ESI 1: Ionic conductance of nanoparticle crystal (NPC)

It has been proved that nanoparticles stacked by evaporation induced self-assembling prefers to be the face-centered-cubic (FCC) structure other than the hexagonal close-packed (HCP) one. Fig.S1(a) shows the FCC lattice (gray points). The interstices in the FCC structure have two kinds: the tetrahedron one (green points) and the octahedron one (red point). Every tetrahedron interstice connects to four adjacent octahedron ones and every octahedron interstice connects to eight tetrahedron ones. The connection between two adjacent interstices is treated as a nanochannel. The nanochannel is equivalent to a straight channel here, and the equivalent principle is that the two nanochannels have the same surface area and volume. It can be calculated that the exposing surface area (S_t) and the interspaceal volume (V_t) in a tetrahedron interstice are $2.21r^2$ and $0.208r^3$, while r is the radium of the nanoparticle. Likewise, the exposing surface area (S_o) and the interspaceal volume (V_o) in an octahedron interstice can be calculated to be $8.16r^2$ and $1.05r^3$. So, the surface area (S) and the volume (V) of one nanochannel are $1.57r^2$ and $0.183r^3$.

According to the equivalent principle, the length (r_s) and the radius (l_s) of the equivalent straight channels are $0.237r$ and $1.04r$, respectively.

The conductance of a nanochannel with constant cross-section is,

$$G \sim 10^3 (\mu_+ + \mu_-) e k_b N_a e \frac{S}{L} + \mu_+ \sigma_s \frac{P}{L}$$

(S1)

where μ, N_A, σ_s, e, S, P, L are the ion mobility, Avogadro constant, channel surface charge density, electron charge, effective cross-section area, cross-section perimeter, and channel length, respectively. Based on Eq. (S1) and the above equivalent relationship, the conductance of the nanochannel constructed by adjacent tetrahedron and octahedron interstices in the NPC can be estimated as,

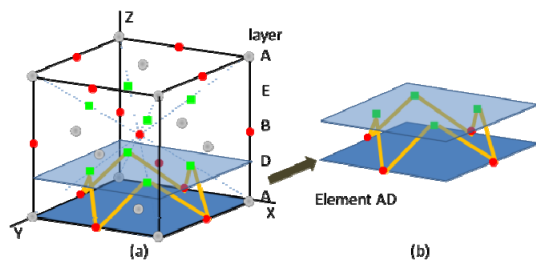$$G_0 \sim 1.64 \times 10^7 (\mu_+ + \mu_-) e k_b r + 1.43 \mu_+ \sigma_s$$

(S2)

Figure S1. Packed nanoparticle with an FCC structure. (a) Schematic illustration of interstices and nanochannels in the FCC structure; (b) calculation unit between layer A and layer D in (a).

Considering the equivalence of X, Y and Z direction in the structure, as shown in Fig. S1(a), the Z direction (crystal direction <001>) is analyzed here. Nanoparticle in the crystal cell can be divided into three layers, layers A, B, and A. All the octahedron interstices in the crystal cell are at the same layer with the nanoparticles, while the tetrahedron ones are between the nanoparticle layers, defined as layers D and E. Therefore, the nanochannel network can divided into four series-connecting independent impedance elements, AD, DB, BE, and EA. Every impedance element is constituted by eight parallel nanochannels, i.e. $G_e = 8G_0$, as shown in Fig.S1 (b). Every impedance element has the same cross-section area (S_e) of $8r^2$ and length (L_e) of $\sqrt{2r}/2$, so the conductivity can be calculated as,

$$Con_z = \frac{G_e L_e}{S_e} = \frac{8G_0 \frac{\sqrt{2}}{2} r}{8r^2} = \frac{G_0}{\sqrt{2}r}$$

(S3)

For a given material, the body conductivity can be characterized by a third-order tensor (3×3 matrix), while the diagonal of the matrix stands for the conductivity in the direction X, Y and Z, and the other elements in the matrix stand for the influence between every two directions. For example, while the electrical field E_X applied in direction X, Con_{XY} means that there will be a current ($E_X Con_{XY}$) in direction Y. For the crystal structure shown in Fig.S1(a), the conductivities in directions X and Y are the same as that in direction Z and the other elements in the conductivity matrix are zeros (for electrical field applied in any direction, there wouldn't current in the other two directions), which means the conductivity of the nanochannel network is isotropic. Therefore, the conductivity along the direction of <111>, exactly the direction for the measurement in this work, is the same as that of <001>, Con_Z here.

The conductance of NPC with the cross-sectional area and the thickness of S_{NPC} and L_{NPC} is,

$$G_{NPC} = Con_z \frac{S_{NPC}}{L_{NPC}} = \left(1.16 \times 10^7 (\mu_+ + \mu_-) e k_b + 2.01 \mu_+ \frac{\sigma_s}{d}\right) \frac{S_{NPC}}{L_{NPC}}$$

(S4)

where d represents the diameter of the nanoparticle.

ESI 2: Microfabrication of the micro-pore chip

As shown in Fig. S2, the micro-pore chip was fabricated by standard silicon fabrication process on a 4 inch, 400μm thick <100> silicon wafer with 3000Å oxide layer onside. Diameter of 20μm micro-pores were firstly patterned on the oxide layer, followed by low pressure chemical vapor deposition (LPCVD) of 1800Å silicon nitride as the protection layer for the following KOH etching. After back side photolithography, silicon nitride and oxide were etched by corresponding RIEs, and then a suspended membrane of 50μm was form after a 350min KOH etching. Then the silicon nitride layer was removed, followed by inductive coupled plasma (ICP) etching through the silicon with the predefined SiO_2 as the etching mask to achieve the micro-pore. At last, another 3000Å thick oxide layer was thermally grown onto the wafer to function as the electrical barrier in the measurement.
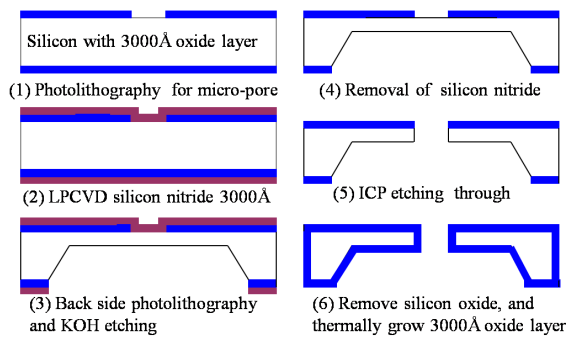

Silicon with 3000Å oxide layer

(1) Photolithography for micro-pore

(2) LPCVD silicon nitride 3000Å

(3) Back side photolithography and KOH etching

(4) Removal of silicon nitride

(5) ICP etching through

(6) Remove silicon oxide, and thermally grow 3000Å oxide layer

Figure S2. Fabrication process of the micro-pore chip (not in scale)

ESI 3: Electrokinetics of the S-NPC

The conductance of a S-NPC constructed by 500nm bare silica
5 nanoparticles with the electrolyte of $10^{-5} \times$ PBS to 1×PBS is
shown in Fig.S3. The insert shows a typical impedance-spectrum
of the S-NPC from 0.1 kHz to 100 kHz (log scale) at the ionic
concentration of 1mM. At low frequency, capacitors of the
electrode pair and their electrical double layers dominate the
10 conductance, while at high frequency (10 kHz~100 kHz), the
impedance levels to stable, which is mainly attributed to the
conductance of the S-NPC. Therefore, the conductance of the S-
NPC reported hereafter was measured at 100 kHz. At high ionic
concentrations, the conductance of the S-NPC varied linearly
15 with the electrolyte concentration, but at low concentrations, the
conductance was insensitive to the buffer concentration, which
meets exactly the electrokinetic property of an individual
nanochannel. This critical concentration c_b can be calculated as
3.1mM in this case (the surface charge density σ_s is estimated as
20 18mC/m^2 as in reference [11]) .
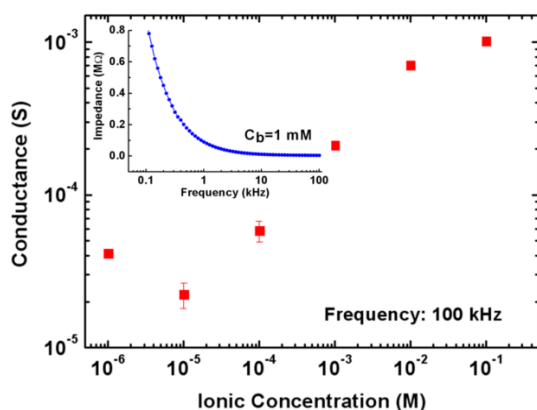

Figure S3. Ionic conductance of the S-NPC constructed by 500nm bare
silica nanoparticles with the ion concentrations varied from 1μM to 0.1M
(log scale) at frequency of 100kHz. Each point stands for three trials.
25 The insert shows a typical impedance-spectrum of the S-NPC from
0.1kHz to 100kHz (log scale) at ion concentration of 1mM.