the membranes were measured. Afterwards the membranes were dried at 70°C and again the weight and dimensions were measured in dry condition. Water uptake was calculated as

$$\emptyset_w = \frac{W_{Wet} - W_{dry}}{W_{wet}} \times 100\%$$

where *Wwet* and *Wdry* are the mass of membranes in wet and dry condition.

Dimensional change is calculated taking the volume difference in dry and wet conditions and is calculated by following equation:

$$\emptyset = \frac{V_{Wet} - V_{dry}}{V_{wet}} \times 100$$

Where V_{wet} and V_{dry} are volume of NTFs in wet and dry condition.

IEC and Ionic conductivity:

IEC refers to the number of mili equivalents of exchangeable charge in polymer. IEC of the membranes was measured by equilibrating the membranes in 1M HCl for 24 h first then in 1M NaCl for further 24h. After that membranes were titrated against 0.1M NaOH solution for exchanged H^+ ions. The IEC was calculated according to the equation:

$$IEC\left(mequiv\ g_{dry\ membrane}^{-1}\right) = \frac{C_{Na^+} V_{sol}}{W_{dry}}$$

where C_{Na^+} is the concentration of Na^+ in the extraction solution and W_{dry} is the dried membrane weight.

Ionic conductivity measurements were carried out after equilibrating the membranes in 1M NaCl. The membranes were sandwiched between two in-house made circular stainless steel electrodes (1.0cm^2). The proton conductivity (κ_m) was calculated from Equation:

$$\kappa_m\ \left(\Omega^{-1}\ cm^{-1}\right) = \frac{L\ (cm)}{R\ (\Omega) \times A\ (cm^2)}$$

where L is the distance between the electrodes used to measure the potential, R is the resistance of the membrane, and A is the surface area of the membrane.

Methanol permeability:

Resistance to methanol crossover of the membranes was evaluated by the measurement of the methanol permeability with a two compartment cell. The concentration of methanol in second compartment was measured as a function of the diffusion time with a refractometer. The methanol permeability (P_M) was obtained by the equation;

$$P_M = \frac{1}{A} \frac{C_{II(t)}}{C_{I(t)} t} V_{II}\ l$$

where A is the effective membrane area, l the membrane thickness, $C_{II(t)}$ the methanol concentration in second compartment at time t, $C_{I(t)}$ the change in the methanol concentration in first compartment at time t, and V_{II} the volume of second compartment. For the suitability of membrane for fuel cell, we calculate the selectivity of the membrane by following equation;

$$S_P = \frac{\sigma}{P_M} \qquad (6)$$

where P_M is the methanol permeability (cm^2/ s), and σ is the membrane conductivity ($S.cm^{-1}$).

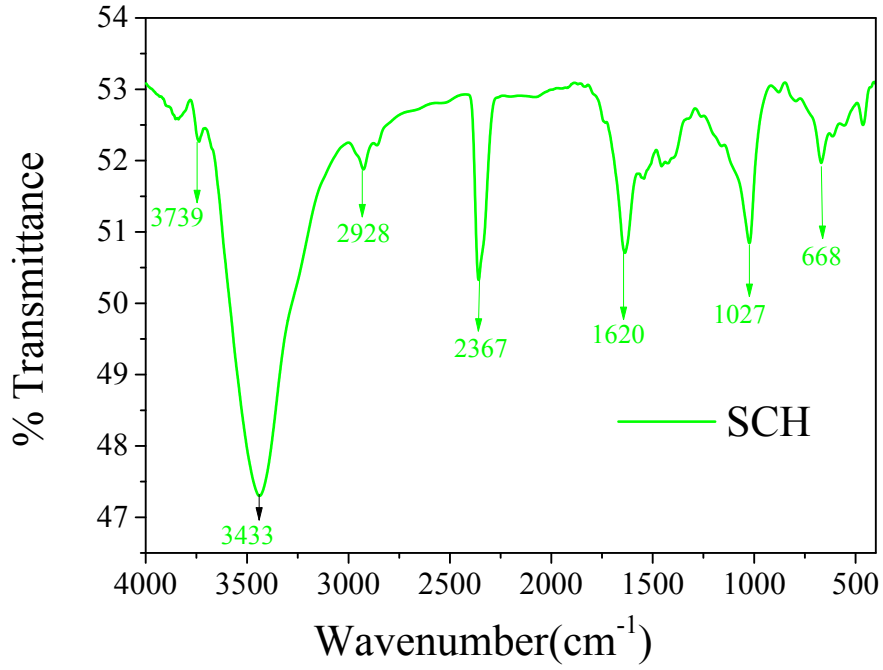

Fig. S1: FTIR spectrum of sulfonated chitosan

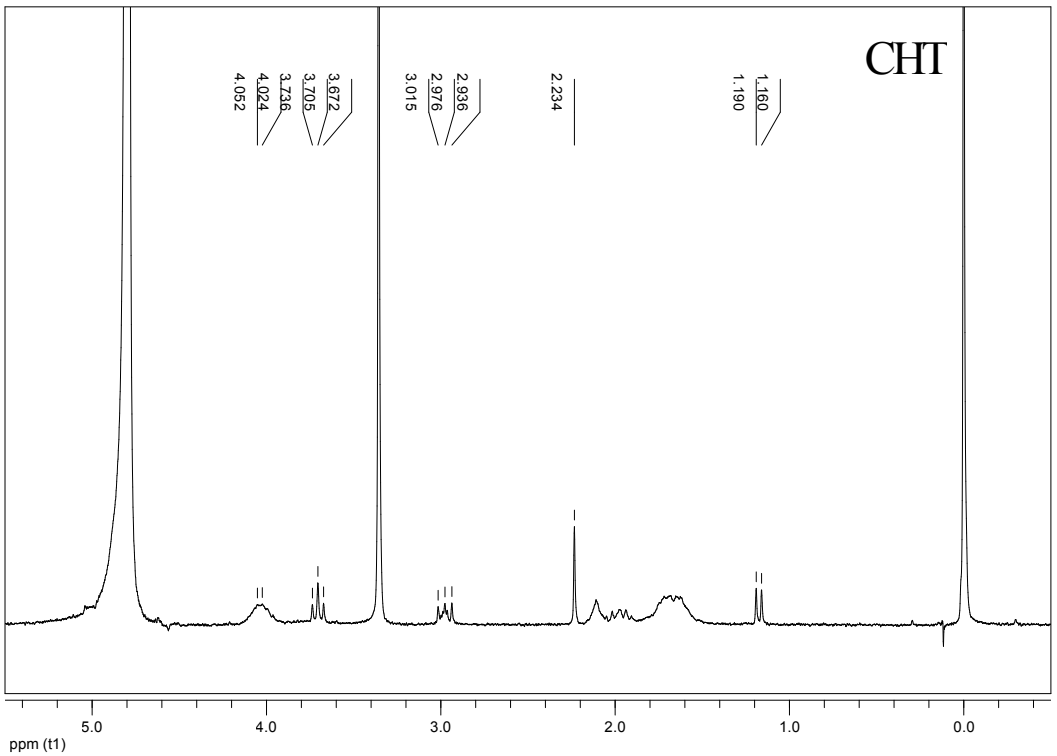

Fig. S2 (a): ^1H NMR spectrum of chitosan

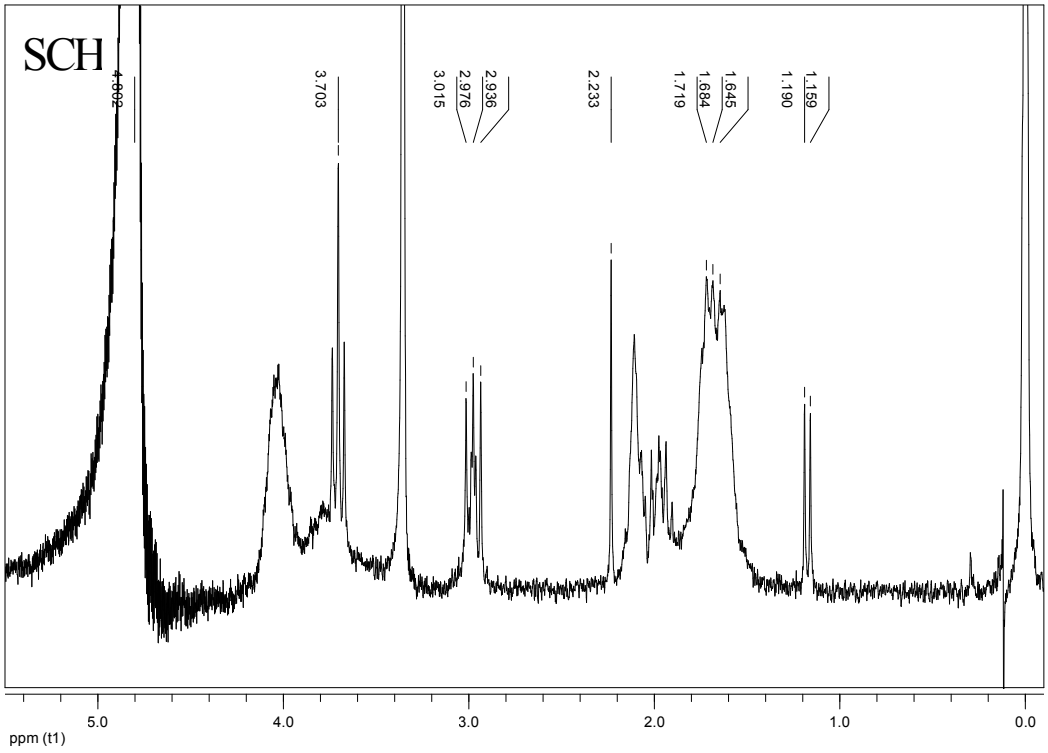

Fig. S2 (b): ^{1}H NMR spectrum of sulfonated chitosan membrane

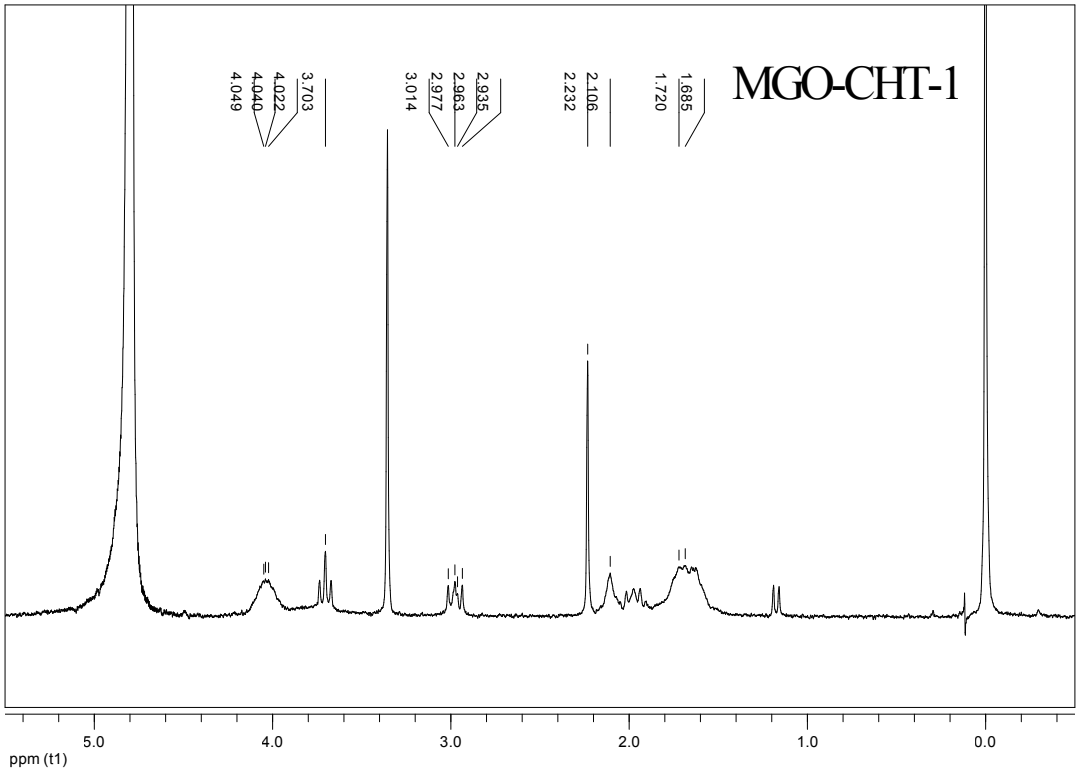

Fig. S2 (c): ^{1}H NMR spectrum of sulfonated chitosan hybrid membrane