Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.


# Supplementary Information for: Current rectification by nanoparticles in bipolar nanopores

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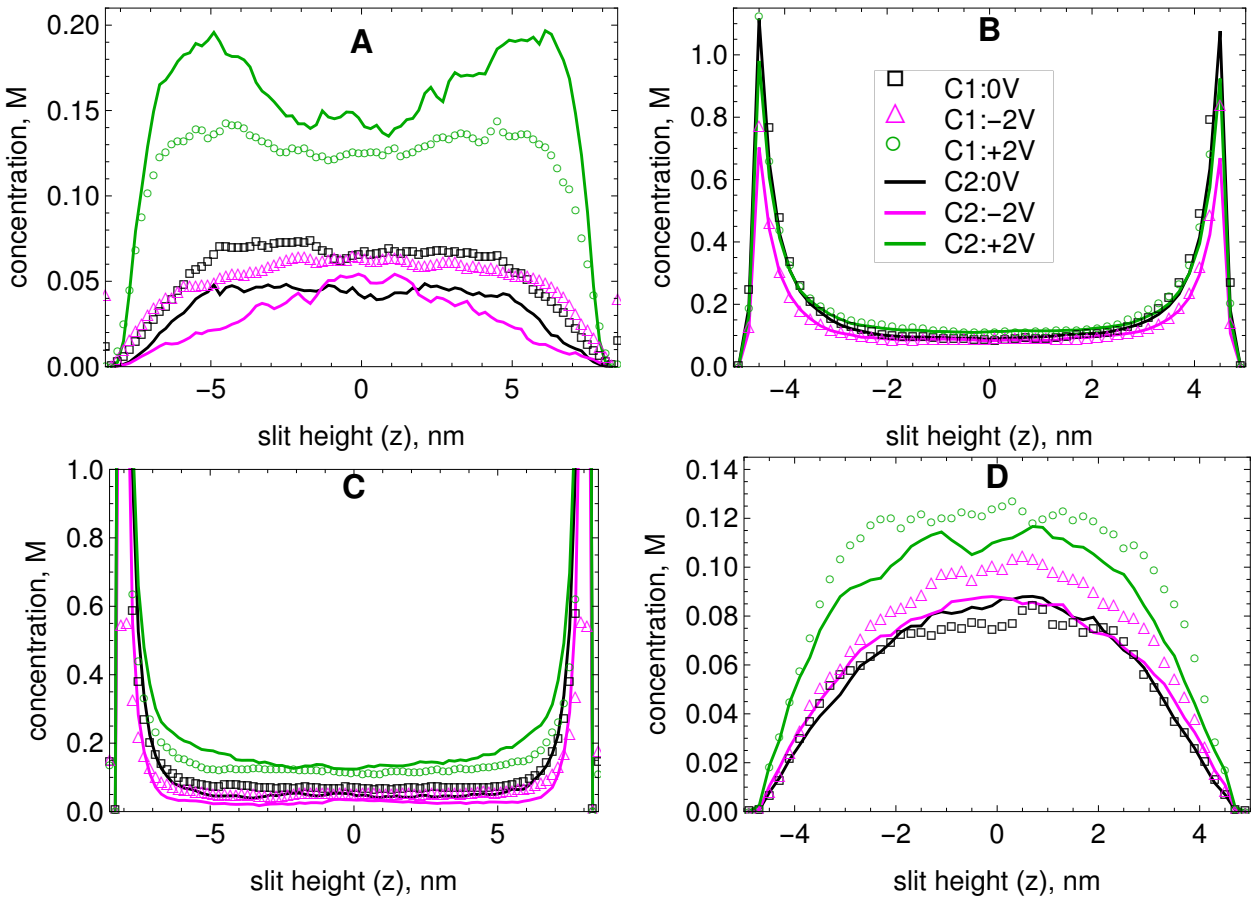


Figure S1: Top Row: Concentration profiles for the cations, $Na^+$, in the two nanopores considered here, the symbols are for C1 and the lines are for C2. Bottom Row: Concentration profiles for the anions, $Cl^-$, in the two nanopores considered here, the symbols are for C1 and the lines are for C2. A) and C) show the concentrations as a function of the channel's height in the wide section of the nanopores. B) and D) show the concentrations as a function of the channel's height in the narrow section of the nanopores.

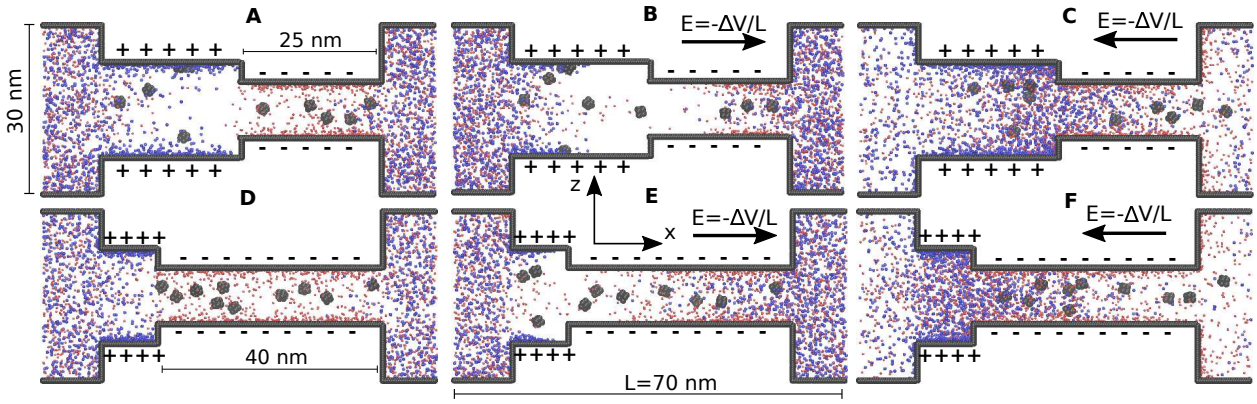


Figure S2: Orthographic projections of steady-state configurations for the two bipolar slit nanopores considered in this work. The top row is for nanopore C1 and the bottom row for nanopore C2. Sodium ions are represented as red dots and Chlorine ions as blue dots. Black dots represent the interaction sites that make up the nanoparticles and the channel walls. The cases shown here are with negatively charged nanoparticles added. The cases with positively charged nanoparticles added are shown in the main text. In A and D no bias is applied (*i.e.* equilibrium). B and E have a negative, $-2$ V, bias applied. And C and F have a positive bias, $+2$ V, applied.

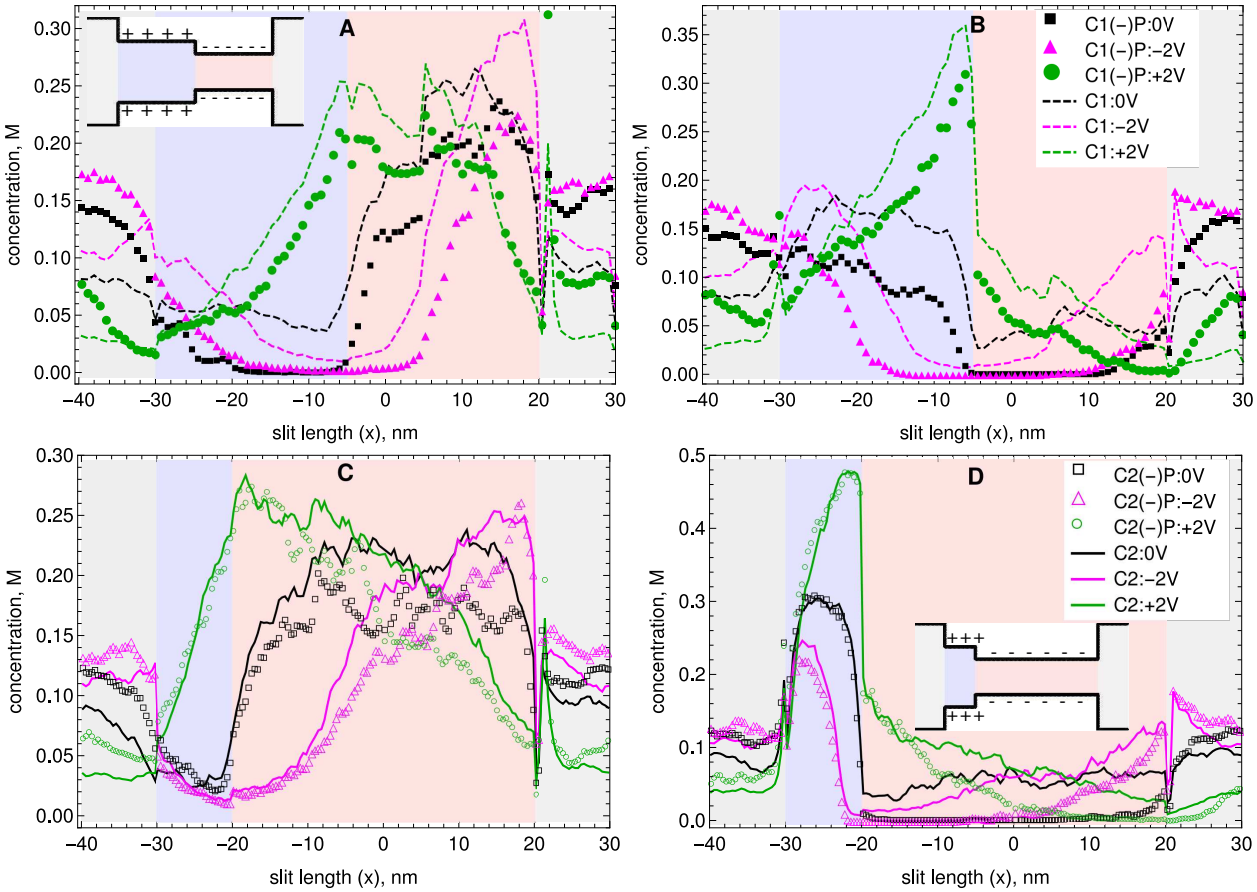


Figure S3: Average concentration as a function of channel length of A) cations and B) anions in C1 at equilibrium and for two different applied voltages with (symbols) and without (dashed lines) the addition of negatively charged nanoparticles. Concentration of C) cations and D) anions in C2 at equilibrium and for two different applied voltages with (symbols) and without (lines) the addition of negatively charged nanoparticles. The background colors indicate the different sections of the nanopores. The insets with the drawings of the nanopores show to which section each color corresponds. The concentration profiles with addition of positively charged nanoparticles are given in the main text.

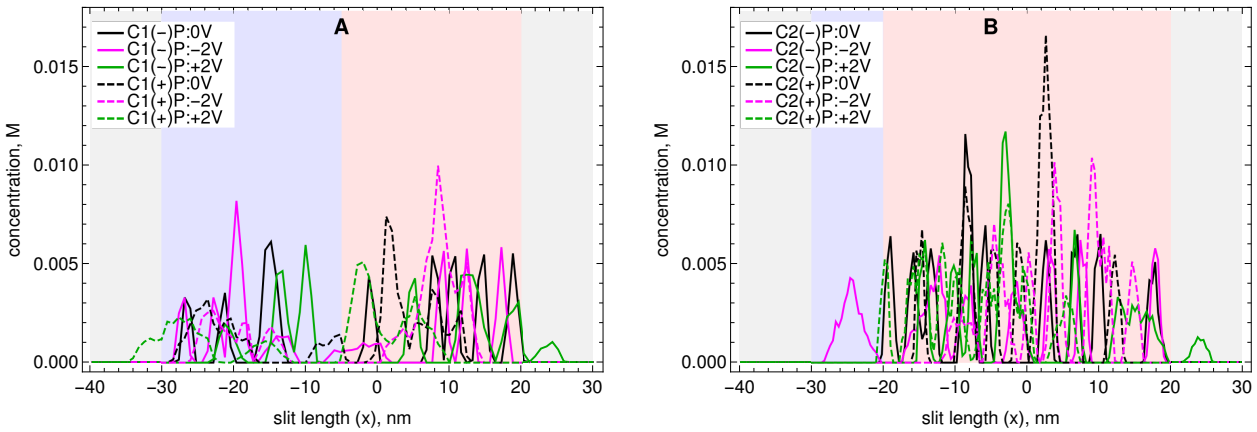


Figure S4: Concentration of nanoparticles as a function of channel length in A) C1 and B) C2 at equilibrium and for two different applied voltages with negatively charged nanoparticles (solid lines) and positively charged nanoparticles (dashed lines). The background colors indicate the different sections of the nanopores. The insets with the drawings of the nanopores show to which section each color corresponds.

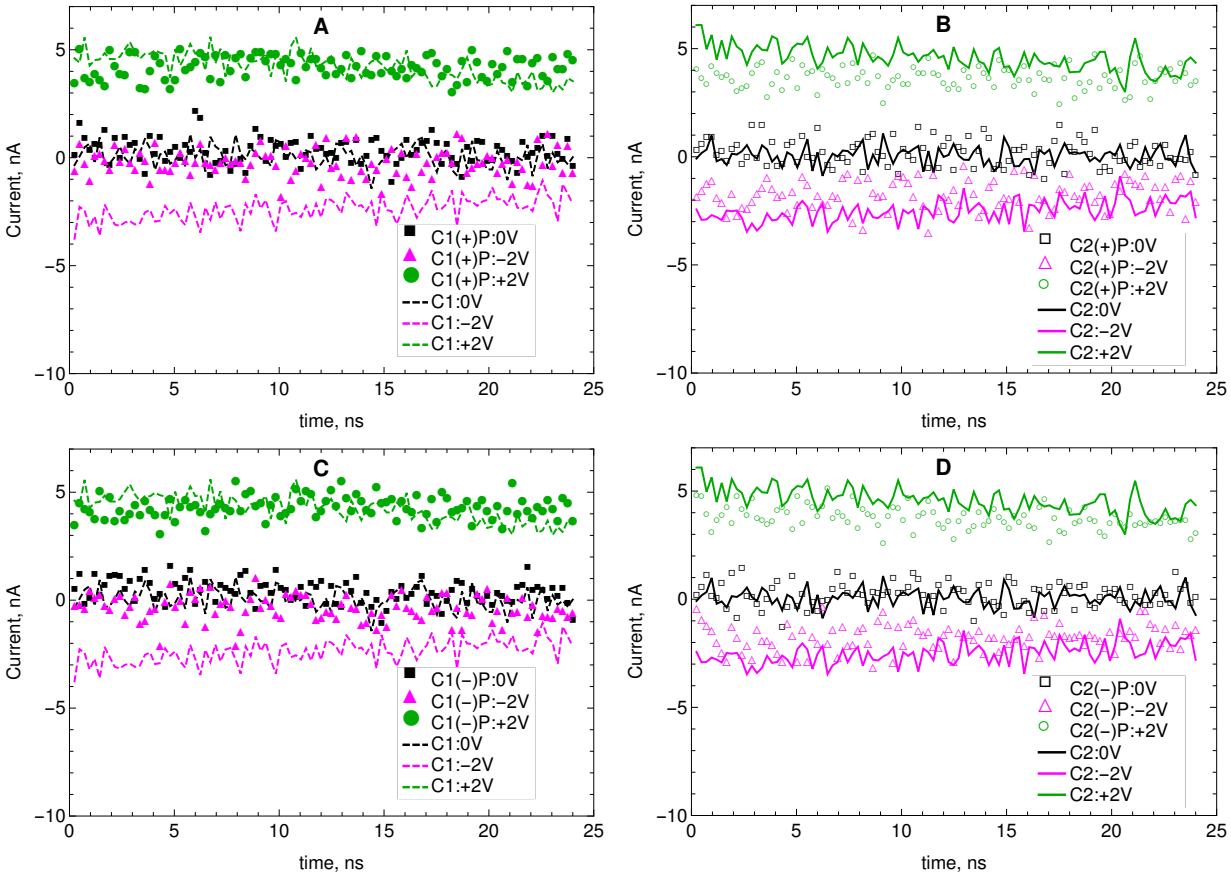


Figure S5: Electric current as a function of time in the last 24 ns of our production runs. This time series data is the one used to calculate the average and the statistical uncertainties of the electric currents reported in the main text. A) Shows the comparison is for C1 with and without positively charged nanoparticles added. B) Shows the comparison is for C2 with and without positively charged nanoparticles added. B) Shows the comparison is for C1 with and without negatively charged nanoparticles added. C) Shows the comparison is for C2 with and without negatively charged nanoparticles added.

Table S1: Summary of the average electric current for the different systems considered in this work. The statistical uncertainties for the average electric currents are calculated using the blocking transformation method of Flyvbjerg and Petersen[1] which is applicable to estimating statistical error in averages of time series data and properly accounts for the correlation in the data.

| Additive | Electric current, nA | | | |
|---|---|---|---|---|
| | $I_{-2V}$ | | $I_{+2V}$ | |
| | C1 | C2 | C1 | C2 |
| None | $-2.4 \pm 0.06$ | $-2.5 \pm 0.05$ | $4.2 \pm 0.13$ | $4.6 \pm 0.09$ |
| Negatively Charged | | | | |
| 10 Particles | $-0.35 \pm 0.06$ | $-1.7 \pm 0.06$ | $4.3 \pm 0.05$ | $3.8 \pm 0.06$ |
| Positively Charged | | | | |
| 10 Particles | $-0.19 \pm 0.06$ | $-1.7 \pm 0.06$ | $4.2 \pm 0.04$ | $3.7 \pm 0.05$ |

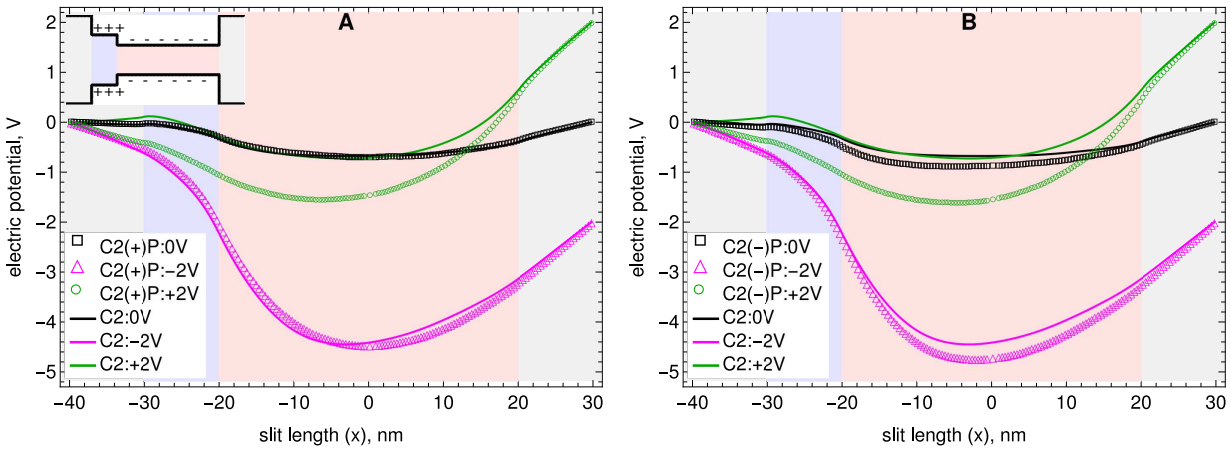


Figure S6: Effect on the electrical potential as a function of channel length for C2 when A) positively charged nanoparticles are added and B) negatively charged nanoparticles are added. The background colors indicate the different sections of the nanopore. The inset with the drawing of the nanopore shows to which section each color corresponds. The electrical potentials in nanopore C1 are given in the main text.

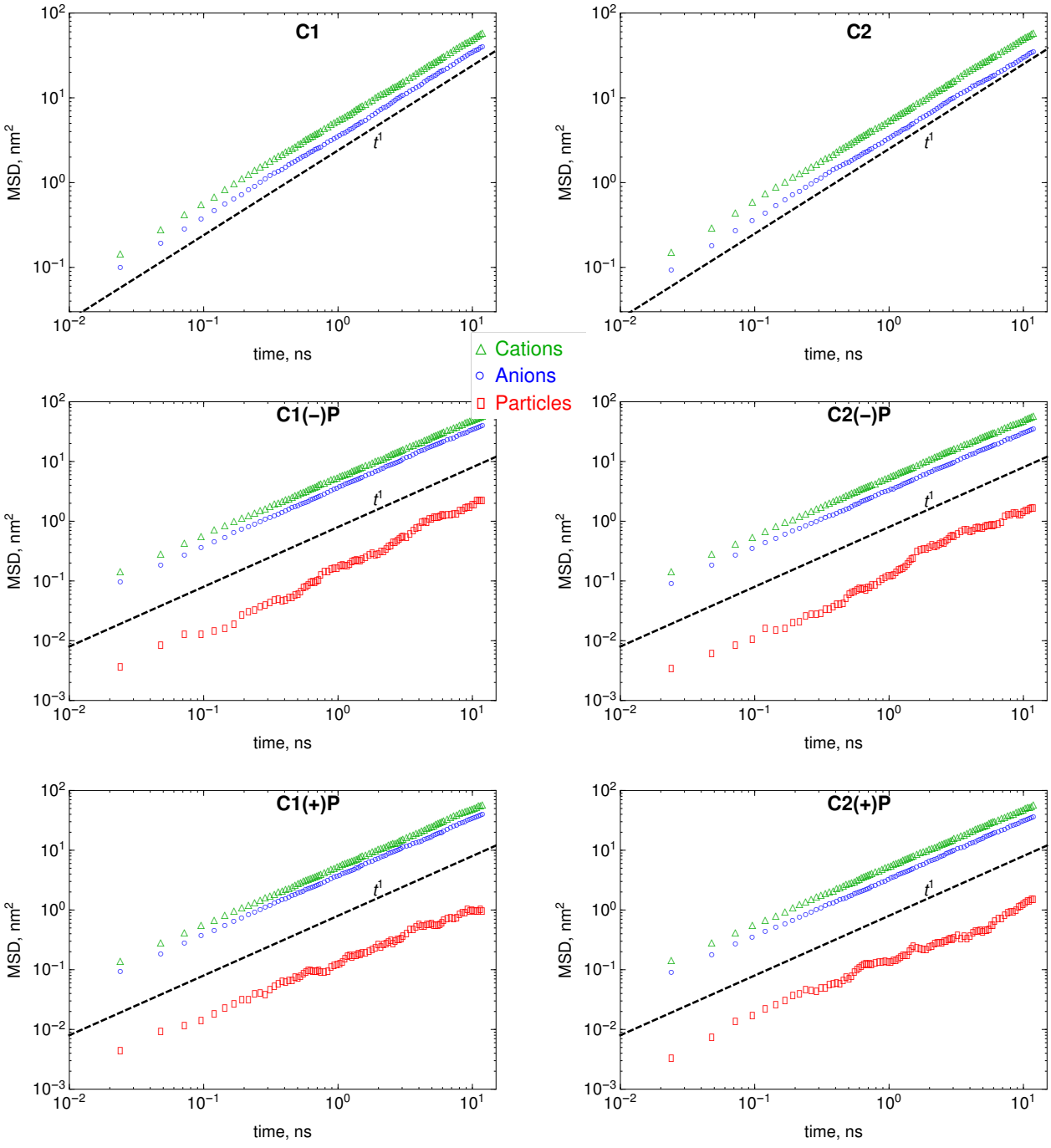


Figure S7: Mean squares displacement (MSD) of the ions, anions and nanoparticles inside the nanopores considered in this work. The MSDs are calculated in the system without applied voltage bias and after the systems have reached equilibrium.

Table S2: Diffusion coefficients for cations, anions and nanoparticles obtained from the mean squared displacements, $\langle \Delta r^2(t) \rangle_{\mathrm{eq}}$, shown in Fig. S7 using the relation, $\mathcal{D} = \langle \Delta r^2(t) \rangle_{\mathrm{eq}} / (6t)$.

| Additive | Diffusivity $\times 10^{-10}$ m$^2$/s | | | | | |
|---|---|---|---|---|---|---|
| | cations | | anions | | particles | |
| | C1 | C2 | C1 | C2 | C1 | C2 |
| None | 9.0 | 9.1 | 6.0 | 5.6 | – | – |
| | Negatively Charged | | | | | |
| 10 Particles | 9.2 | 9.1 | 6.1 | 5.6 | 0.28 | 0.23 |
| | Positively Charged | | | | | |
| 10 Particles | 8.9 | 9.0 | 6.2 | 5.6 | 0.22 | 0.22 |

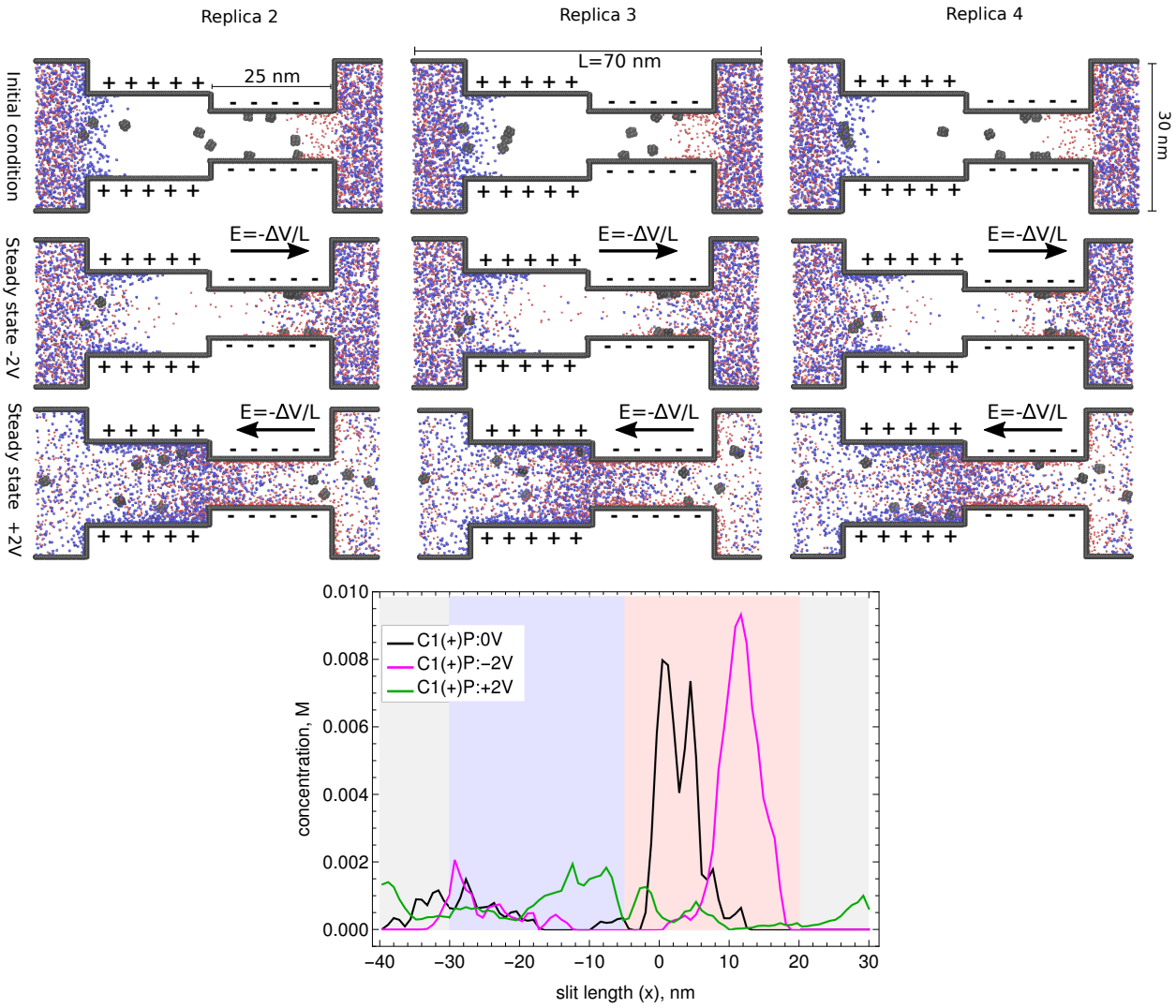


Figure S8: Orthographic projections of nanopore C1 with positively charged nanoparticles added. Three replicas of the simulation starting from different initial conditions (top row) are shown. The second and third rows correspond to steady-sates for negative, $-2$ V, and positive, $+2$ V, bias respectively. These replicas were performed using a larger damping factor for the nanoparticles, namely $\tau_{\mathrm{m}}^{\mathrm{np}} = 79 \times 10^{-15}$ s. The bottom row shows the steady-state nanoparticle concentration as a function of the channel length obtained from averaging the four replicas done for C1 with positively charged nanoparticles.

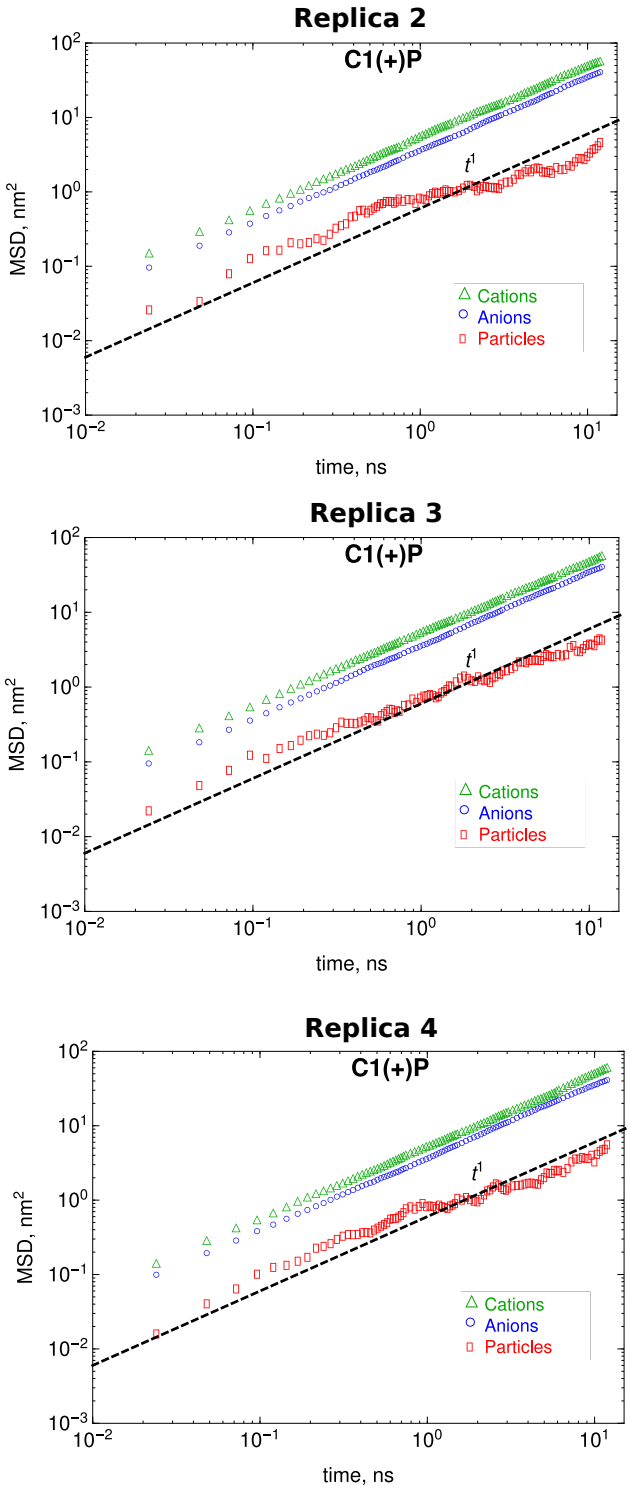


Figure S9: Mean squares displacement (MSD) of the ions, anions and nanoparticles inside nanopore C1 with positively charged nanoparticles added. The MSDs are calculated in the system without applied voltage bias and after the systems have reached equilibrium. These replicas were performed using a larger damping factor for the nanoparticles, namely $\tau_{\mathrm{m}}^{\mathrm{np}} = 79 \times 10^{-15}$ s.

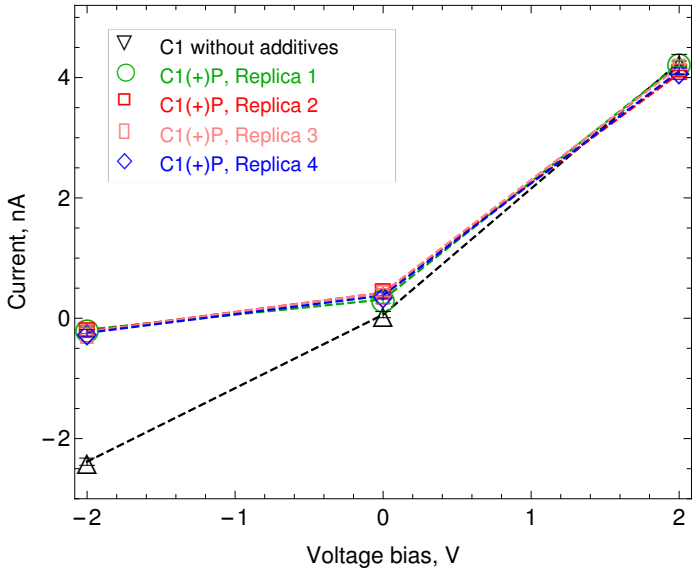


Figure S10: Current-Voltage relationship for nanopore C1 without additives and with positively charged nanoparticles added. Replica 1 was performed with $\tau_m^{np} = 10 \times 10^{-15}$ s while replicas 2, 3 and 4 were performed with $\tau_m^{np} = 79 \times 10^{-15}$ s.

Table S3: Summary of the average electric current for the different replicas of the simulations of nanopore C1 with positively charged nanoparticles. Replica 1 was performed with $\tau_m^{np} = 10 \times 10^{-15}$ s while replicas 2, 3 and 4 were performed with $\tau_m^{np} = 79 \times 10^{-15}$ s. The statistical uncertainties for the average electric currents are calculated using the blocking transformation method of Flyvbjerg and Petersen[1] which is applicable to estimating statistical error in averages of time series data and properly accounts for the correlation in the data.

| Replica | Electric current, nA | | Rectification ratio |
|---|---|---|---|
| | $I_{-2V}$ | $I_{+2V}$ | $\lvert I_{+2V}\rvert / \lvert I_{-2V}\rvert$ |
| 1 | $-0.19 \pm 0.06$ | $4.2 \pm 0.04$ | $22.3 \pm 7.3$ |
| 2 | $-0.22 \pm 0.07$ | $4.1 \pm 0.05$ | $18.8 \pm 5.7$ |
| 3 | $-0.22 \pm 0.06$ | $4.2 \pm 0.05$ | $18.6 \pm 5.5$ |
| 4 | $-0.24 \pm 0.05$ | $4.1 \pm 0.05$ | $16.9 \pm 4.0$ |

Table S4: Contributions to the total electric current from the different components of the solution for the systems with positively charged nanoparticles added.

| | C1 | | C2 | |
|---|---|---|---|---|
| | +2 V | - 2 V | +2 V | -2 V |
| Cations | 2.44 nA | -0.18 nA | 2.73 nA | -1.32 nA |
| Anions | 1.77 nA | 0.0033 nA | 0.94 nA | -0.37 nA |
| Particles | 0.017 nA | -0.0071nA | 0.010 nA | -0.012 nA |
| Total | 4.2 nA | -0.19 nA | 3.7 nA | -1.7 nA |

Table S5: Contributions to the total electric current from the different components of the solution for the systems with negatively charged nanoparticles added.

| | C1 | | C2 | |
|---|---|---|---|---|
| | +2 V | - 2 V | +2 V | -2 V |
| Cations | 2.64 nA | -0.37 nA | 2.88 nA | -1.37 nA |
| Anions | 1.67 nA | 0.028 nA | 0.90 nA | -0.33 nA |
| Particles | 0.017 nA | -0.011 nA | 0.014 nA | -0.023 nA |
| Total | 4.3 nA | -0.35 nA | 3.8 nA | -1.7 nA |

Table S6: Contributions to the total electric current from the different components of the solution for the systems without any nanoparticles added.

| | C1 | | C2 | |
|---|---|---|---|---|
| | +2 V | - 2 V | +2 V | -2 V |
| Cations | 2.6 nA | -1.51 nA | 3.1 nA | -1.71 nA |
| Anions | 1.53 nA | -0.88 nA | 1.43 nA | -0.80 nA |
| Total | 4.2 nA | -2.4 nA | 4.6 nA | -2.5 nA |

# References

(1) Flyvbjerg, H.; Petersen, H. G. Error estimates on averages of correlated data. *The Journal of Chemical Physics* **1989**, *91*, 461–466.