Supplemental Information for

Capacitive-pulse model for nanoparticle sensing by single conical nanochannels

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1. Solving Poisson−Nernst−Planck (PNP) equations

The transport process is simulated by numerically solving PNP equations, i.e. Eqs. (1) (2) and (3),

$$\vec{J}_i = -D_i(\nabla c_i + \frac{z_i F}{RT} c_i \nabla \phi) \tag{1}$$

$$\nabla \cdot \vec{J}_i = 0 \tag{2}$$

$$\nabla^2 \phi = -\frac{F}{\varepsilon} \sum_i z_i c_i \tag{3}$$

where $\vec{J}_i$ is the ion flux, D_i, c_i, and z_i are the diffusion coefficient, concentration and the charge number of species i, respectively, and F, R, T, ε, and ϕ are the Faraday constant, gas constant, temperature, the dielectric constant of the medium, and the local potential, respectively. The calculation is performed with a two-dimensional axial-symmetric geometry for a charged conical nanochannel. The boundary conditions are respectively given as the following:

at nanochannel wall (segment DE in Figure S1):

$$\nabla_\perp \phi = -\frac{\sigma}{\varepsilon}, \quad \vec{J}_{i\perp} = 0, \ i = +, -$$

at walls facing reservoirs (segments CD and EF in Figure S1) :

$$\nabla_\perp \phi = 0, \quad \vec{J}_{i\perp} = 0, \ i = +, -$$

at the end of the reservoir at the tip side (segment GH in Figure S1):

$$\phi = 0, \quad c_i = c_0, \ i = +, -$$

at the end of the reservoir at the base side (segment AB in Figure S1):

$$\phi = \phi_0, \quad c_i = c_0, \ i = +, -$$

where ϕ_0 is the applied voltage, and σ corresponds to the surface charge density.

2. Two-dimensional axial-symmetric geometry for the Comsol simulation

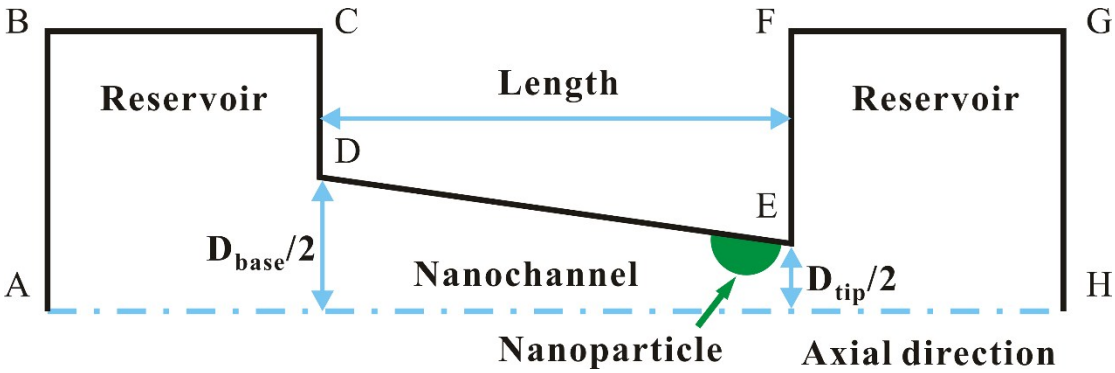

Fig. S1 Schematic illustration of two-dimensional axial-symmetric geometry for studying the transport of nanoparticles through a nanochannel. The dimensions in this figure are distorted for clarity. The modeled geometry consists of a nanochannel and two reservoirs. The modeled geometry consists of a nanochannel and two reservoirs. The tip entrance (point E) is located at axial direction 0 μm, while value of 12 μm corresponds to the base entrance (point D). The nanoparticle is assumed to adsorb on the channel wall. The nanochannel has a length of 12 μm with the entrance diameters of 97 nm and 500 nm for the tip and base sides, respectively. The inner surface of the nanochannel is negatively charged as -0.03 C/m^2. The nanoparticle is assumed as 60 nm in diameter and stayed in the location near the nanochannel wall 5 nm from the tip entrance. To simplify the calculation and avoid singularity, the adsorbed nanoparticle was treated as a ring structure containing the same total volume, and the surface charge density on the nanoparticle-occupied region was set as the sum of the surface charge densities that the nanoparticle originally carried and the covered channel surface originally contained. Two reservoirs of 1 μm × 1 μm containing 100 mM KCl are attached to the two entrances of the nanochannel, respectively.

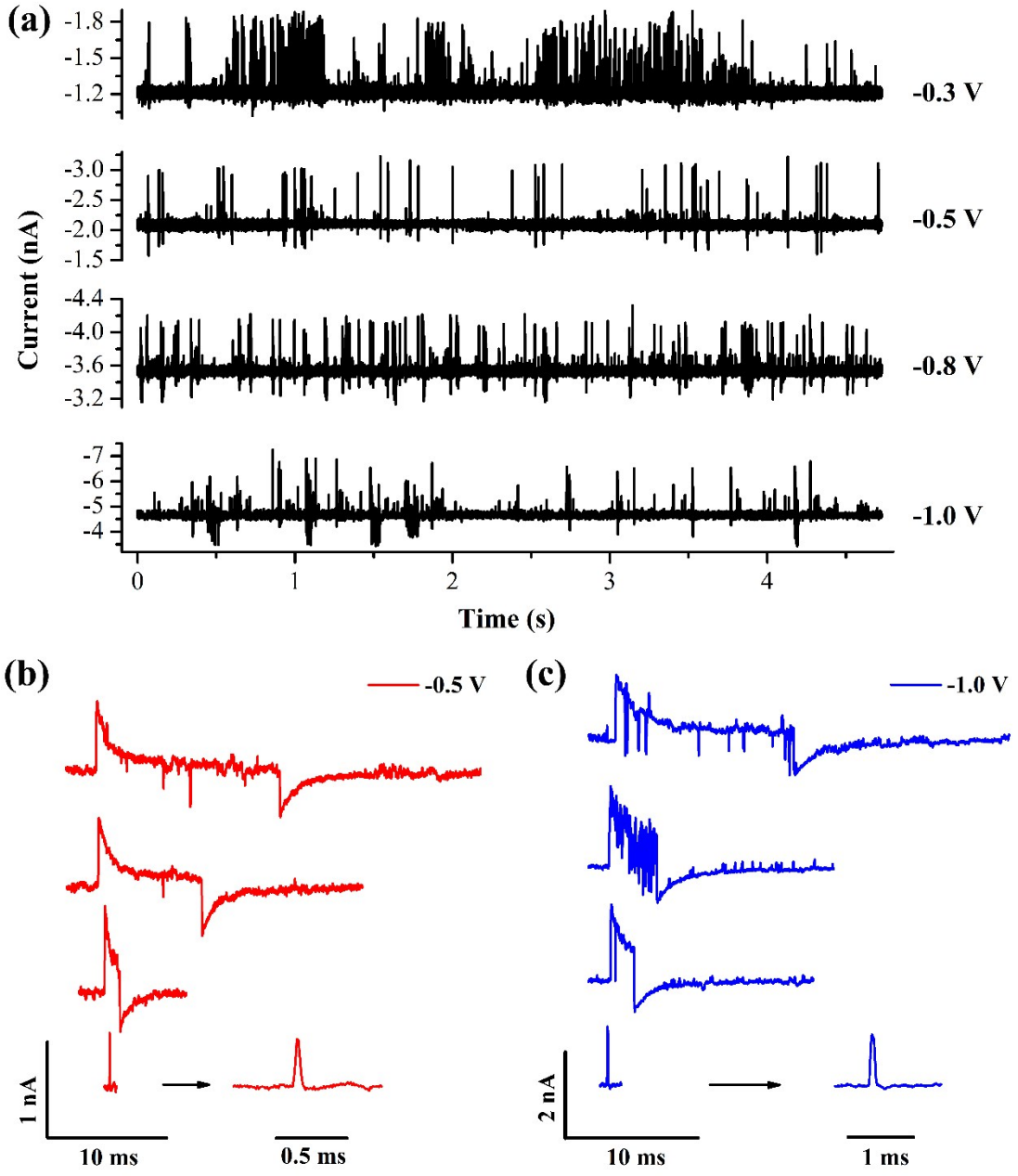

Fig. S2 (a) Current traces under different applied voltages of -0.3 V, -0.5 V, -0.8 V and -1.0 V, respectively, while the polystyrene (PS) nanoparticles (274 μeq/g, 60 nm in diameter) transport through a nanochannel with the tip diameter of 97 nm. The chamber on the tip side of the nanochannel was filled with the solution containing 10^{11}/mL PS nanoparticles dispersed in 100 mM KCl with 0.1% TritonX-100, whereas

the chamber on the base side contained only 100 mM KCl and 0.1% TritonX-100. (b) and (c) show a few examples of the waveshapes for biphasic pulses at -0.5 V and -1.0 V, respectively. Note that a monophasic pulse can be viewed as a biphasic pulse with very short dwell time.

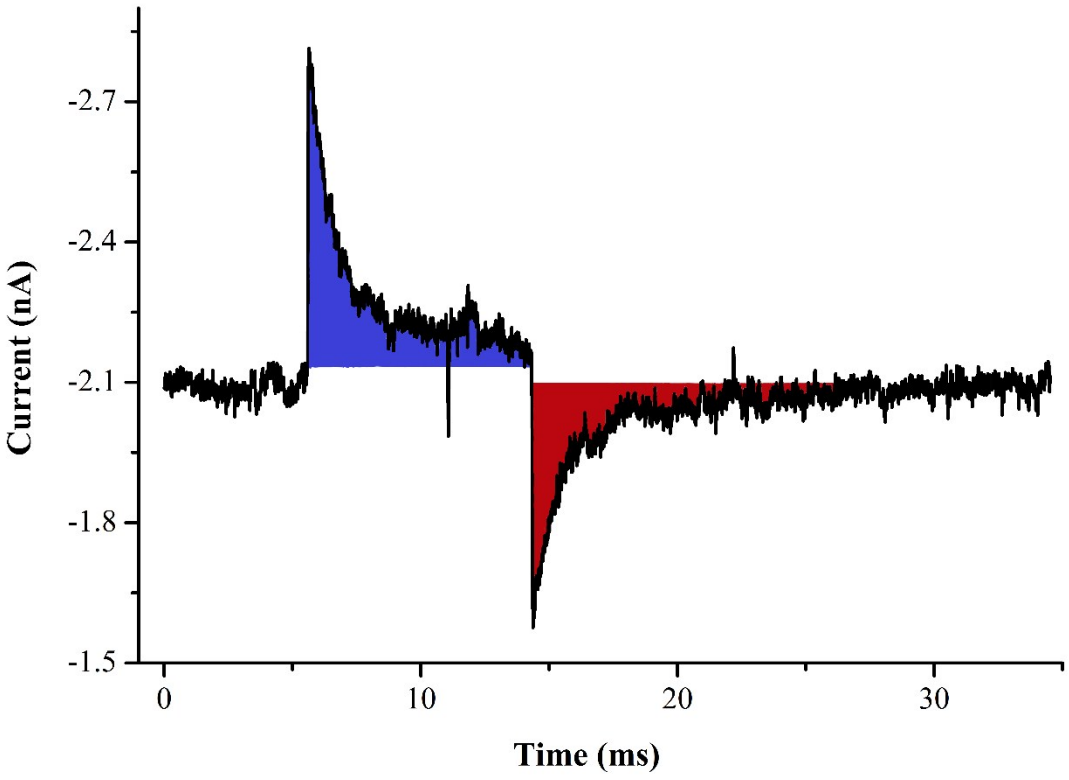

Fig. S3 A typical biphasic pulse. The integral area of the blue region (1.12 pA·s) was almost the same as the integral area of the red region (1.09 pA·s), suggesting that the total number of the ions entered into the nanochannel due to the nanoparticle was approximately equal to the number of ions that left the nanochannel.

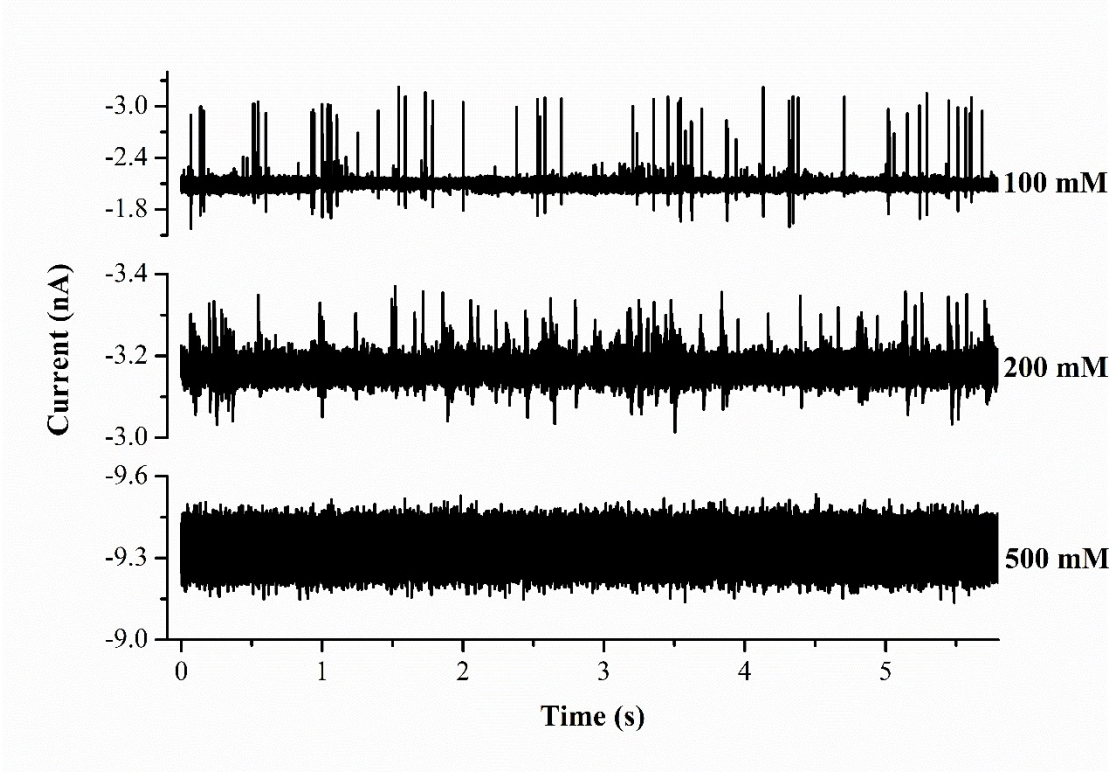

Fig. S4 Current traces under various concentrations of 100 mM, 200 mM, and 500 mM, respectively, while the PS nanoparticles (274 μeq/g, 60 nm in diameter, 10^{11}/mL) transport through a nanochannel with the tip diameter of 97 nm.

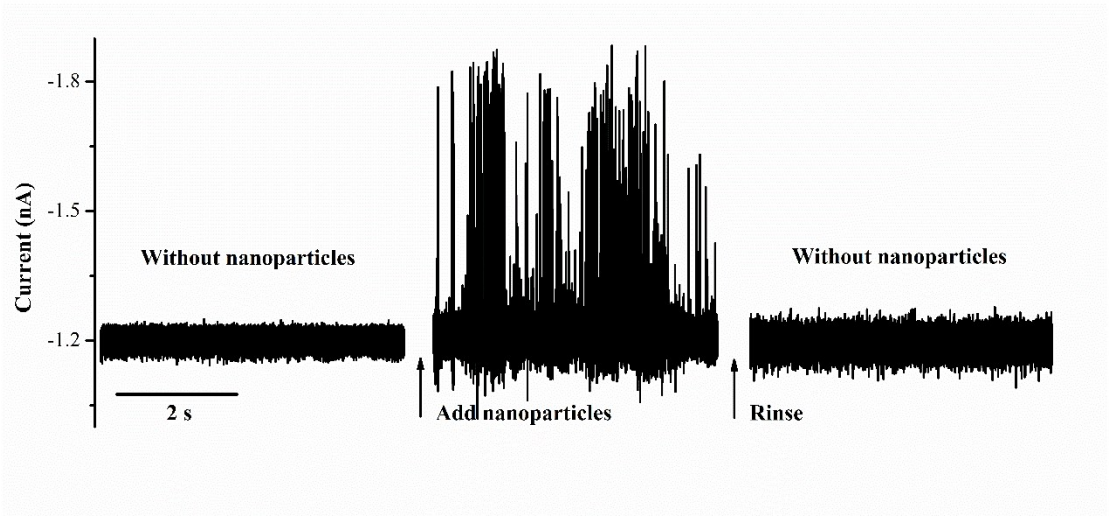

Fig. S5 (a) Current traces under applied voltage -0.3 V with the measurement sequence of (1) without PS nanoparticles, (2) adding nanoparticles, and (3) without

nanoparticels again, by using a nanochannel with tip diameter of 97 nm in 100 mM KCl.

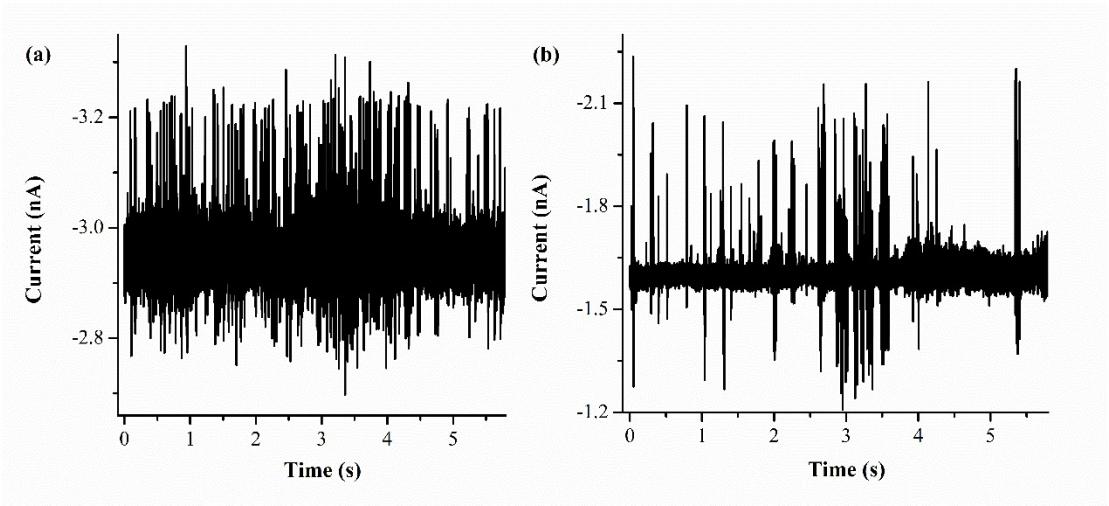

Fig. S6 (a) Current traces under applied voltages of -0.5 V, while the PS nanoparticles (274 μeq/g, 60 nm in diameter) transport through nanochannels with the tip diameter of 175 nm (a) and 80 nm (b), respectively. The chamber on the tip side of the nanochannel were filled with the solutions containing 10^{11}/mL (a) and 10^{10}/mL (b) PS nanoparticles dispersed in 10 mM KCl with 0.1% TritonX-100, whereas the chamber on the base side contained only 10 mM KCl and 0.1% TritonX-100.