

## Supplementary Information

### Microfluidic synthesis of chitosan-based nanoparticles for fuel cell application

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#### Experimental procedure

##### 1. Materials and methods

Chitosan solutions of different concentration were prepared by dissolving 0.25% (w/v) chitosan (medium molecular weight, 280,000 g/mol, degree of deacetylation 83%, Fluka) in 2% (w/v) hydrochloric acid (Sigma-Aldrich) solution and stirring for 24 h. Once dissolved, the chitosan solution was filtered with a syringe 0.45  $\mu\text{m}$  Nylon syringe filter. ATP (Adenosine 5'-triphosphate disodium salt hydrate, Sigma) was dissolved in deionized (DI) water at the concentration 1  $\text{mg}\cdot\text{ml}^{-1}$ .

For bulk synthesis experiments, the chitosan solution was flush mixed with an equal volume of ATP solution and the formation of chitosan-ATP nanoparticles started spontaneously via the ATP initiated ionic gelation mechanism. The nanoparticle suspensions were gently stirred for 60 min at room temperature before being subjected to further analysis.

Microfluidic devices were fabricated with poly(dimethylsiloxane) (PDMS) using a standard micromolding process. To make the master molds, silicon wafers were spincoated with SU-8 50 photocurable epoxy to a thickness of 60  $\mu\text{m}$ . Baking, lithography, and development procedures were performed in EPFL center for micronanotechnology (CMi) to obtain negative microchannels on the wafer. The wafers were annealed at 150  $^{\circ}\text{C}$  to eliminate surface cracks in SU-8. The resulting mold, after thermal annealing, was treated with self-assembly monolayer of trimethylethoxy silane by placing a few drops of the chemical under the hood along with the wafers and leaving it for 40 min for preventing from sticking of PDMS to the mold. PDMS (Sylgrad 184) monomer and curing agent were mixed in a weight ratio of 10:1, pored over the mold, degassed in desiccators and cured in oven at 80  $^{\circ}\text{C}$  for 1 h. After curing, PDMS was removed from the mold and in-/outlet holes were punched using a 150  $\mu\text{m}$  diameter puncher. The PDMS component was then bonded to a glass slide using oxygen plasma (100 mW, 1 min). The resulting device had two inlets for ATP aqueous solution and one for chitosan solution streams, and one outlet. The water stream was split into two in order to achieve two water streams at the flow focusing (T-) junction. The mixing channel was 150  $\mu\text{m}$  wide, 60 $\mu\text{m}$  high and 1 cm long. Moreover, the mixing time,  $\tau_{mix}$ , can be estimated from the diffusion timescale<sup>1</sup> as Supplementary Equation S1.

$$\tau_{mix} \sim \frac{w_f^2}{4D} \approx \frac{w^2}{9D} \frac{1}{(1 + 1/R)^2} \quad (S1)$$

where,  $w$  is channel width (150  $\mu\text{m}$ ),  $D$  is  $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  and  $R$  is the ratio of flow rate of the polymeric stream to the total flow rate of ATP ( $R = 0.03-0.1$ ) controlled using syringe pumps and silicon rubber tubing.  $w_f$  can be estimated as the width of the focused chitosan stream (when  $R < 1$ ). Above equation predicts a mixing time in the range of 2.5-23 ms in our case.

Membranes were prepared using CS-ATP NPs at 2.0 wt% which was suspended in Nafion<sup>®</sup> solution at room temperature and stirred for 2.5 h. The resultant mixture was ultra-sonicated for 5 min intervals was cast on Petri dishes and incubated at room temperature overnight and then dried at 70°C for 8-10 h. Finally, fabricated membranes annealed at 120°C for 12 h. A similar procedure was carried out to prepare membranes based on unfilled recast Nafion.

Membrane electrode assemblies (MEAs) were prepared via the catalyst painting technique.<sup>2-4</sup> Pt-black and Pt-Vulcan XC72 were used as catalysts for the anode and cathode, respectively. The catalysts were mixed with Nafion<sup>®</sup> solution and several drops of glycerol. The suspension was brushed directly ( $2 \text{ mg.cm}^{-2}$ ) onto the membranes, and hot-pressed to increase the contact area between the catalysts and membranes. The area of the tested membranes was  $3 \times 3 \text{ cm}^2$  and MEAs were fabricated using a  $200 \text{ kg.cm}^{-2}$  hot-press at 120°C for 90 s for each side of membranes.

## 2. Characterization

Transmission electron microscopy (TEM; CM200-FEG-Philips) was used to characterize the chitosan based nanoparticles. A dilute suspension of CS-ATP NPs was prepared from which the particles were deposited onto the Cu grid that supported a carbon film. The particle shape and sizes were characterized via diffraction (amplitude) contrast and, for crystalline materials, by high resolution (phase contrast) imaging. TEM with LaB6 source operated at 200 kV accelerating voltage. The images were characterized using ImageJ software with at least 20 different measurements.

Dynamic light scattering (DLS) measurement performed at our measurements with DLS (Zetasizer 3000HS, Malvern Instruments Ltd., Worcestershire, UK) at backscattering mode at 173° for water diluted systems in the DLS cuvettes.

Two types of water, freezing (free) and nonfreezing (bound) water molecules, in the membranes were detected by melting transitions in differential scanning calorimetry (DSC; Perkin-Elmer) with a liquid nitrogen-cooled heating element. The temperature scale of the calorimeter was calibrated with In. All of the samples were weighed ( $5 \pm 0.2$  mg) and enclosed in an aluminum pan. An empty aluminum pan was also used as the reference. Each sample was first cooled from 25°C to -50 °C and then heated to 40°C at a heating rate of 5 °C.min<sup>-1</sup>. Reported data are the average of three determinations.

The amount of bulk water in the samples was calculated by integrating the peak area of the endotherm melting. The degree of crystallinity for water that is obtained from the heat of fusion of pure ice was used as the standard.<sup>5</sup> The weight fraction of free water ( $\omega_f$ ) to the fully-hydrated membranes can be estimated from the total melting enthalpy ( $\Delta H_m$ ) that is obtained by integration of the transition heat capacity ( $\Delta C_p$ ) over the broad melting temperature interval. The weight fraction of free water ( $\omega_f$ ) was calculated based on Supplementary Eq. S2:

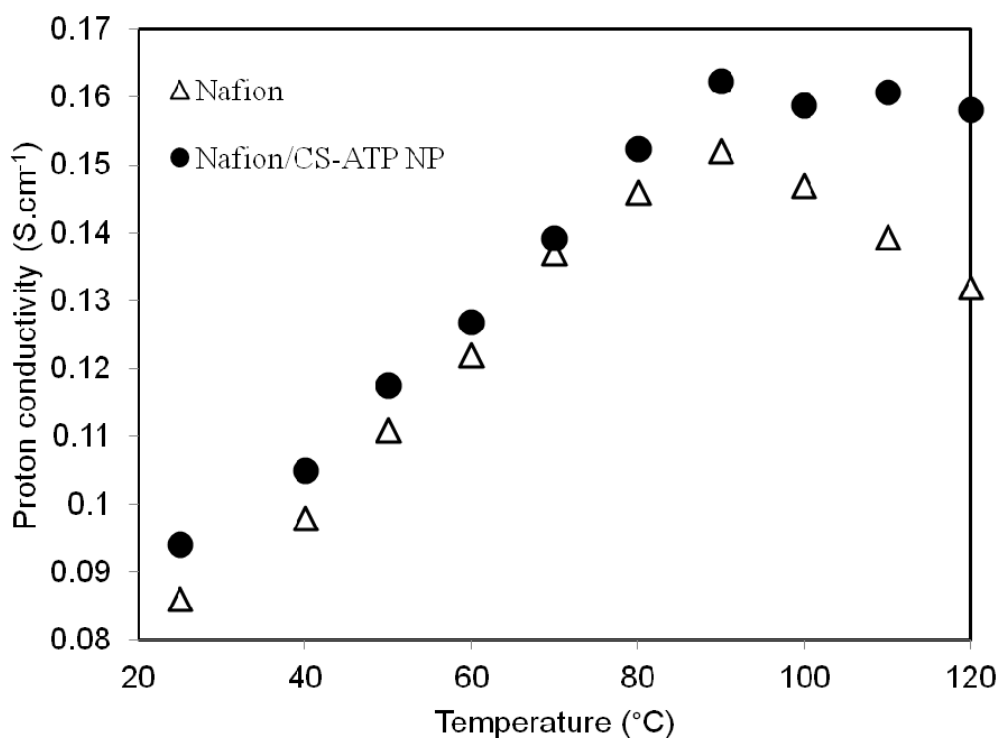
$$\omega_f = \frac{\Delta H_m}{Q_{melting}} = \frac{\int \Delta C_p dT}{Q_{melting}} \quad (\text{S2})$$

where  $Q_{melting}$  is the heat of fusion of bulk ice (334 J/g). The weight fraction of bound water ( $\omega_b$ ) is calculated by subtracting the amount of freezing water ( $\omega_f$ ) from the total water uptake ( $\omega_t$ ). The bound water degree ( $\chi$ ) is also defined as a ratio of the amount of bound water to the total water uptake<sup>2</sup>.

CS-ATP also improved water-retention ability of the membranes. After drying at 100°C for 4 h under vacuum, and exposing in 40% R.H. the nanocomposite membranes<sup>6</sup> contained about 22.5 wt% water, which is much higher than 11 wt%, which is reported for the pure Nafion membrane.

Small angle X-ray scattering (SAXS) analysis of the membranes was carried out by using a diffractometer equipped with Cu K source and Kratky SAXS apparatus. The water swelled samples were used in a sealed sample holder at 25°C. The chamber was maintained under vacuum. The intensity of the X-ray scattering is plotted versus the scattering vector,  $q$ , defined as  $q = (4\pi/\lambda) \sin \theta$ , where  $\lambda$  is the X-ray wavelength and  $2\theta$  is the scattering angle.

The proton conductivity of the fully hydrated membranes was measured at room temperature via the AC electrochemical impedance spectroscopy method, using a Solartron Interface 1260 gain phase analyzer over the frequency range of 1-10<sup>6</sup> Hz. The conductivity values were calculated from the  $\sigma = L \cdot R^{-1} \cdot A_e^{-1}$  formula, where  $L$  is the membrane thickness,  $A_e$  is the cross-sectional area of the membrane and  $R$  is the resistance. Bekktech Conductivity Cell has been used to measure the bulk conductivity of membranes. For conductivity measurements, the samples were put into humidity control chamber to reach to their equilibrium hydrated state for conductivity measurement. The obtained data are reported as the average of at least three samples. The standard deviation (S.D.) was found to be less than 8% for all measurements.



**Supplementary Figure S1.** Proton conductivity of prepared Nafion/CS-ATP nanocomposite membranes as a function of temperature in comparison with pristine membranes.

The oxygen permeability of membranes were determined using constant pressure/variable volume method at 25 °C via laboratory made test cell using the following equation:  $P = Q.l./[A.(p_1-p_2)]$ , where  $Q$  is the flow rate of the permeate molecules through the membrane,  $l$  is the membrane thickness,  $A$  is the effective membrane area,  $p_1$  and  $p_2$  are the absolute pressures of feed side and permeate side, respectively. The permeability coefficient is expressed in Barrer units ( $\times 10^{10} \text{ cm}_{(\text{STP})}^3 \text{ cm.cm}^{-2}.\text{s}^{-1}.\text{cmHg}^{-1}$ ). Permeability measurements were performed on at least three multiple samples, and obtained results have been reported as the average with standard deviation (S.D.) lower than 15%.

The PEMFC single cell was composed of stainless steel as the end plates and flow fields, two carbon papers as the gas diffusion layers (GDL, TGP-H-120 Toray), silicon rubber sheets as the sealants and a membrane electrode assembly (MEA). The performance of the single cell was evaluated at 40% R.H for hydrogen and oxygen flows into the anode and cathode sides at 120°C. The cell temperature as well as the temperature of anode and cathode sides was fixed at 120°C, which was controlled by preheating the fuels. The relative humidity (RH) was fixed at 70% RH. Hydrogen and oxygen was introduced to the cell with gradual pressure increase to 138 kPa, and the cell was allowed to run for half an hour before collecting the polarization curves data. All single cell performance tests were performed on multiple samples and the results are presented as the mean values. Kinetic parameters derived based on curve fitting on cell potential ( $E$ ) versus current density ( $I$ ) data points to the following equation:  $E = E_0 - b \cdot \text{Log} I - R \cdot I$ , (Supplementary equation S3), where  $E$  and  $I$  are the measured cell potential and current,  $b$  is the Tafel slope, and  $R$  accounts for the linear variation of overpotential with current density primarily due to ohmic resistance.<sup>7</sup>

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