Electronic supplementary information

Gold nanoparticle embedded microchannel array for enhanced power generation

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Procedure for determination of EDL thickness inside microfluidic channels

Determination of EDL thickness of the working fluid during flow at a fixed inlet pressure was necessary in order to support the hypothesis regarding increase of EDL thickness for flow of ultrapure water in PDMS and PDMS-AuNP micro fluidic channels. The EDL thickness was estimated using Debye Huckel's parameter (Eq. 1).

$$\frac{1}{k} = \sqrt{\frac{\in_r \in_0 k_b T}{2z^2 e^2 \eta_0}} \tag{1}$$

Where 1/k is the EDL thickness, ε is the effective dielectric constant of the working fluid inside the micro fluidic channel, k_b is the Boltzmann constant, T is the absolute temperature, z is the valence of ions, e is the charge on proton, η_0 is the bulk concentration of ions in the working fluid in mol/m^3 and ε_0 is the permittivity of free space. In Eq. 1, z is equal to 1, η_0 is 10^{-7} mol/L or (10^{-7} mol/LX1000L/m^3XAvagardo number) mol/m^3, T is 298.15 K (room temperature of 25°C), e is 1.602X10^{-19}C, k_b is 1.3807X10^{-23} J/K, ε_0 is 8.85X10^{-12} F/m.

In order to evaluate the effective dielectric constant ε_r of the working fluid a PDMS micro fluidic channel with and without embedded AuNP was fabricated. The channel had a channel width of 1 mm, length 5 cm and height of 56 µm. The PDMS channel had an inlet and an outlet as hollow stainless tubes. The channel area near to the outlet was exposed with UV laser radiation with laser power of 0.5 W using the same CNC based laser used for mold fabrication in our experiments. The exposure was controlled such that the exposed portion has a length of 1 cm from the outlet of the channels. UV exposure leads to adhesion of the conducting ink since the area of exposure becomes hydrophilic in nature. Electrode of size 1 cm (equal to length of UV exposed portion) and breadth 1mm (breadth of channel) was printed using silver conductive ink employing Voltera VOne PCB printer. The thickness/ height for the printed footprint was 20 µm which is the also the repeatability of the PCB printer. The printed electrode is such that it was in contact with outlet stainless steel tube. Thus the outlet tube acted as fluid outlet and one of the electric terminals. The micro channels were attached to a cell cast acrylic sheet employing scotch tape. Prior to attachment, same silver conducting ink was printed on the acrylic sheet with dimensions 1 cmX 1 mm which is also the electrode area (A). The printed PDMS as well as acrylic were baked for 30 min at 90°C so that the printed ink gets adhered rigidly. The cured ink on PDMS as well as acrylic sheet was thoroughly washed in DI water to check the adhesion of the ink to the surfaces. A hole was drilled in the sheet in order to accommodate a current collector which remains in contact with the printed electrode on the acrylic sheet. The hole accommodating the current collector was rigidly sealed with industrial glue to avoid leakage. This current collector and the outlet stainless tubing acted as the connections for a potentiostat. The printed electrodes on the PDMS channel and the acrylic sheet acts as a parallel plate capacitor inside the micro channel with the effective working fluid as the dielectric medium. Since the print height from both sides (PDMS channel and acrylic sheet was 20 µm, i.e. 40 µm in total) the electrode gap (d) was calculated from the difference of net channel height and net print height (56µm-40µm= 16µm). The arrangement along with the dimensions of the printed ink on PDMS as found under a microscope is shown in Fig S1.

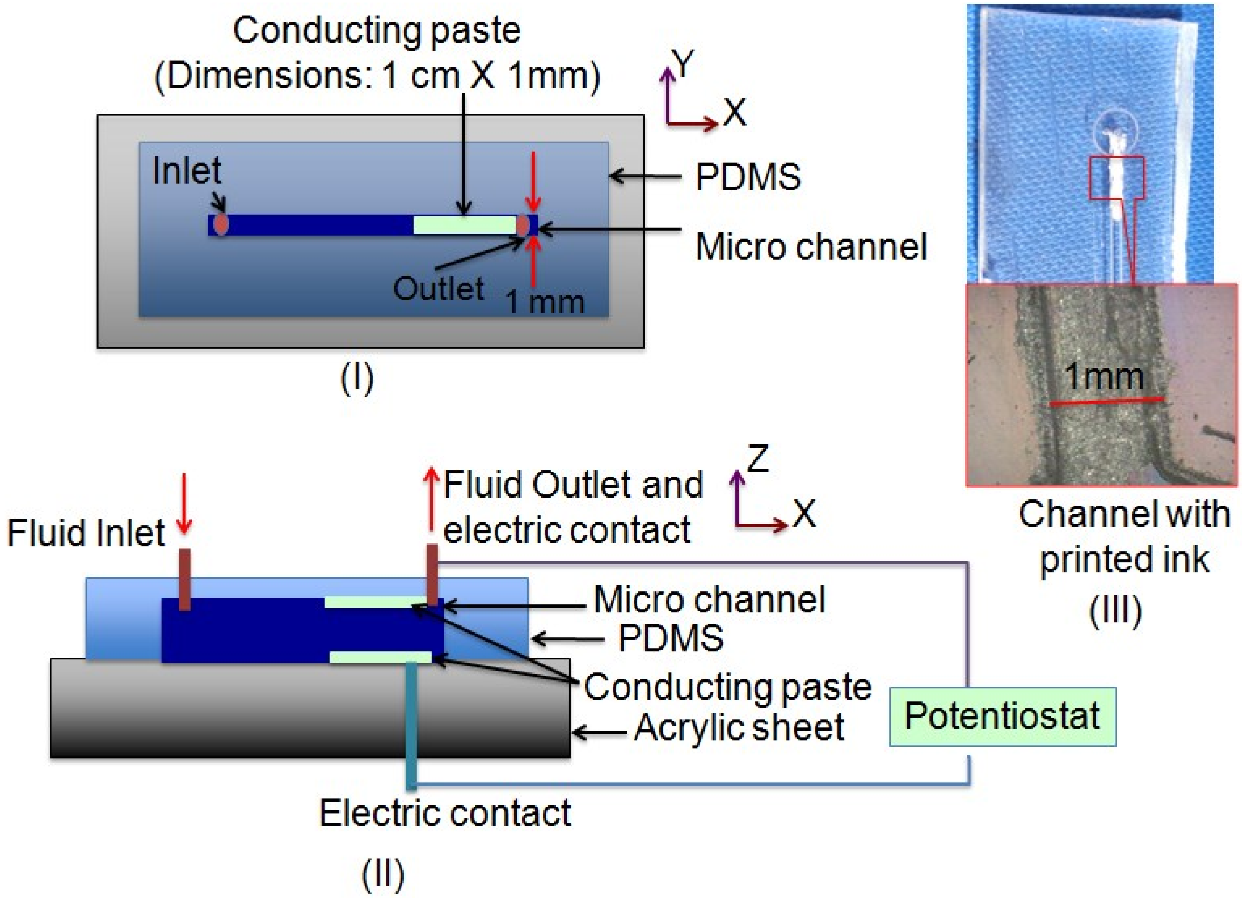

Fig S1 (I) Top view of the fabricated micro fluidic channel (II) Side view of the fabricated micro fluidic channel (III) The micro fluidic channel and the adhesion of ink as seen under microscope.

The cyclic voltammetry (I-V) plots were recorded employing a potentiostat (Model: PARSTAT4000). The capacitance (C) pertaining to the working fluid inside the micro fluidic channel under stationary as well as flow conditions were found using Eq. 2.

$$C = \frac{i_{avg}}{sA} \qquad (2)$$

The cyclic voltammetry plots for ultrapure water as working fluid under pressure and stationary conditions in the PDMS micro fluidic channels with and without AuNP are shown in Fig S2. The plotted curves are drawn with 10-point moving average data filter which enhances smoothing of data and is available in the potentiostat software.

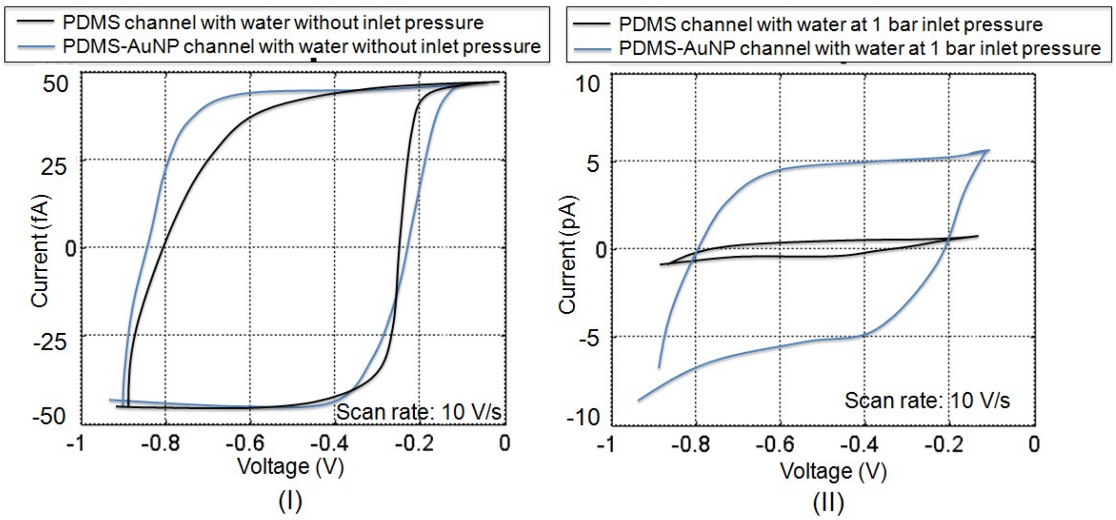

Fig S2

Cyclic voltammetry plots for PDMS channels with and without AuNP (I) without pressure flow (II) with pressure flow

Where, i_{avg} is the average of the peak recorded current in the I-V plots for the anodic and cathodic sweeps, s is the scan rate and A is the effective area of the electrodes. Since a parallel plate capacitor is formed inside the micro channel, Eq. 3 is valid and the dielectric constant of the working fluid can be found.

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \tag{3}$$

The calculated parameters from cyclic voltammetry and EDL thickness for ultrapure water as working fluid are summarized in Table S1.

Channel type and conditions	**i_{avg} from Cyclic voltammetry**	**Effective dielectric constant (ε_r)**	**EDL thickness**
PDMS channel without pressure	44.25 fA	79.98	0.97 µm
PDMS channel with 1 bar inlet pressure	0.542 pA	980.81	3.4 µm
PDMS-AuNP channel without pressure	44.23 fA	79.97	0.97 µm
PDMS-AuNP channel with 1 bar inlet pressure	5.216 pA	9425.6	10.54 µm

Calculation of power density from I-V curves

The power generated at 1 bar inlet pressure for the flow of ultrapure water was calculated from the I-V curves. In order to plot the I-V curves, the current density was obtained by varying the external resistances and placing them in series with the wires to measure the current values at 1 bar inlet pressure. The overall electrode area for electron transfer was 0.18 cm^2 found from the diameter of hollow stainless steel tubes which were used both as fluid inlet/ outlets and current collector. The maximum power was determined from the I-V plots as shown in Fig S3.

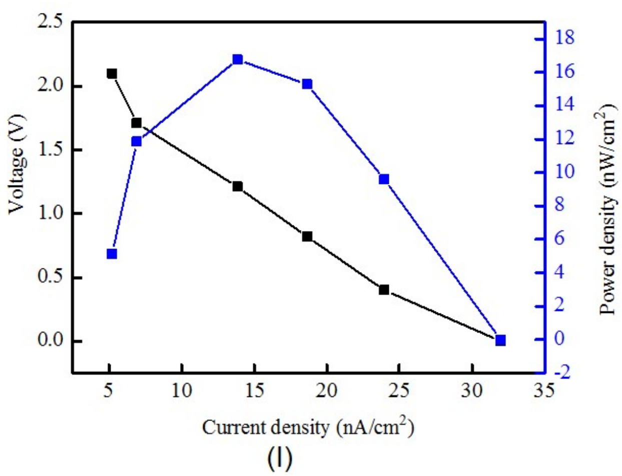

Fig S3 The I-V curve for (I) PDMS micro channel (II) PDMS-AuNP micro channel with ultrapure water at 1 bar inlet pressure as working fluid

The maximum power density was 16.8 nW/cm^2 and 4.3 μW/cm^2 for PDMS and PDMS-AuNP micro channel respectively.

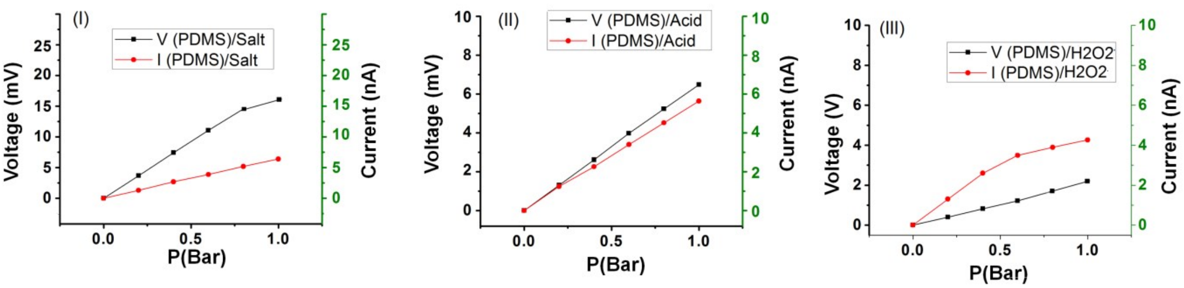

Fig S4 Streaming potential and current versus input pressure in (I) PDMS micro channel array with 0.1 M NaCl solution as fluid (II) PDMS micro channel array with 0.1 M HCl solution as fluid (III) PDMS micro channel array with 40% H_2O_2 solution as fluid