TÉCNICO LISBOA

Nanotechnology

Electrostatic Control of Ions and Molecules in Nanofluidic Transistors

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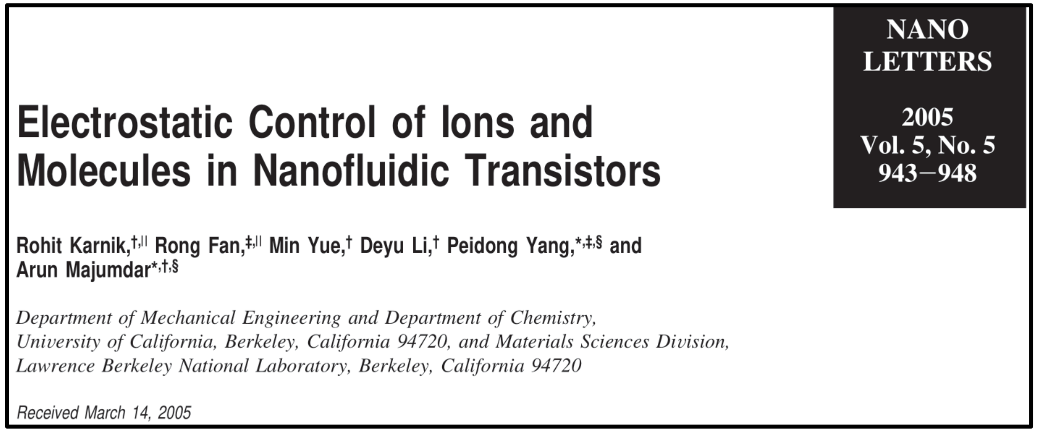
Summary

Nanofluidic transistor

- Based on metal-oxide-solution (MOSol) system;
- similar to metal-oxide-semiconductor field-effect transistor (MOSFET);
- integrated nanofluidic circuits → manipulation of ions and biomolecules in sub-femtoliter volumes.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Electrostatic Control of Ions and Molecules in Nanofluidic Transistors

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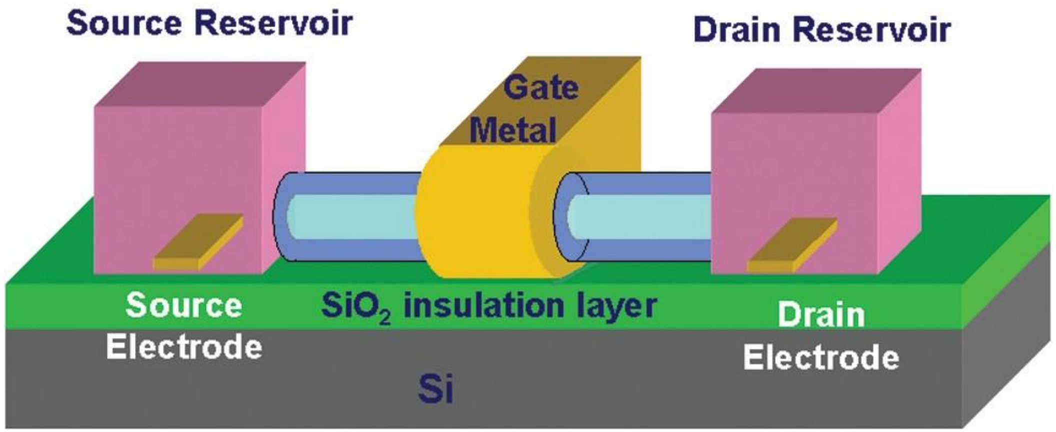
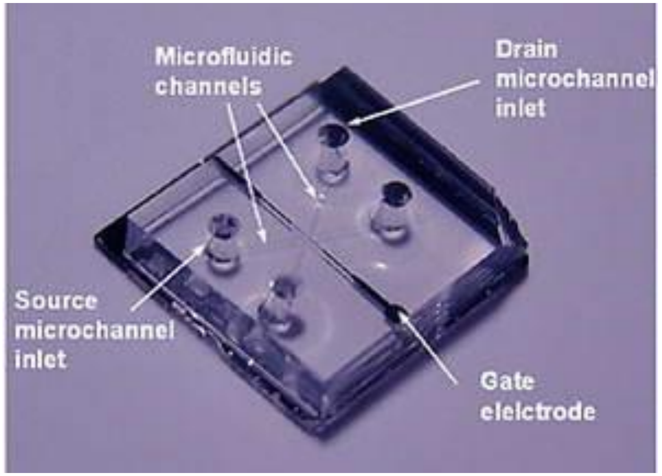
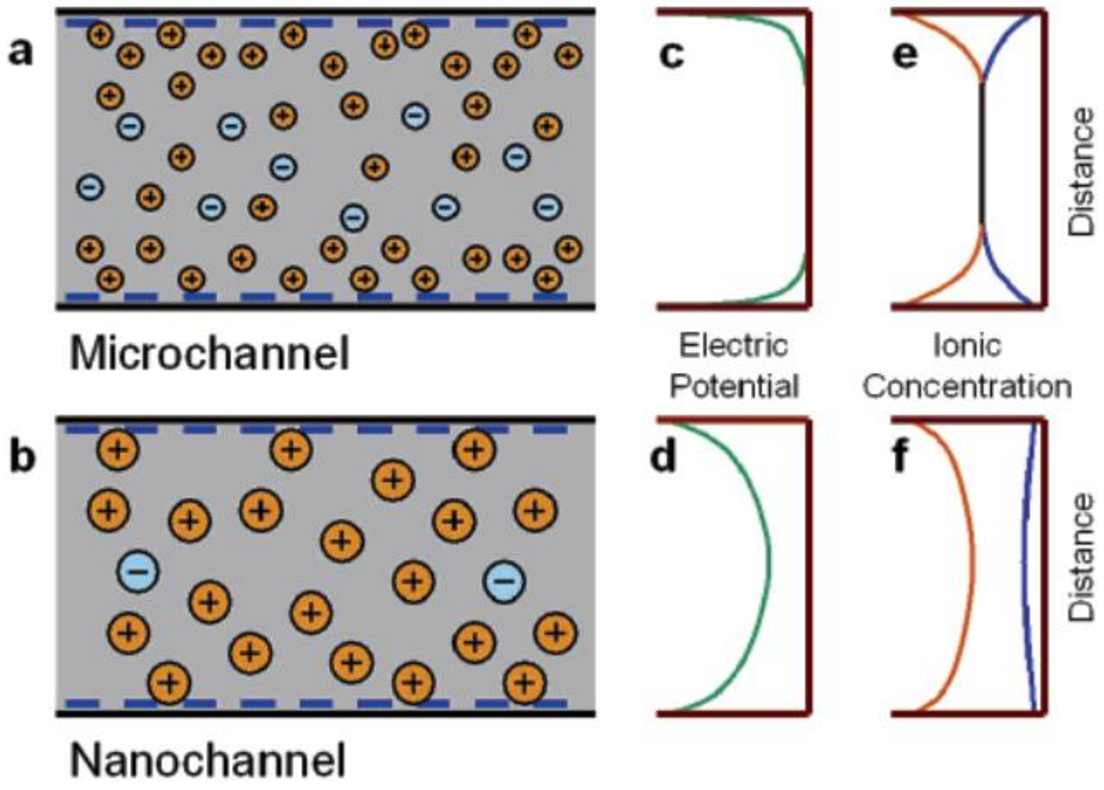
► **This work uses fluorescence and electrical measurements to demonstrate that gate voltage modulates the concentration of ions and molecules in the channel and controls the ionic conductance.**





Surface charge effects

- Similarly to MOSFETs, field effect modulation for higher level of controllability and logic operation → could advance the development of large-scale nanofluidic circuits.



- **Counterion** concentration (orange), **coion** concentration (blue), electric potential and ionic concentration

→ **Debye length:** $l_D \propto n^{-1/2}$ (n - ion concentration)

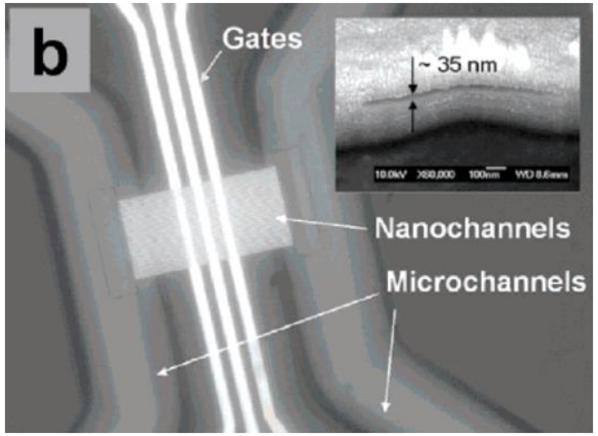
- Due to counterion shield, electric potential decays to its bulk value over l_D;
- typically 1-100nm for aqueous solutions.

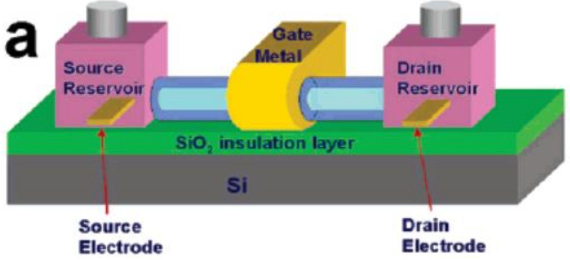
⇩

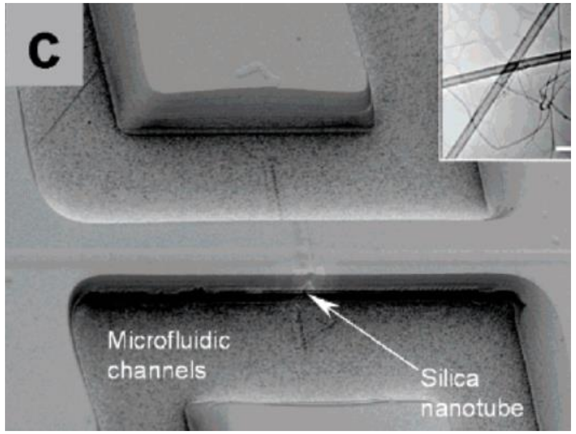
→ **Microchannels:** l_D much smaller than channel → bulk of the solution shielded from surface charge (most of the solution **neutral**); direct electrostatic manipulation is not possible;

→ **Nanochannels** with at least one dimension $\lesssim l_D$: electrostatic fields can penetrate throughout the channel, enabling **manipulation** using surface charge or field-effect.

Nanofluidic transistor devices







<u>Two types of fluid confinement:</u>

2-dimensional nanochannel transistor

→ 30 **nanochannels** (120μm long, 1μm thick) connected by two microchannels, ran across by 3 gate electrodes;

→ **etching** 35nm thick and patterned poly-silicon layer;

→ made completely by **optical lithography**.

- **Ag/AgCl electrodes** in the microfluidic channels/chambers for applying electrical bias and generating ionic current.

1-dimensional nanotube transistor

→ Metallic gate electrode covered by a silicon dioxide patterned film, **bonding with PDMS cover**;

→ tubes (internal diameters 10-100nm) connected on both ends to microfluidic channels;

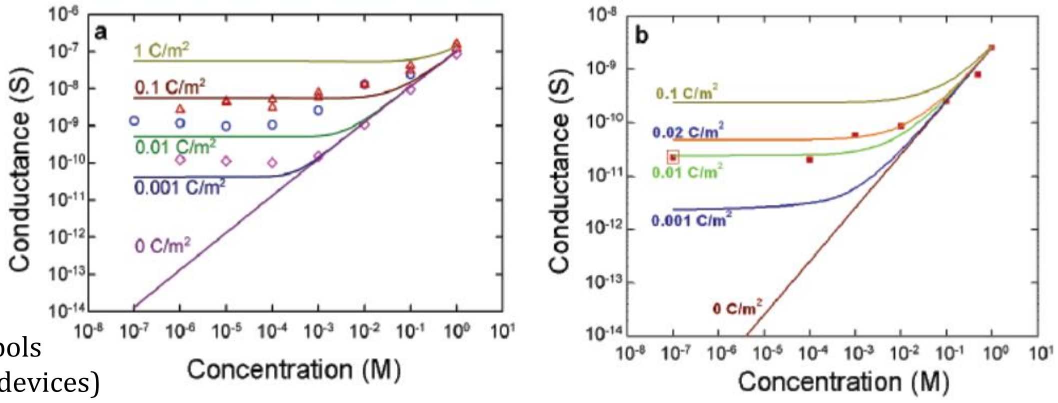
→ **partial oxidation** of silicon <u>nanowires</u> and **etching** of the remaining silicon core to obtain the silica <u>nanotubes</u> (separate synthesis and subsequent integration with microfabricated channels and gate electrodes).

Electrostatic effects in nanochanels

- **Surface charge increases with KCl concentration;**

(a) nanochannel: surface charge densities between 0.002 and 0.1C/m^2;

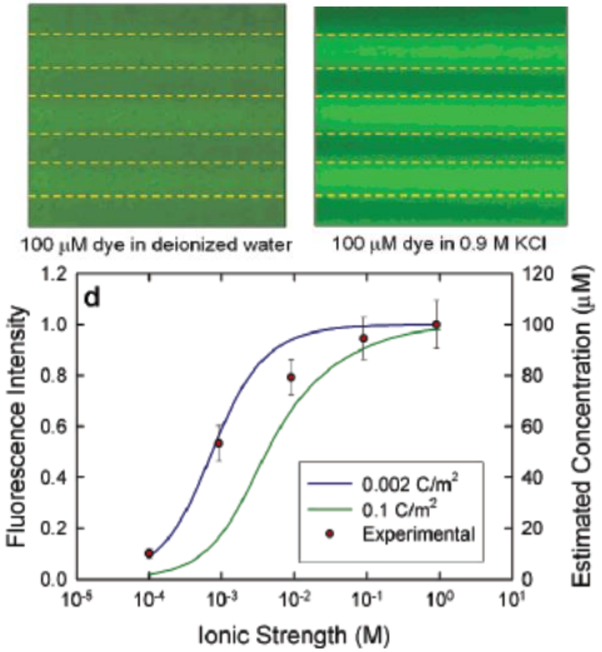
(b) nanotube devices: surface charge densities between 0.01 and 0.02C/m^2.



(different symbols represent different devices)

Fluorescence images

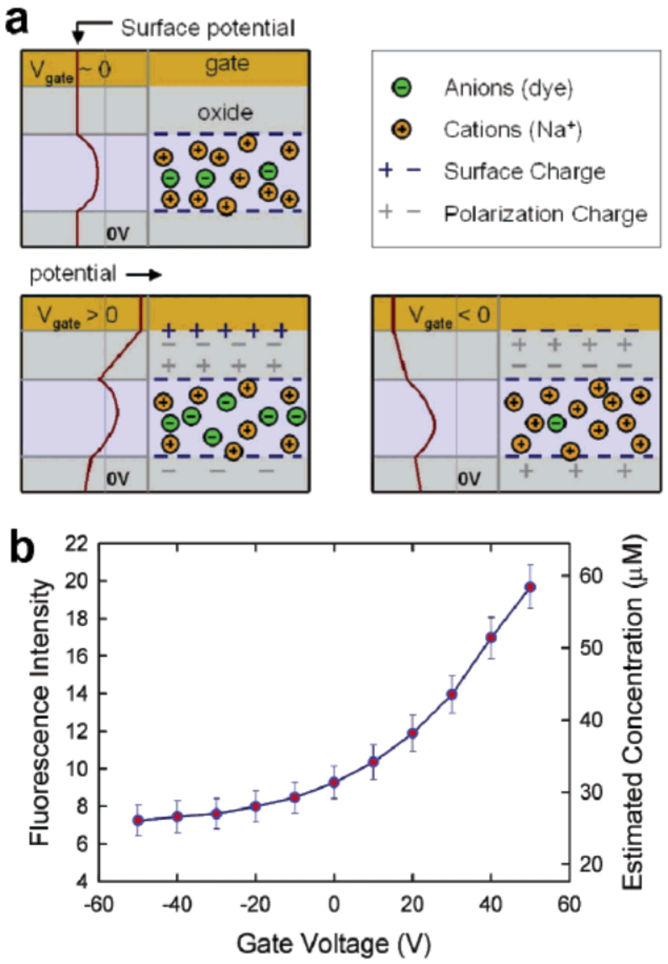
(dots outline three nanochannels, each 1 μm wide)



- **Negatively charged dye** in the nanochannels while **KCl** concentration varied;
- **deionized water** → most dye molecules excluded; **0.9M KCl** → dye molecules can enter the nanochannel (surface charge is shielded);
- dye concentration in 0.9M KCl with **bulk value** of 100μM (1.0 fluorescence intensity);
- **fluorescence** intensity represents the actual amount of dye in the nanochannels;
- as ionic strength decreases from 0.9M to 100μM, l_D increases to ≈30nm and effect of surface charge extends throughout the nanochannel – fluorescence decreases.

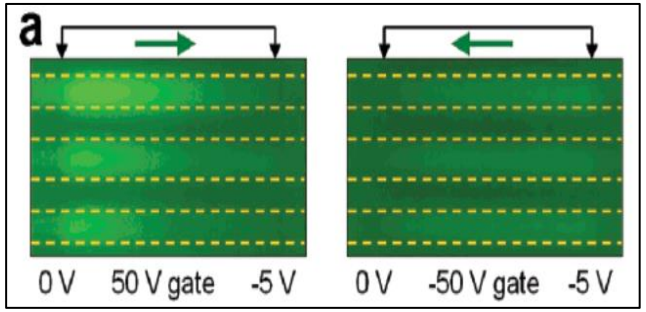
Field-effect modulation of ionic concentration

► **Gate voltage to control ionic concentration in nanochannels** (↔ carrier density modulation in MOS systems via capacitive coupling between the gate electrode and the semiconductor)



- Low salt concentrations → external charges (e.g., generated by **applied gate voltage**) can affect electric potential in nanochannel when $l_D \sim l$;
- **negatively charged dye** (100μM bulk value), fluorescence intensity below the gate electrode as a function of the gate voltage;
- **negative gate voltage** → dye repelled;
- **positive gate voltage** → dye concentration enhanced by a factor of 2 when 50V applied, change in surface charge of $\approx 3\text{mC/m}^2$;
- better control over ionic concentrations → low surface charge (determines the inherent ionic concentration in the nanochannels).

Field-effect control in nanofluidic transistors (1)



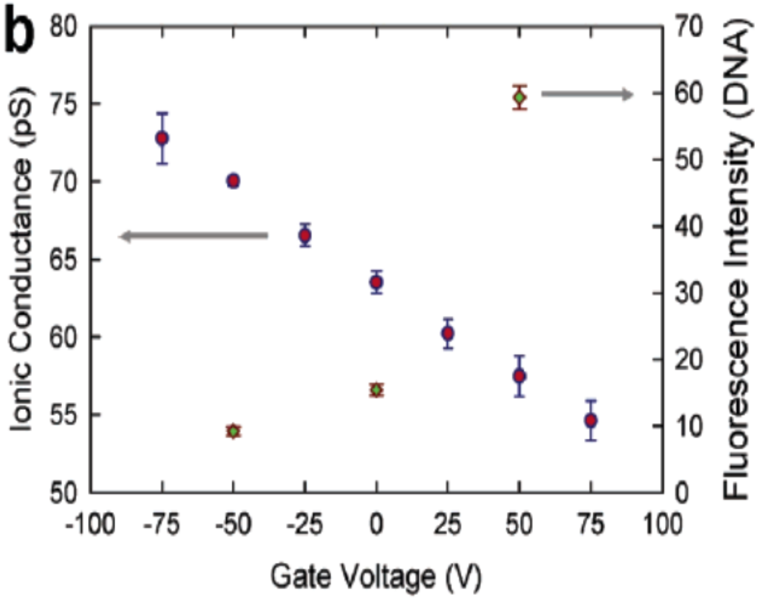
(green arrows for concentration gradients, vertical arrows for edges of gate electrodes; dots outline 3 nanochannels, each 1 μm wide)

- Fluorescence intensity while **gate <u>and</u> S-D** (5V) **voltages** in **2-dimensional nanochannel transistors;**
- **controllable concentration gradients** below the gate, direction of gradients switched by changing the gate voltage polarity;
- gate and S-D bias control **magnitude of the concentration enhancement** - 50 V and 5 V (resp.) led to 10-fold enhancement.

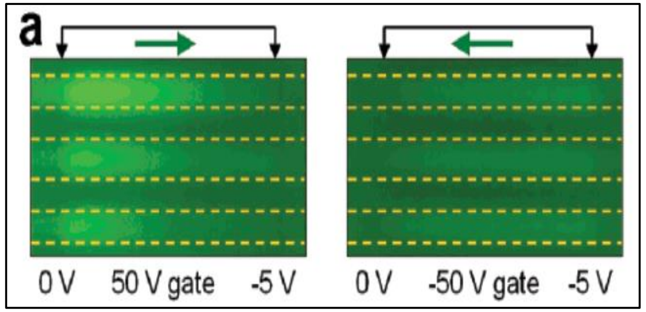
- As gate voltage changed from -75V to 75V, **ionic conductance** monotonically **decreased**;
- **inherent negative** surface charge in the nanochannel → most of the current is carried by the **cations**. Hence:

→ **<u>negative</u> gate voltage** (increases cation concentration) **increases conductance**;

→ **<u>positive</u> gate voltage** (depletes the cations) **decreases conductance**.



Field-effect control in nanofluidic transistors (2)



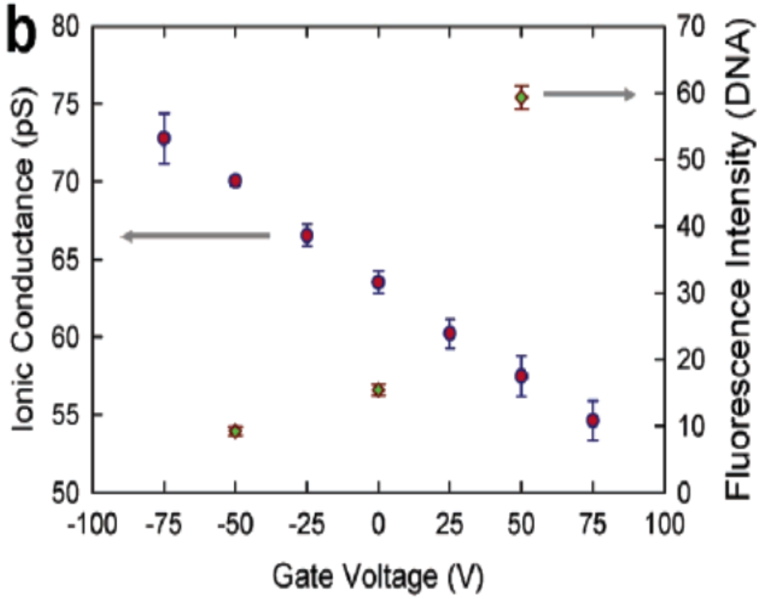
(green arrows for concentration gradients, vertical arrows for edges of gate electrodes; dots outline 3 nanochannels, each 1 μm wide)

MOSFET → control electrical conductance

► Nanofluidic transistor to **tune the ionic environment, control transport and concentrations of ions or particular charged biomolecular species.**

- **Fluorescence intensity** of labeled single-stranded DNA (ssDNA) in 1mM KCL controlled by factor of 6 with gate voltage → **suggests that flow control of charged biomolecules is feasible**;

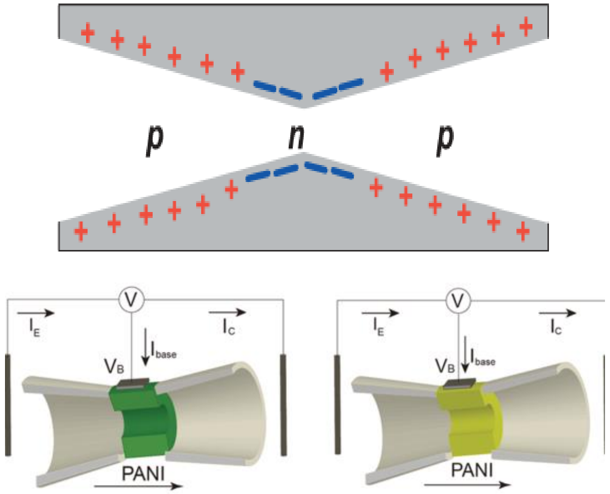
- in <u>deionized water</u>, no fluorescence was observed → DNA molecules excluded due to negative charge; in <u>1mM KCl</u>, surface charge partially shielded, **enables gating control**.



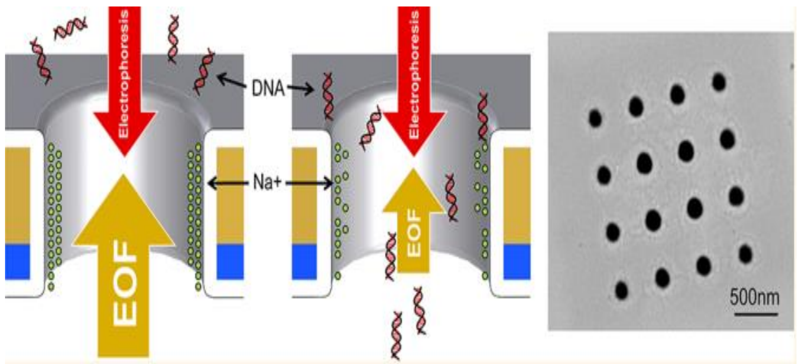
Conclusion

- ✓ This work demonstrated that it is possible to **electrostatically control ion transport** in **2-dimensional nanochannel transistors** and **1-dimensional nanotube transistors**;
- ✓ if high dielectric constant materials employed to fabricate nanochannel wall, enhanced field effect due to stronger capacitive coupling is expected;
- ✓ multivalent species (such as biomolecules) → **gating control enhanced**;
- ✓ unique tool for **biological and chemical analyses in sub-femtoliter volumes**.

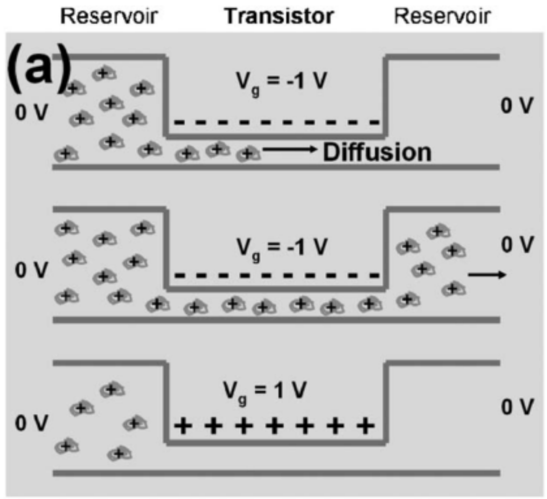
► **Similarly to MOSFETs, the nanofluidic transistor has the potential to be the building block of integrated nanofluidic circuits for manipulating biomolecules with single-molecule precision and control.**



Nanofluidic PNP bipolar transistors



Control of DNA capture and passage



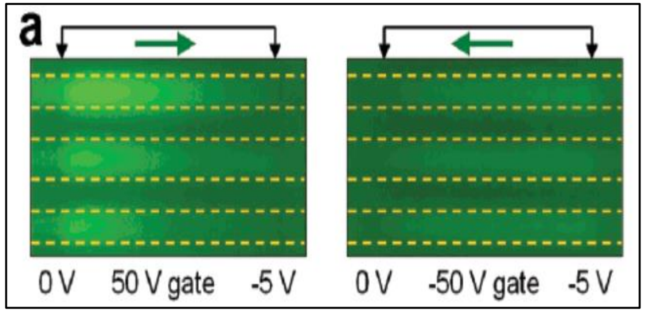
Field-effect control of protein transport

Thank you!

References

- ✓ Karnik R.; Fan R.; Yue M.; Li D.; Yang P.; Majumdar A., Electrostatic Control of Ions and Molecules in Nanofluidic Transistors, Nano Letters, **2005**, *5*, 943-948. *DOI: 10.1021/nl050493b*;
- ✓ Kalman E.; Vlassiouk I.; Siwy Z., Nanofluidic Bipolar Transistors, Advanced Materials, **2008**, *20*, 293-297. *DOI: 10.1002/adma.200701867*;
- ✓ Hu Y.; Hua Y.; Pan Z.; Qian J.; Yu X.; Bao N.; Huo X.; Wu Z.; Xia X., PNP Nanofluidic Transistor with Actively Tunable Current Response and Ionic Signal Amplification, Nano Letters, **2022**, *22*, 3678-3684. *DOI: 10.1021/acs.nanolett.2c00312*;
- ✓ Karnik R.; Castelino K.; Majumdar A., Field-effect control of protein transport in a nanofluidic transístor circuit, Applied Physics Letters, **2006**, *88*, 123114. *DOI: 10.1063/1.2186967*;
- ✓ Paik K.; Liu Y.; Tabard-Cossa V.; Waugh M.; Huber D.; Provine J.; Howe R.; Dutton R.; Davis R., Control of DNA Capture by Nanofluidic Transistors, ACS Nano, **2012**, *6*, 6767-6775. *DOI: 10.1021/nn3014917*.

Attachment



(green arrows for concentration gradients, vertical arrows for edges of gate electrodes; dots outline 3 nanochannels, each 1 μm wide)

Field-effect control in nanofluidic transistors (3)

- Differential ionic conductance (slope of I/V curves) of the **nanotubes**;
- insets illustrate electric potential from the gate electrode and across the nanotube when applying gate voltage, which modulates ionic density and conductivity.

- ► Gate voltage shifts **potential** diagram across oxide, changes effective surface charge density and potential on inner wall surface;
- ► when nanotube size is comparable to Debye length, ionic conductance depends only on ξ potential and effective surface charge → enables **gate control of ionic conductance**;
- ► for gate voltage from -20V to +20V, ionic conductance decreases from 105pS to 45pS, due to depletion of cations → **p-type transistor** behavior.