Fabrication and investigation of single track-etched nanopore and its applications

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Fabrication and Investigation of Single Nanopore

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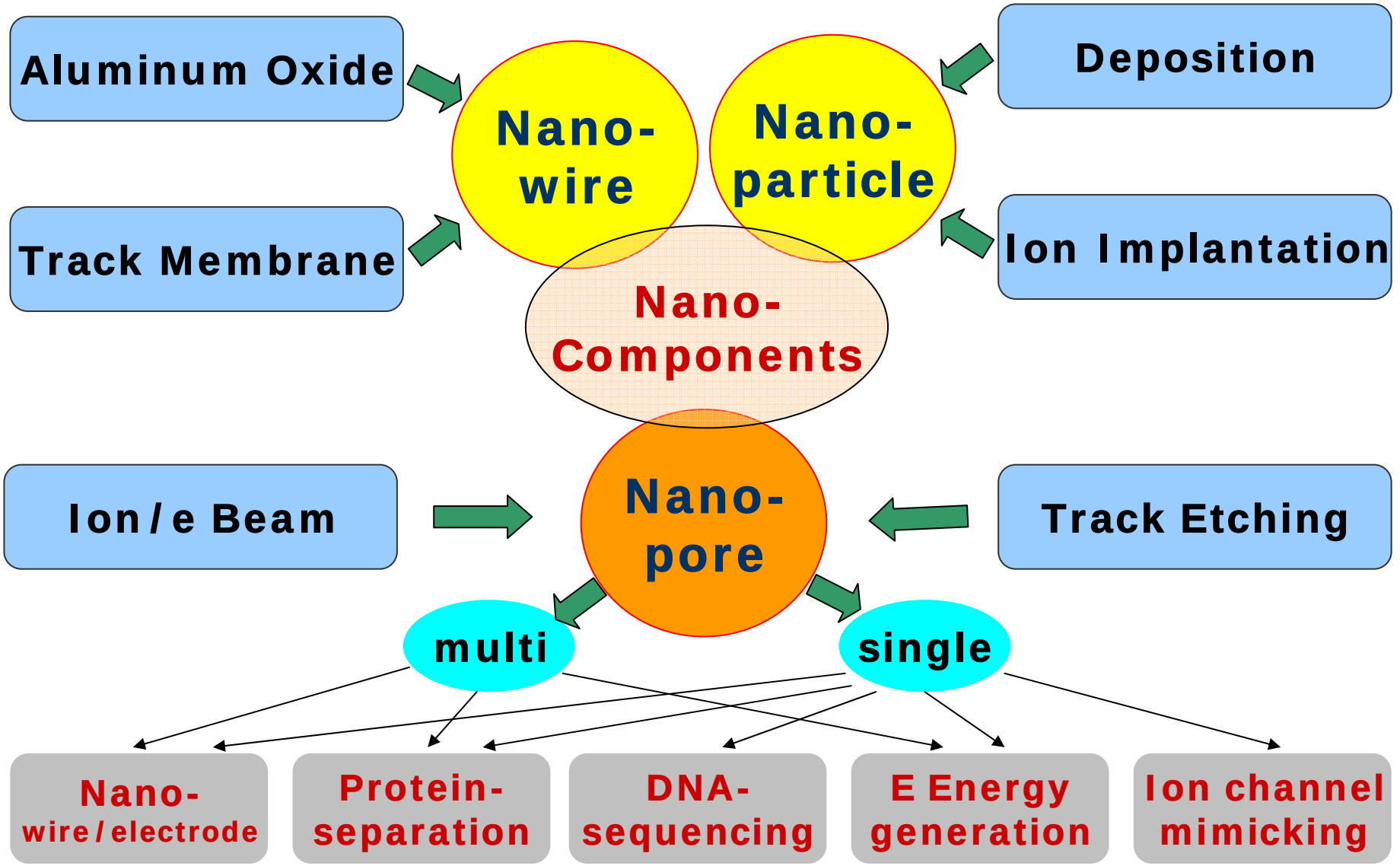

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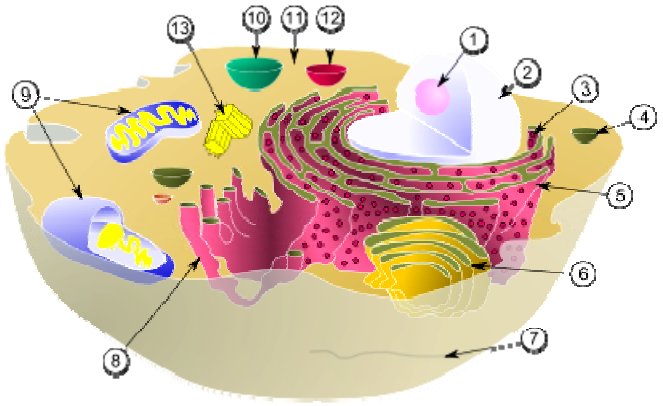

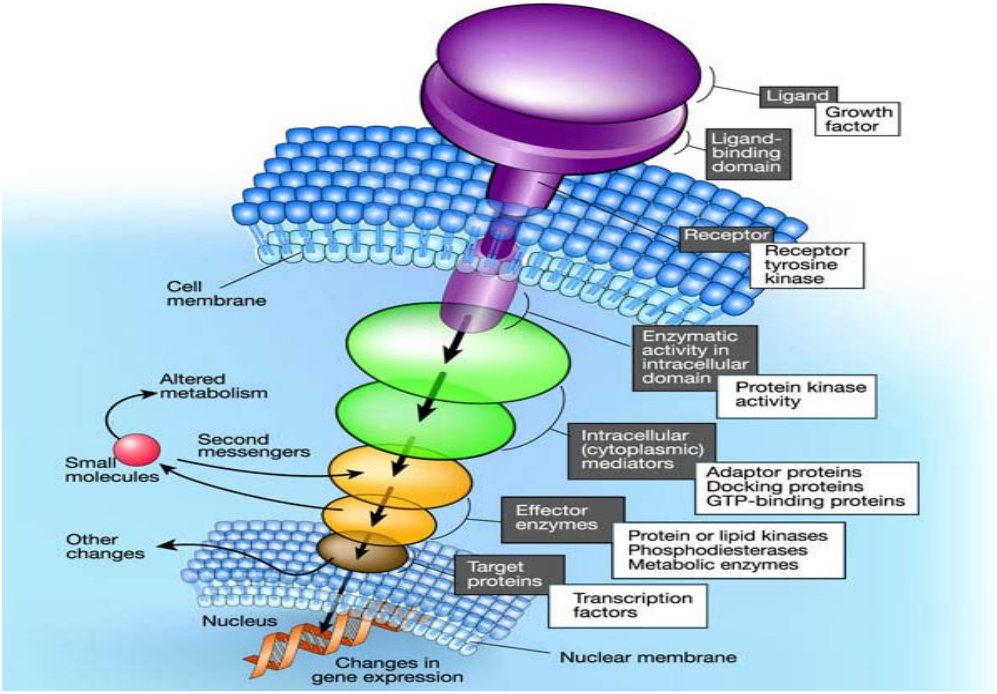

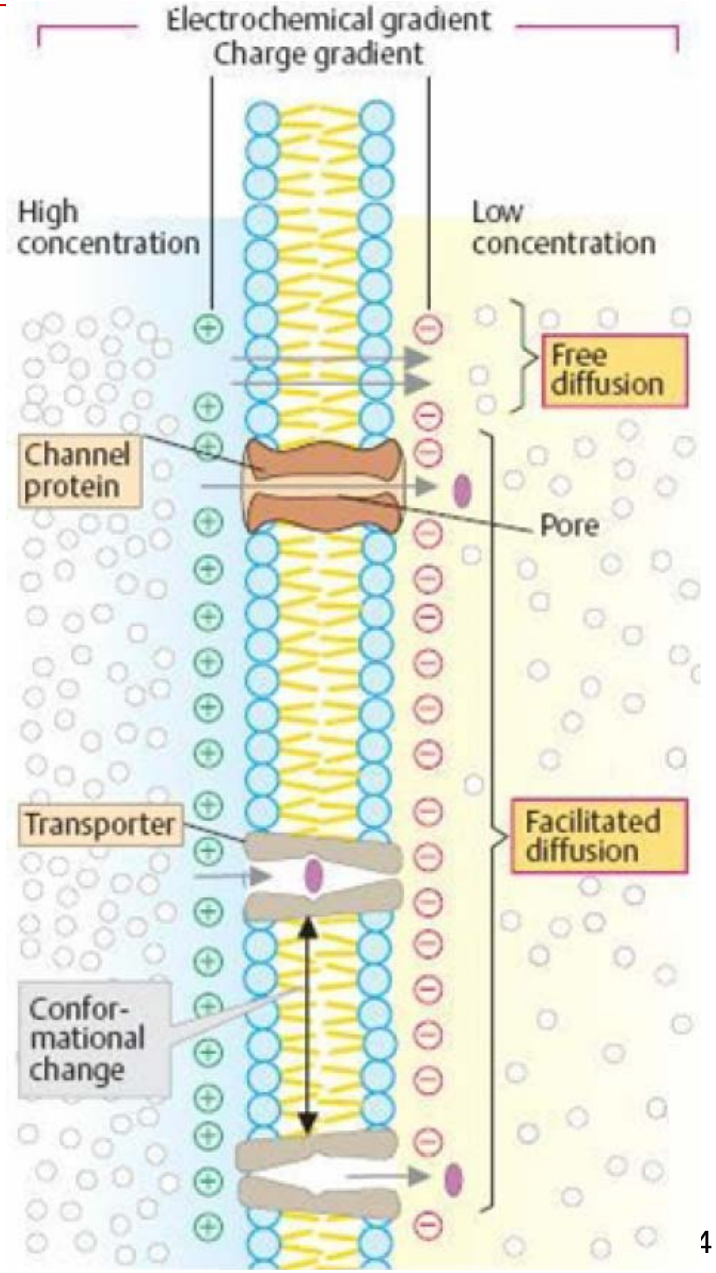

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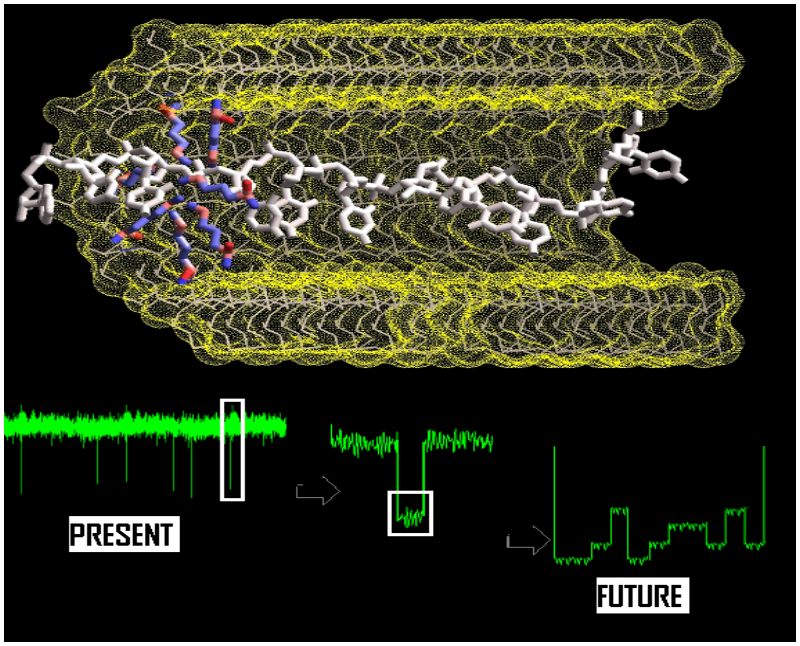
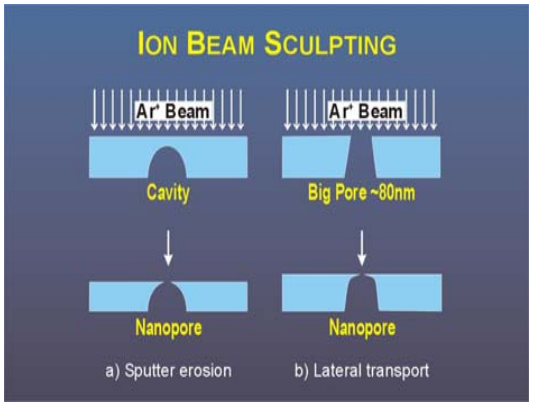
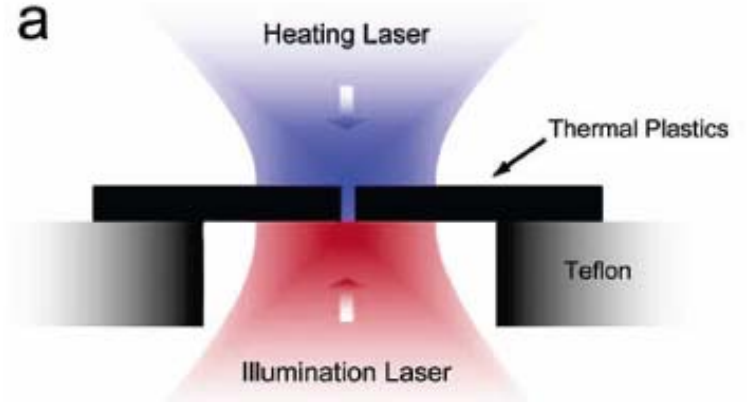


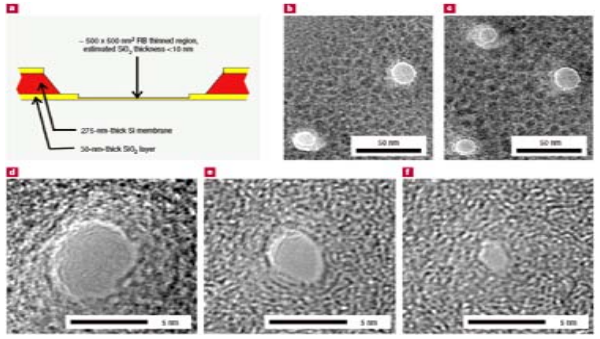


Jiali Li, *et al*. / Nature,2001,Vol. 412(12)

Z. Siwy, *et al*. Phys. Rev. Lett, 2002
Mara A, *et al*. Nano Lett, 2004

Nano Lett., Vol. 6, No. 11, **2006**





A. J. STORM, et al./Nature Materials,2003, Vol. 2

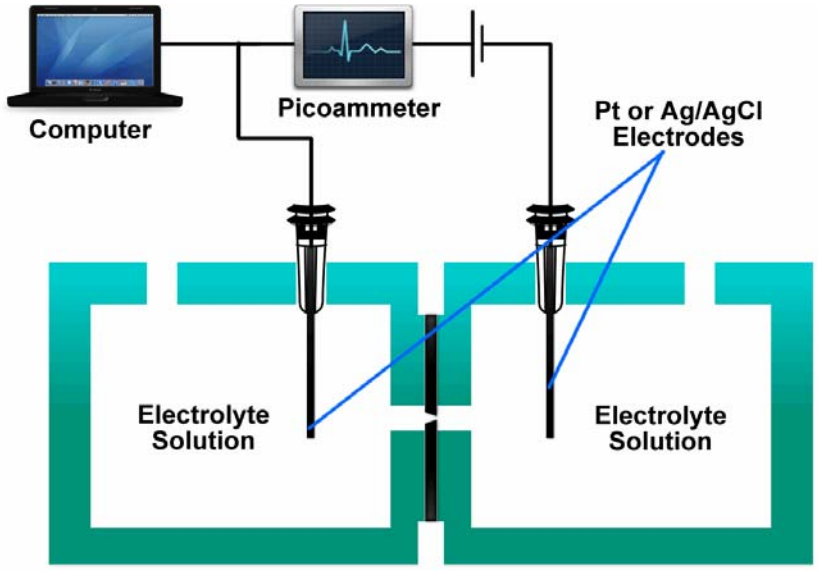
Contents

- Asymmetric properties of ion transport in nanopore both in experiment and in theory
- Electric energy generation in single track-etched nanopore
- Thermal responsive nanochannels based on single conical nanopore
- Fabrication of synthetic nanopore-DNA system
- Controllable fabrication of nanopore in Silicon based materials

Fabrication and Investigation of Single Nanopore

Fabrication of single conical nanopore in PET membrane

- The PET membranes were irradiated by single heavy ion at UNILAC of GSI.
- The irradiated PET was etched from one side; stopping medium was used to stop the etching process as soon as the nanopore was etched through.
- A picoammeter was used to monitor the moment of the breakthrough.

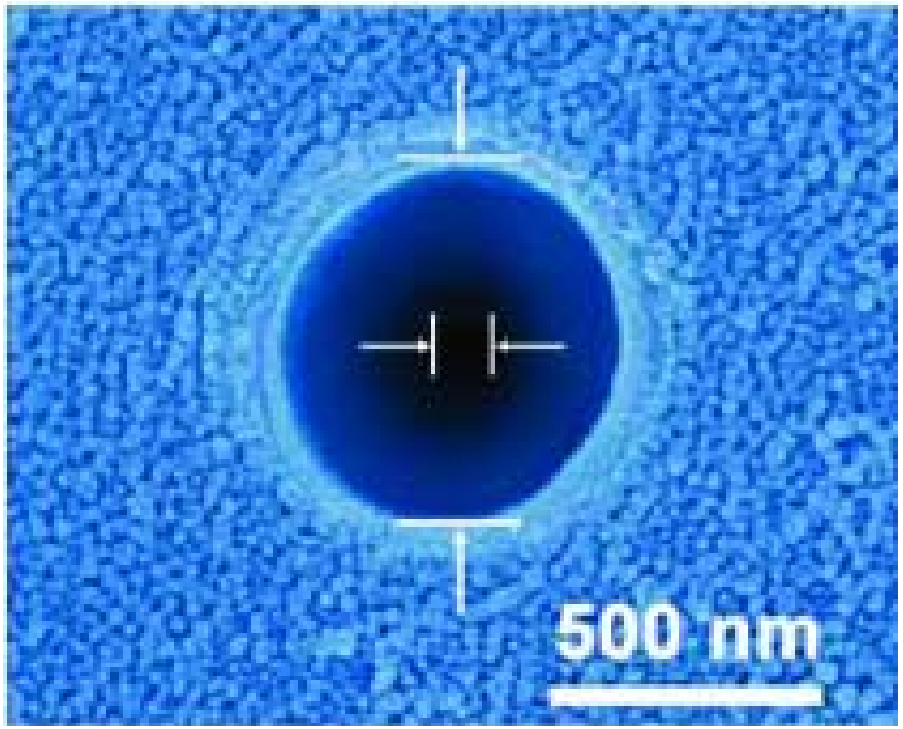


Etchant: 9M NaOH

Stopping solution: 1M KCl +1M HCOOH

Fabrication and Investigation of Single Nanopore

- Following these steps, conical nanopores in PET membrane with tip diameter from 1.5nm to tens of nm have been fabricated successfully



$$d_{tip} = \frac{4LI}{\pi k(c)UD}$$

d_{tip}: diameter of the tip end

L: length of the pore

D: diameter of base end

$K(c)$: specific conductivity of the electrolyte (KCl)

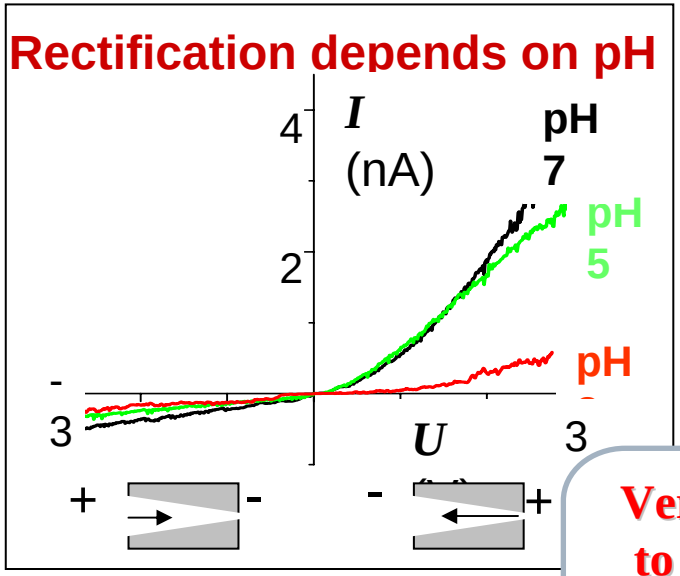
Fabrication and Investigation of Single Nanopore

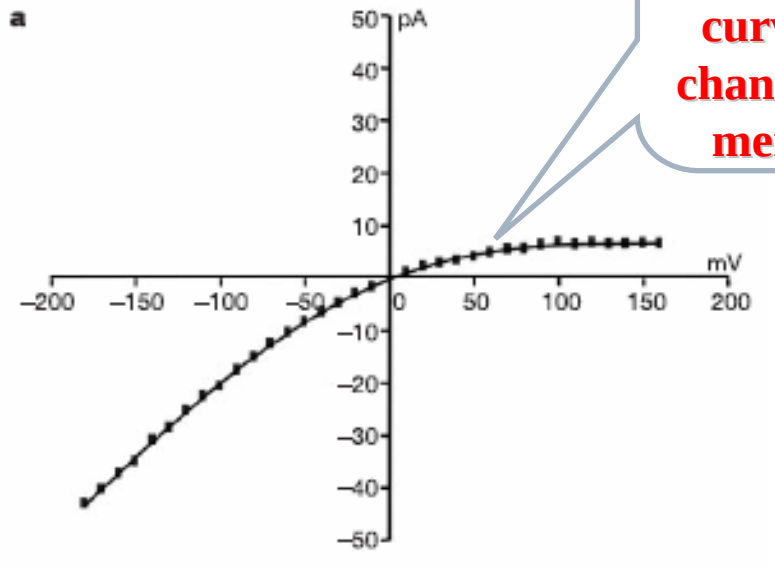
Ion Transport properties in nanopore

- There were extensive researches on exploring the basic physical properties of ion transport in a conical nanopore both in experiment and in theory.
- A synthetic conical nanopore in a PET membrane exhibits asymmetric properties of ion transport that resemble those in biological ion channels, such as current rectification and ionic selectivity.

Fabrication and Investigation of Single Nanopore

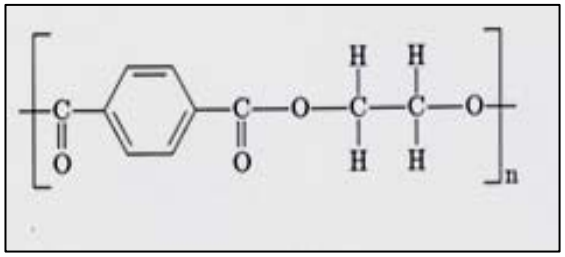
Rectification depends on pH

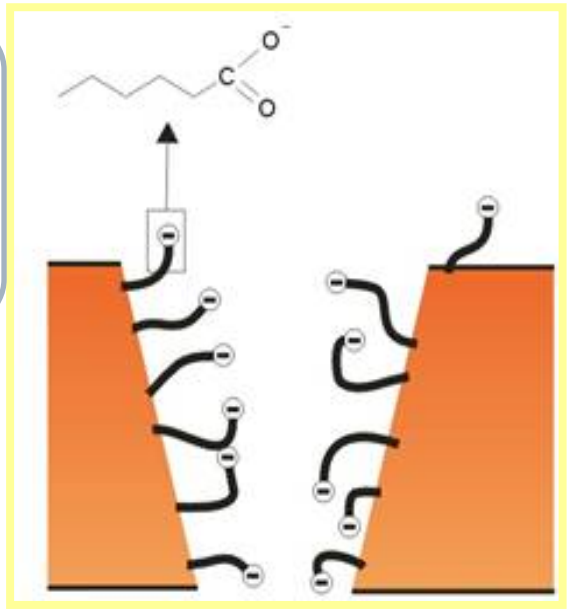




Very similar to the I—V curve of ion channel in cell membrane

Pores are negatively charged

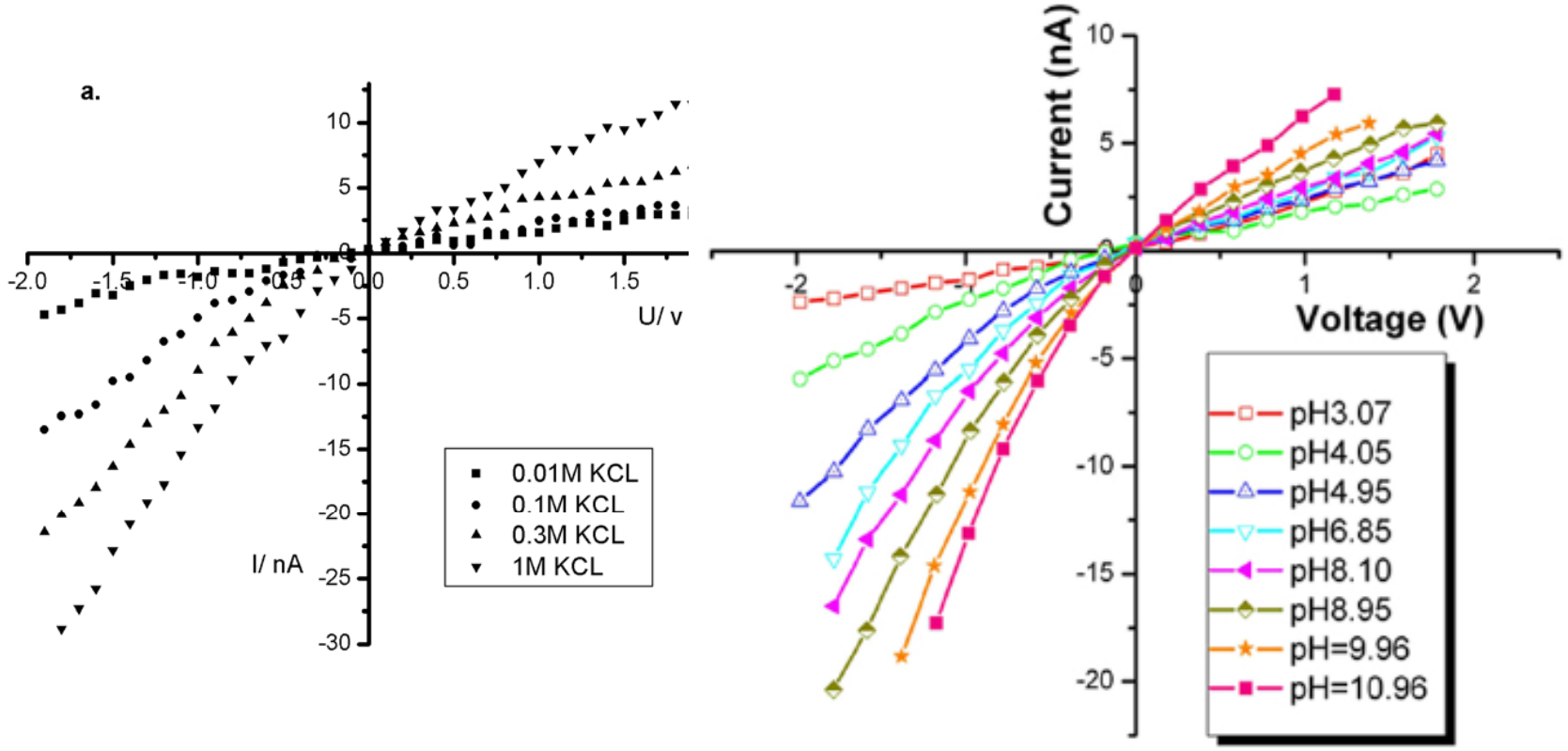




Pores are cation selective

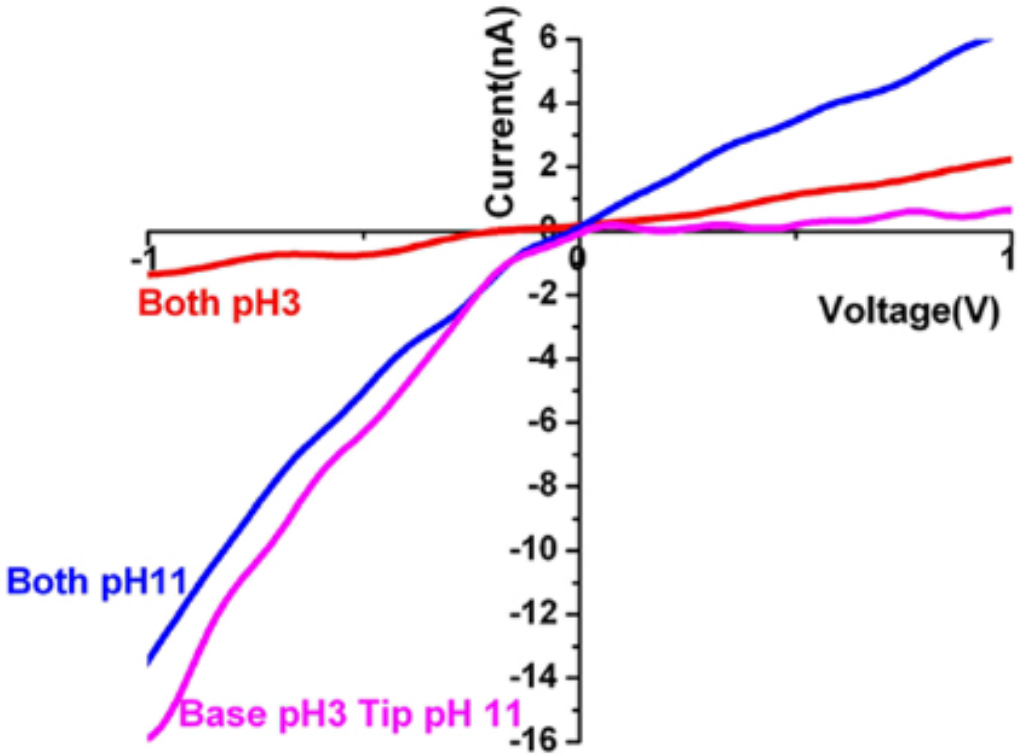
Fabrication and Investigation of Single Nanopore

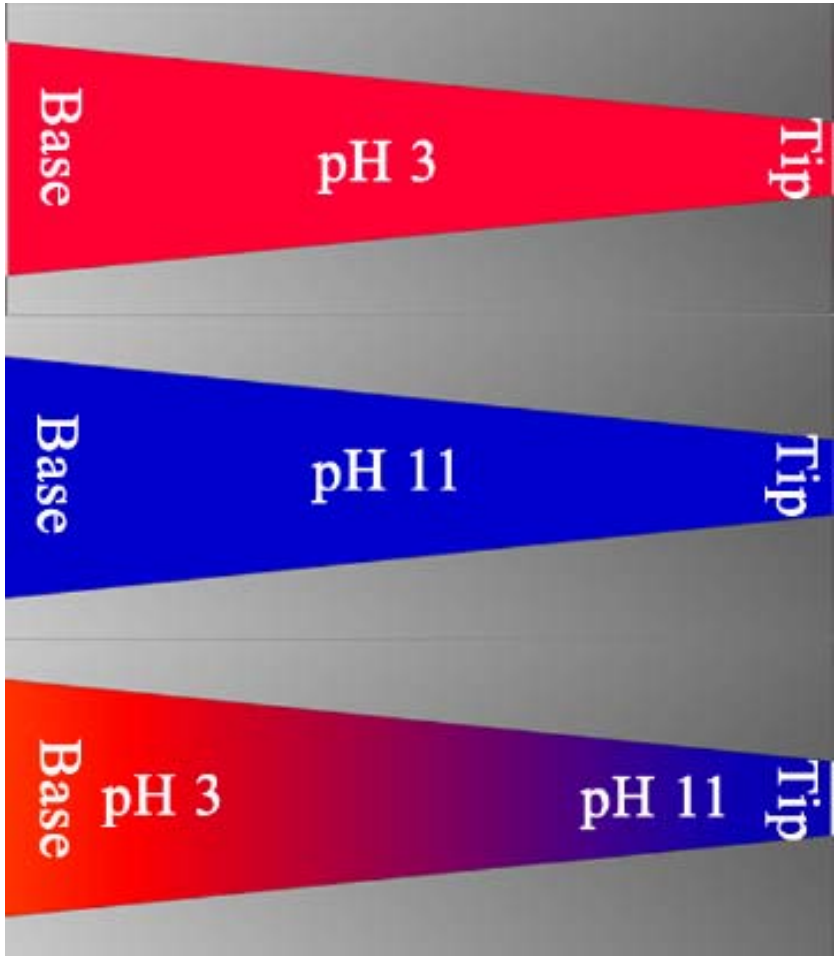
- **Experimental studies of asymmetric properties of ion transport in nanopore**
  - Ion-current rectification (diode-like I-V curve) was verified
  - The rectification effect is influenced by c(M) and pH value



Fabrication and Investigation of Single Nanopore

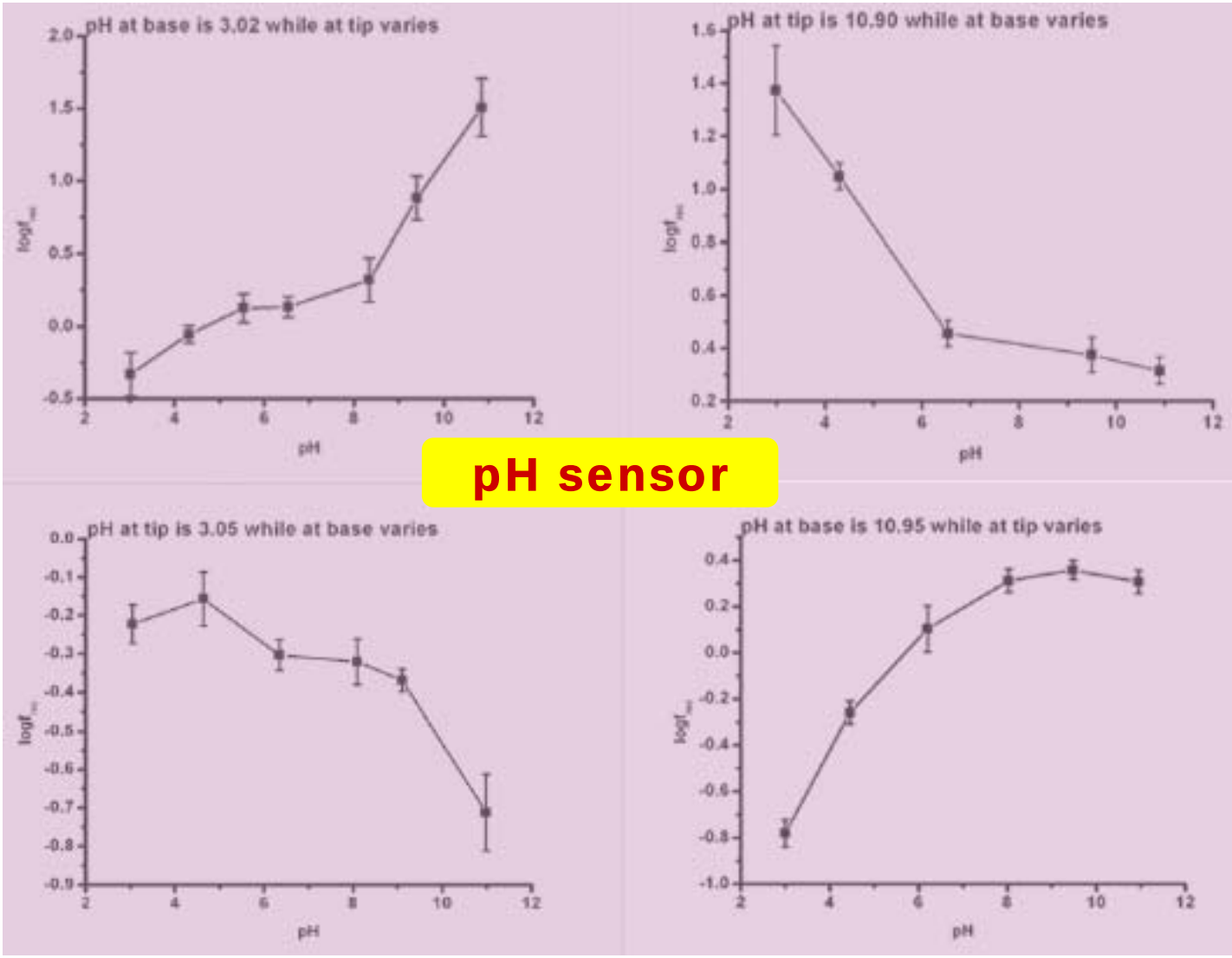
- I-V curves at different pH environments





Fabrication and Investigation of Single Nanopore

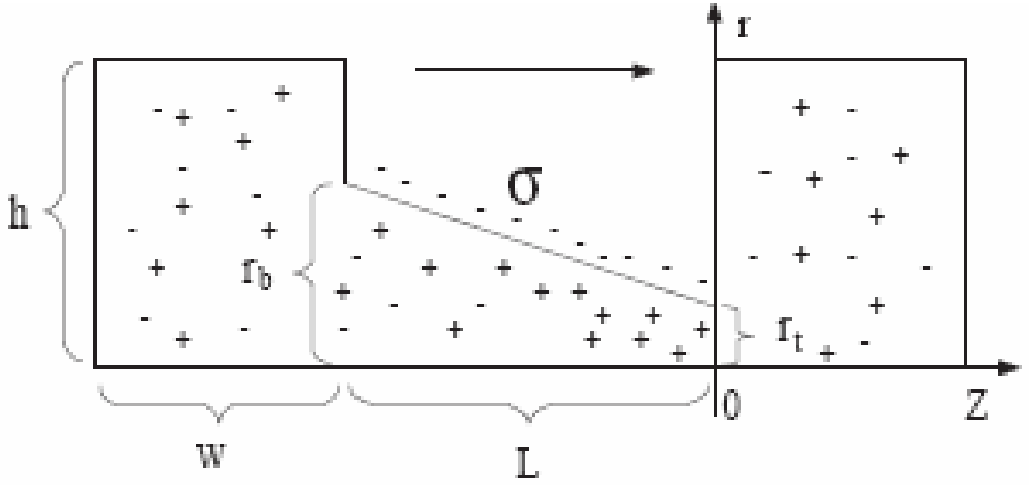
Rectification in asymmetric pH environments



Fabrication and Investigation of Single Nanopore

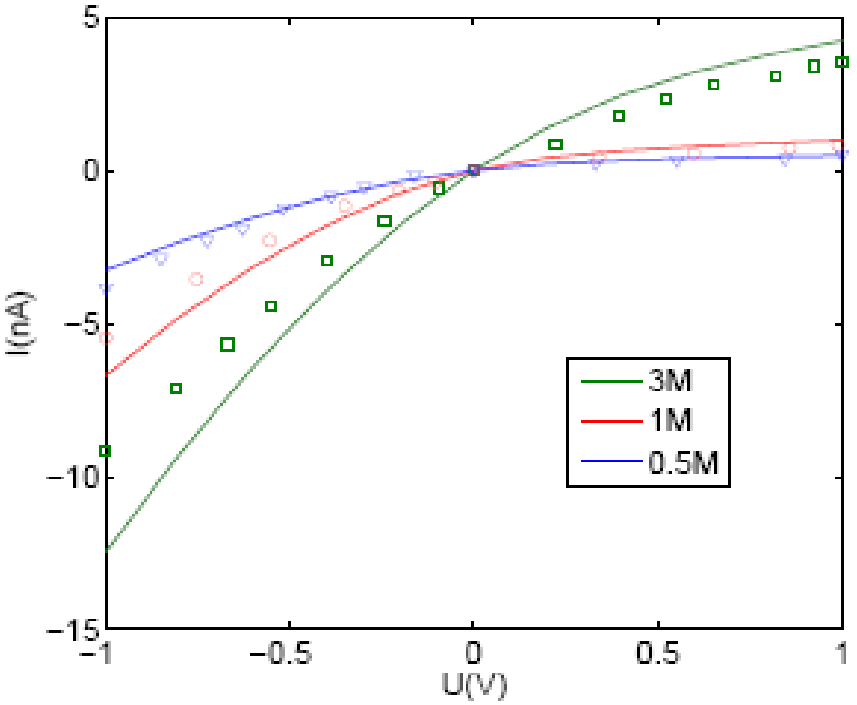
- **Theoretical study on asymmetric properties of nanopores based on PNP equations**
  - Finite element method was used to solve 3-D PNP equations
  - There is no free parameters in our model; all were taken from experimental data, including surface charge density , the size of the nanopore , ion concentration of KCl , and diffusion coefficients.

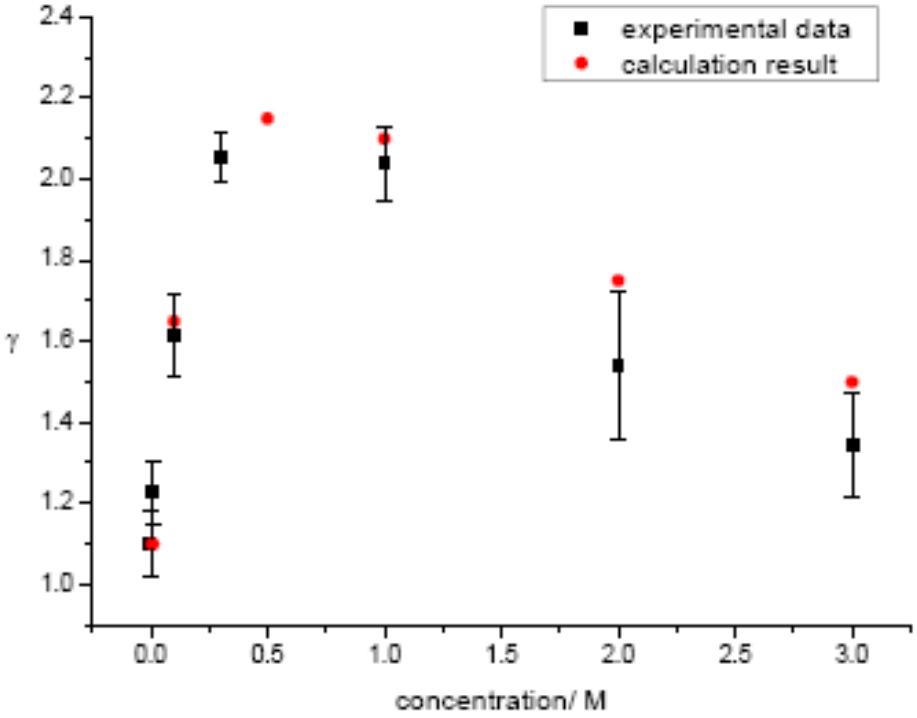
$$\nabla^2\phi = -\frac{e}{\varepsilon\varepsilon_0}\left(n_+ - n_-\right) \qquad J_i = -D_i\left(\nabla n_i + \frac{ien_i}{kT}\nabla\phi\right), i = +,-$$



Fabrication and Investigation of Single Nanopore

- Our theoretical calculation results consist with the experimental data well (from GSI's and ourselves)

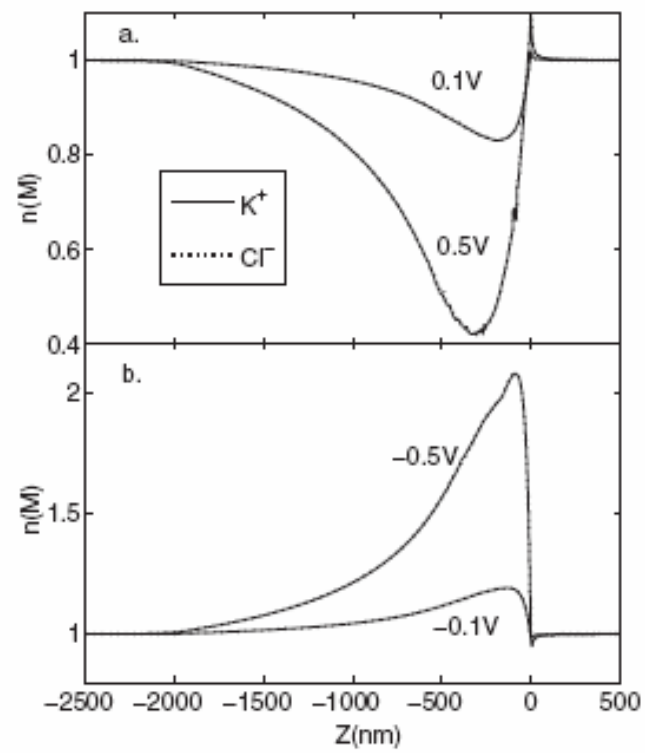


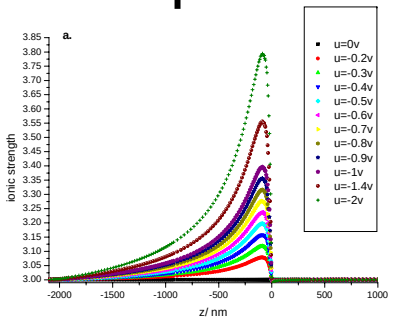


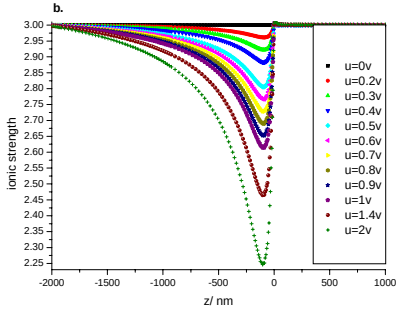
$$\gamma = I(-U)/I(+U)$$

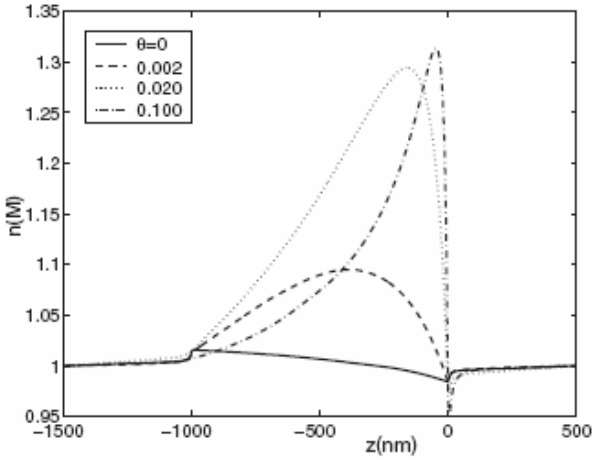
Fabrication and Investigation of Single Nanopore

- This current rectification effect is contributed to ion-enrichment and ion-depletion effect





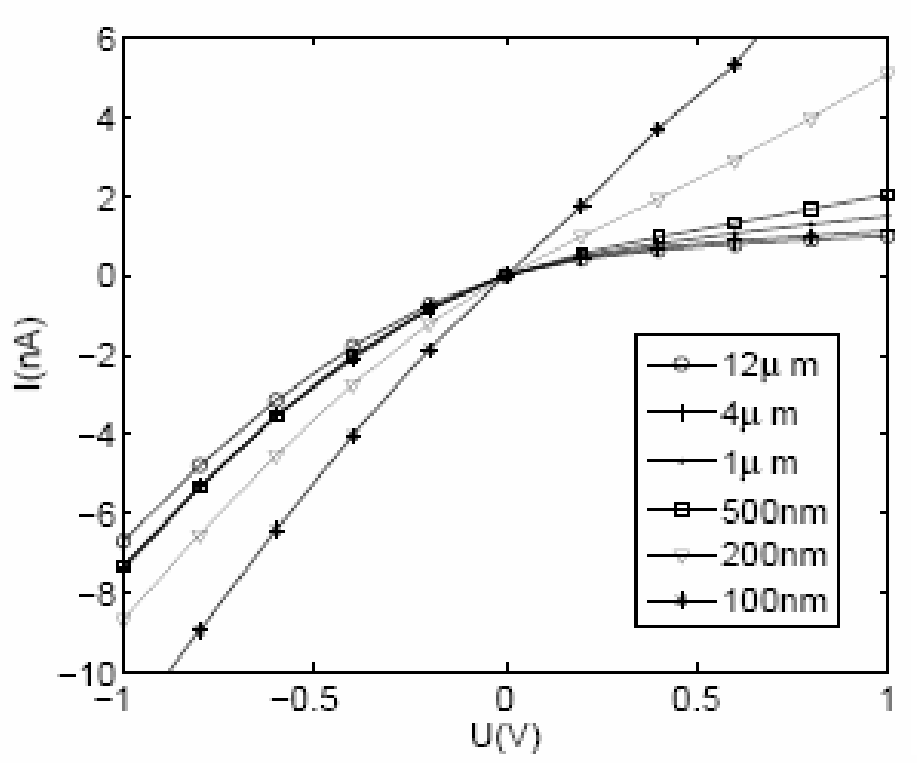


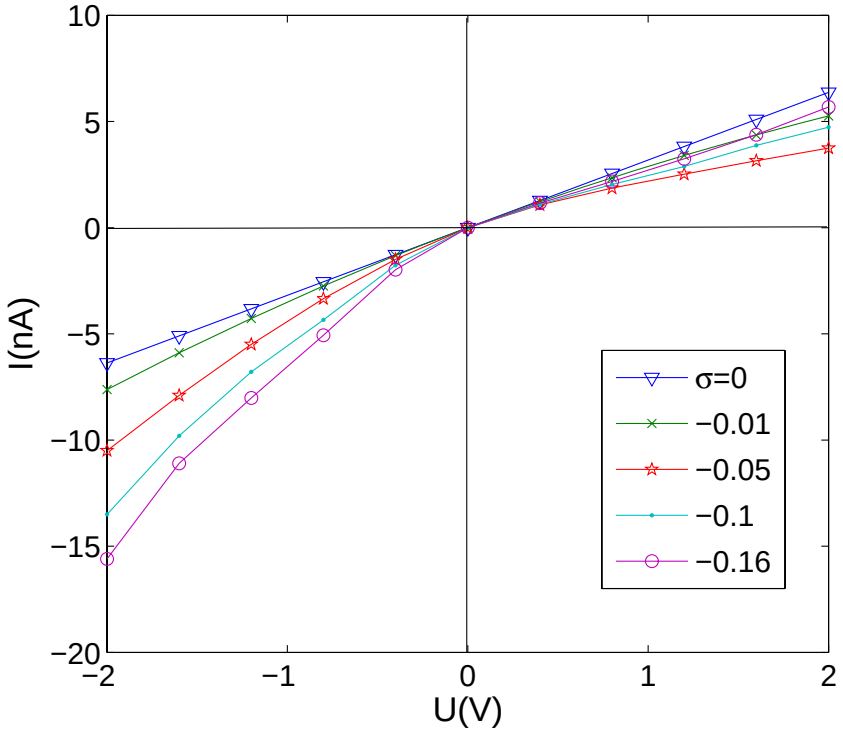


The particular shape of the conical pore causes ion greatly enriched or depleted in the mid of the pore. The conductivity of the pore is adjusted by the applied voltage and cone angle.

Fabrication and Investigation of Single Nanopore

- A relatively long length is indispensable for the conical pore to have rectification effect; a conical pore with the length comparable to its tip diameter is impossible to have the rectification effect.

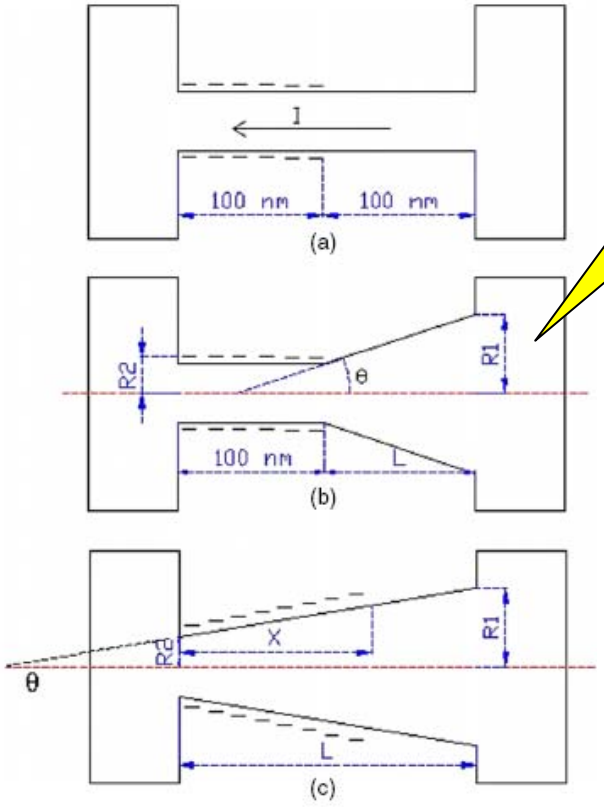




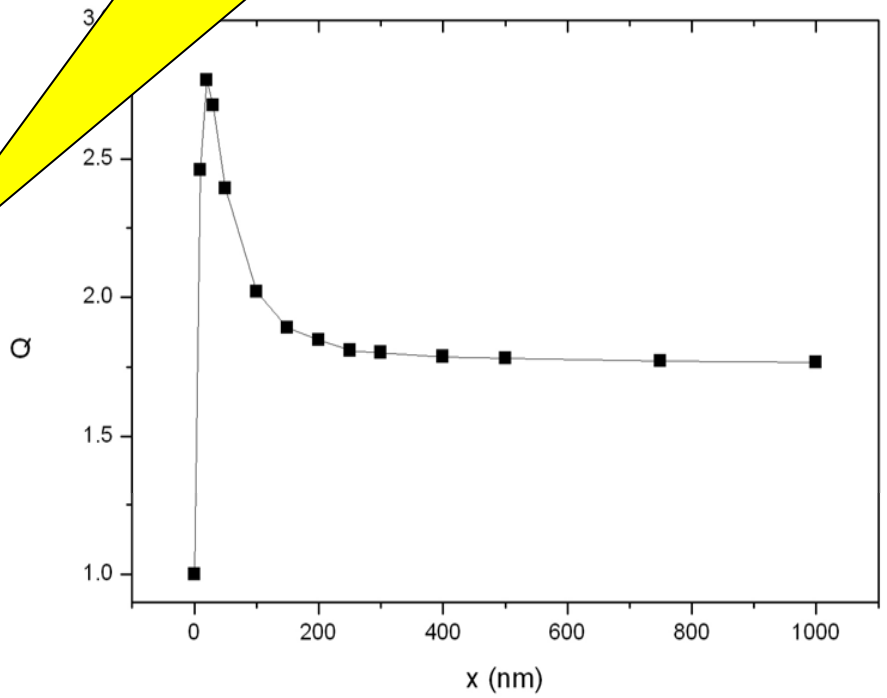
Phys. Rev. E, 2007

Fabrication and Investigation of Single Nanopore

- For a long conical nanopore charged homogeneously, the electrical and geometrical properties of the section near nanopore's tip with a length of hundreds of nanometer are mainly responsible for the ionic current rectification.



electrophoresis



J. Phys. D, 2007

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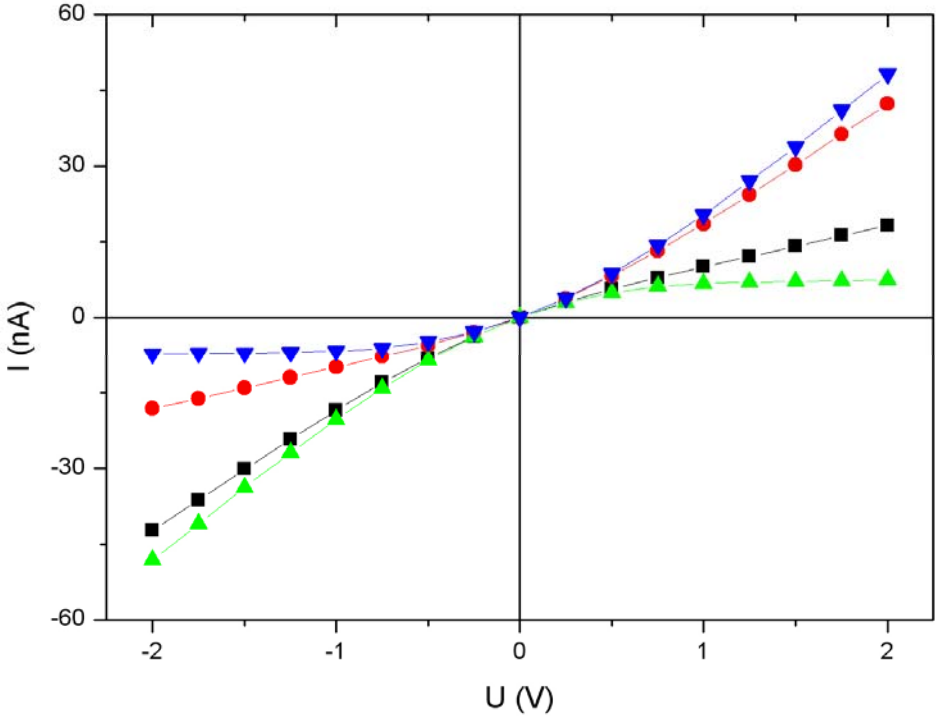
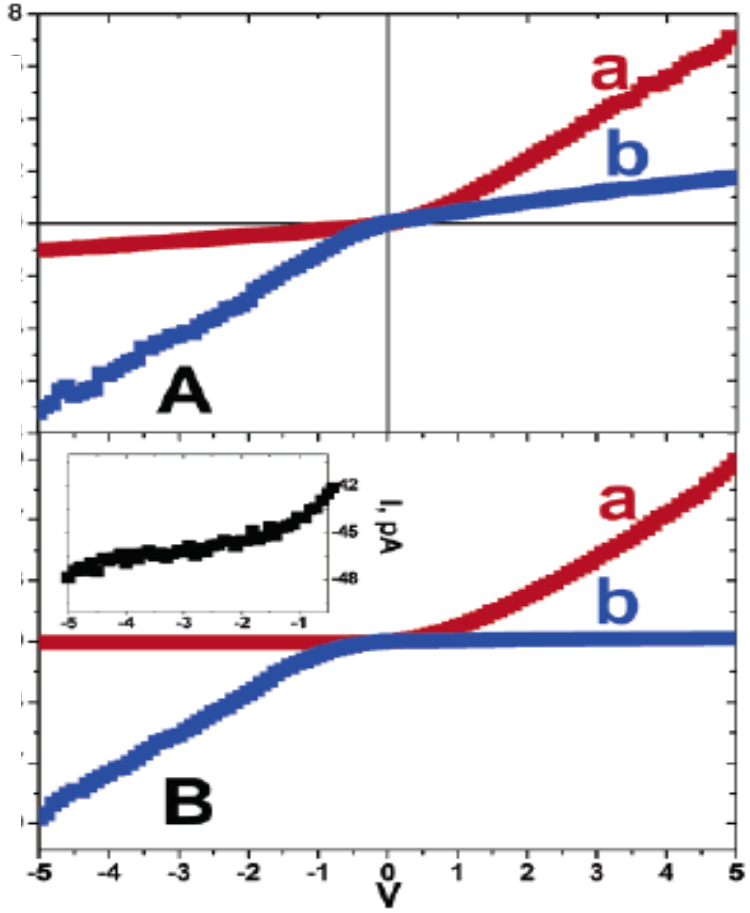
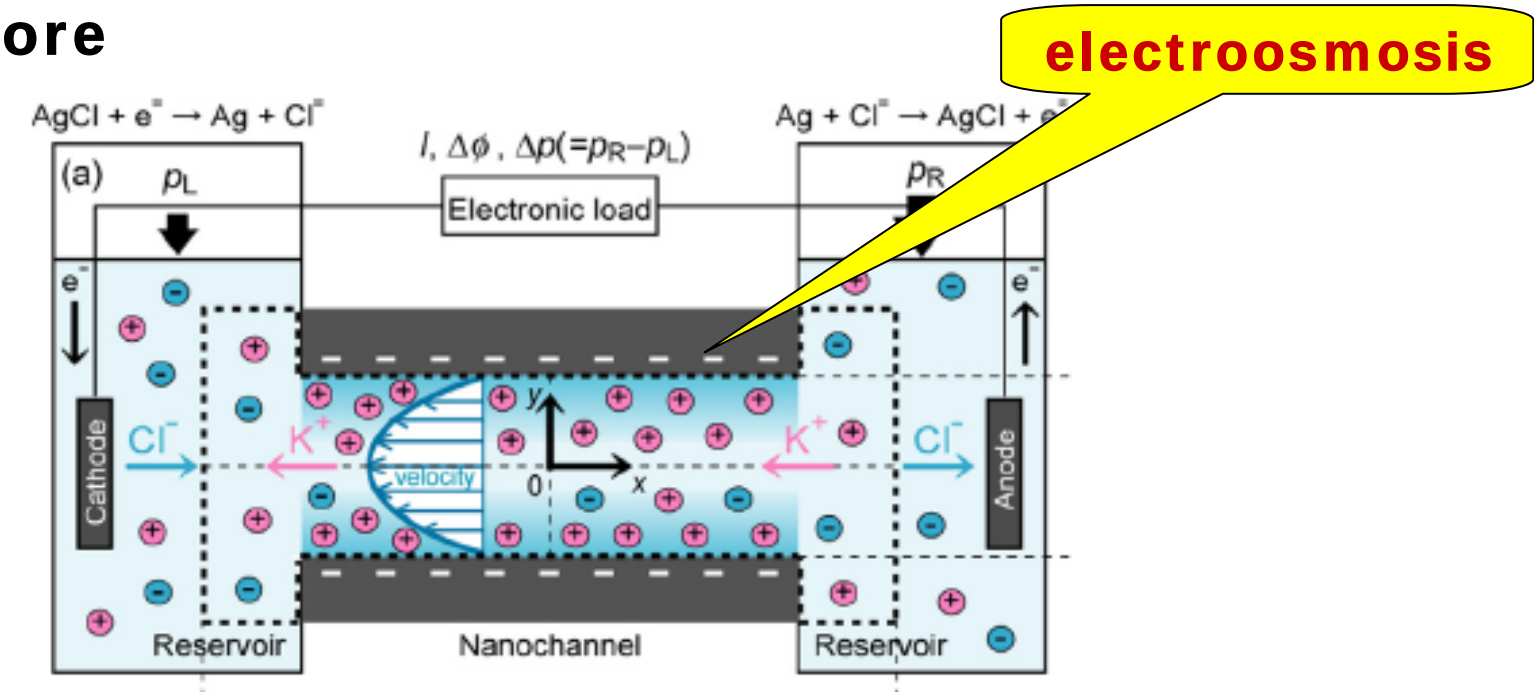




Fabrication and Investigation of Single Nanopore

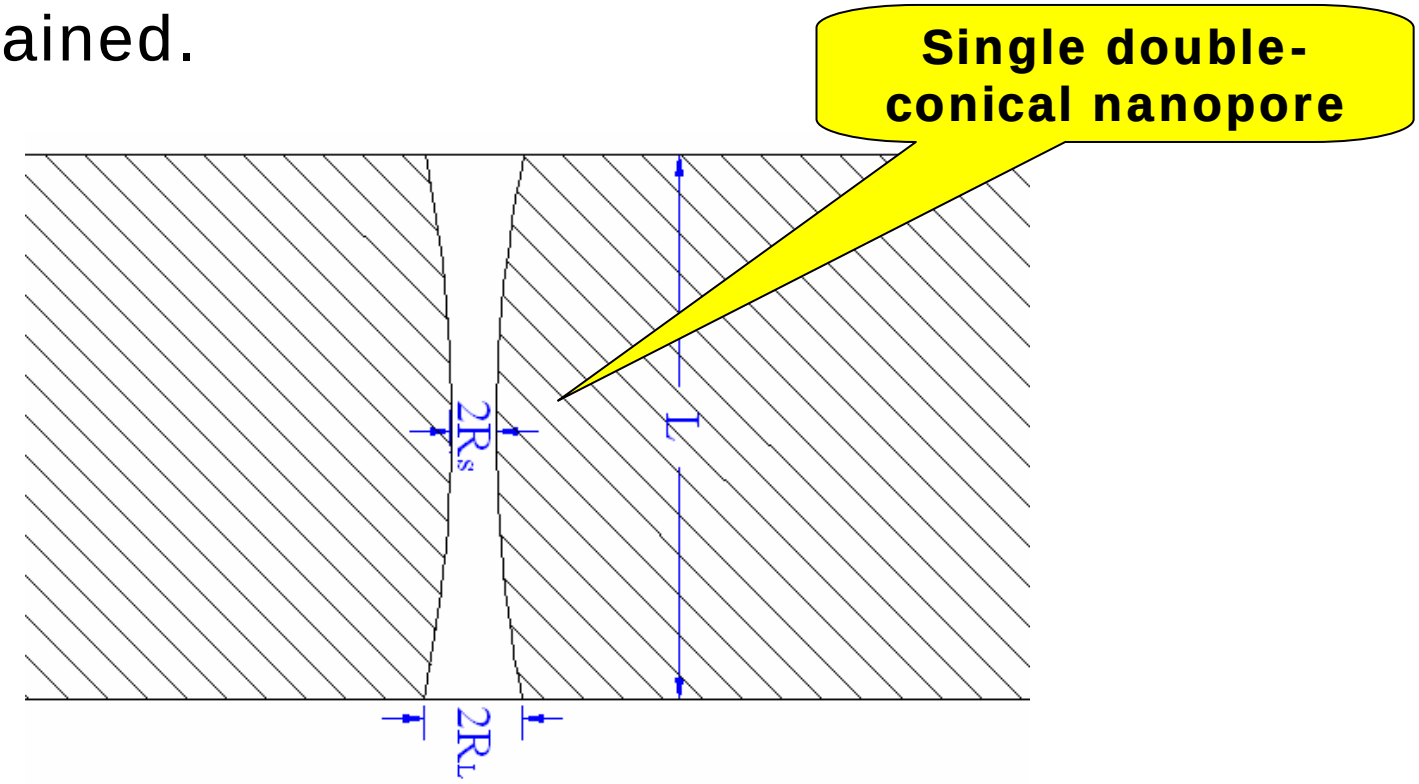
- **Electric Energy Generation in Single Track-etched Nanopore**



A pressure-gradient-driven flow inside nanofluidic channels that have a surface charge can be used to generate streaming current and potential. This process forms the basis for electro-chemo-mechanical energy conversion in nanofluidic batteries.

Fabrication and Investigation of Single Nanopore

- The chemical etching was performed from both sides of the PET foil simultaneously, and a double-conical shaped nanopore with very small angles was obtained.

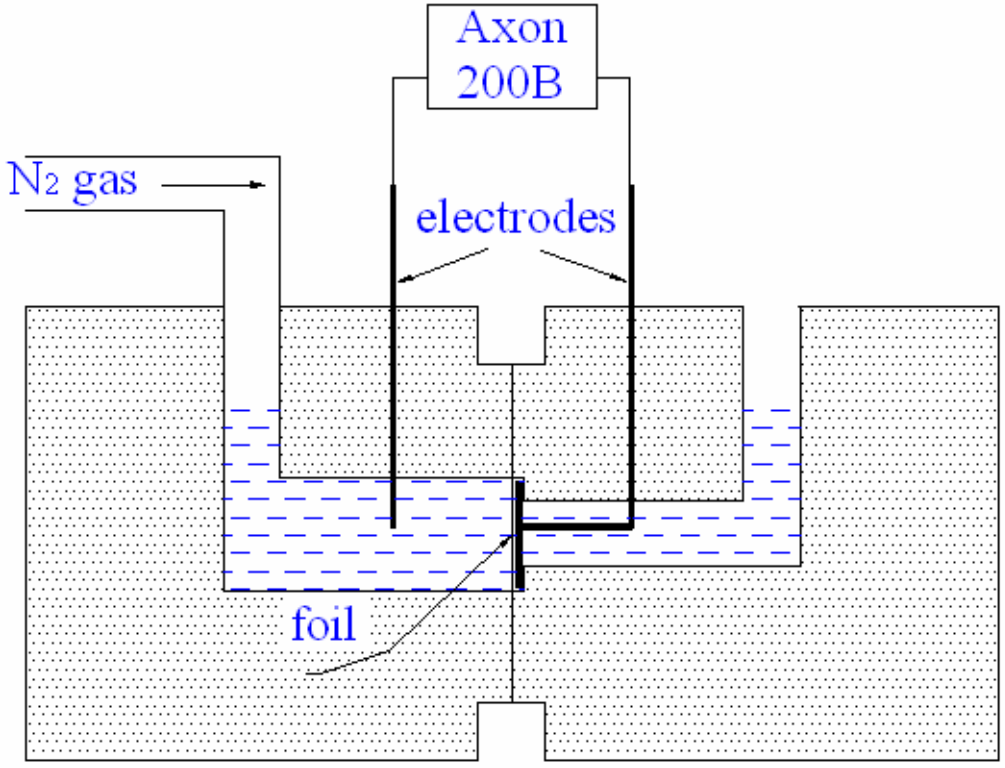


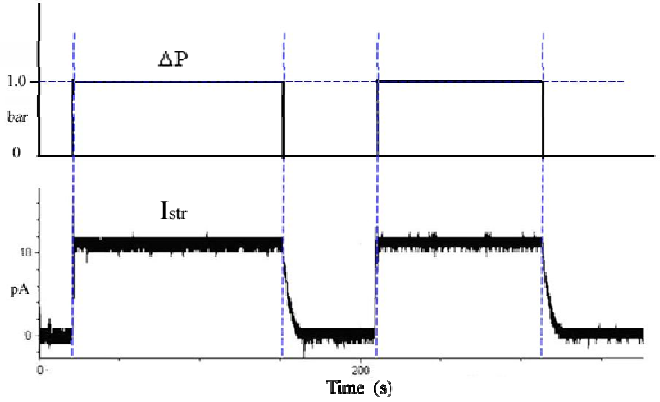
72nm / 160nm (sample Ⅰ), 72nm /160nm (sample Ⅱ)

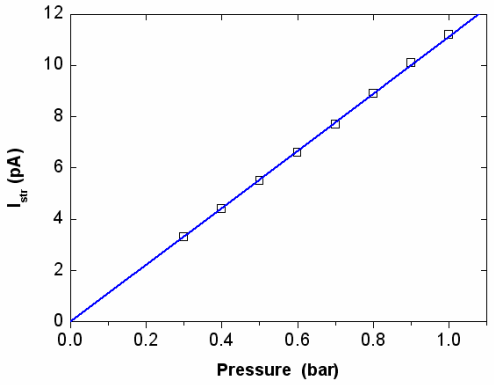
32 nm /120 nm (sample Ⅲ) and 31 nm /120 nm (sample Ⅳ)

Fabrication and Investigation of Single Nanopore

- The streaming current (I_{str}) was recorded directly with a patch clamp (Axon 200B) .
- As pressure was applied I_{str} increased instantaneously, and then kept stable. After the external pressure was removed, I_{str} dropped back to zero again.

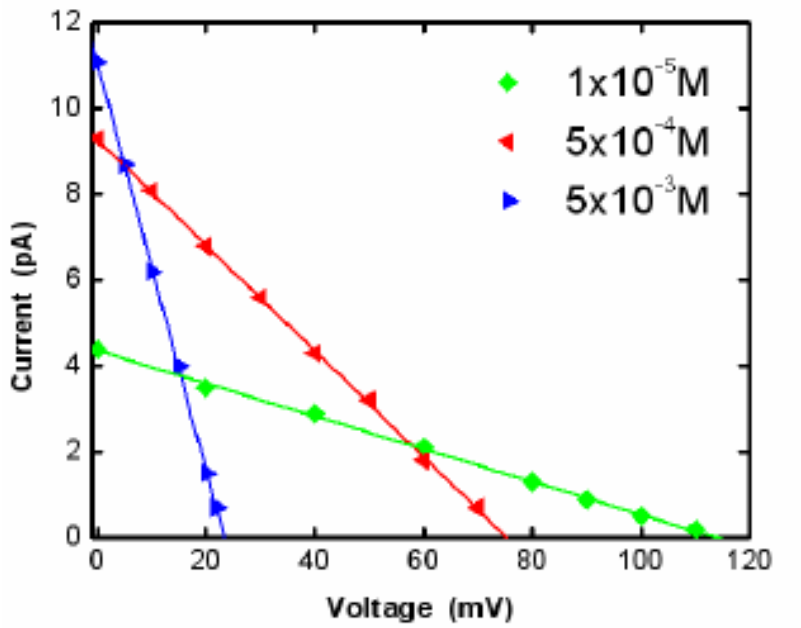


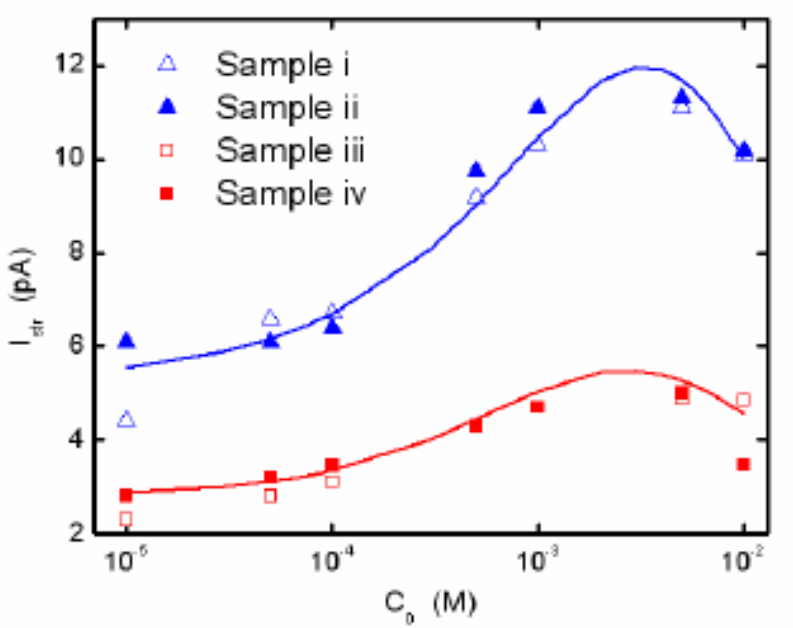




Fabrication and Investigation of Single Nanopore

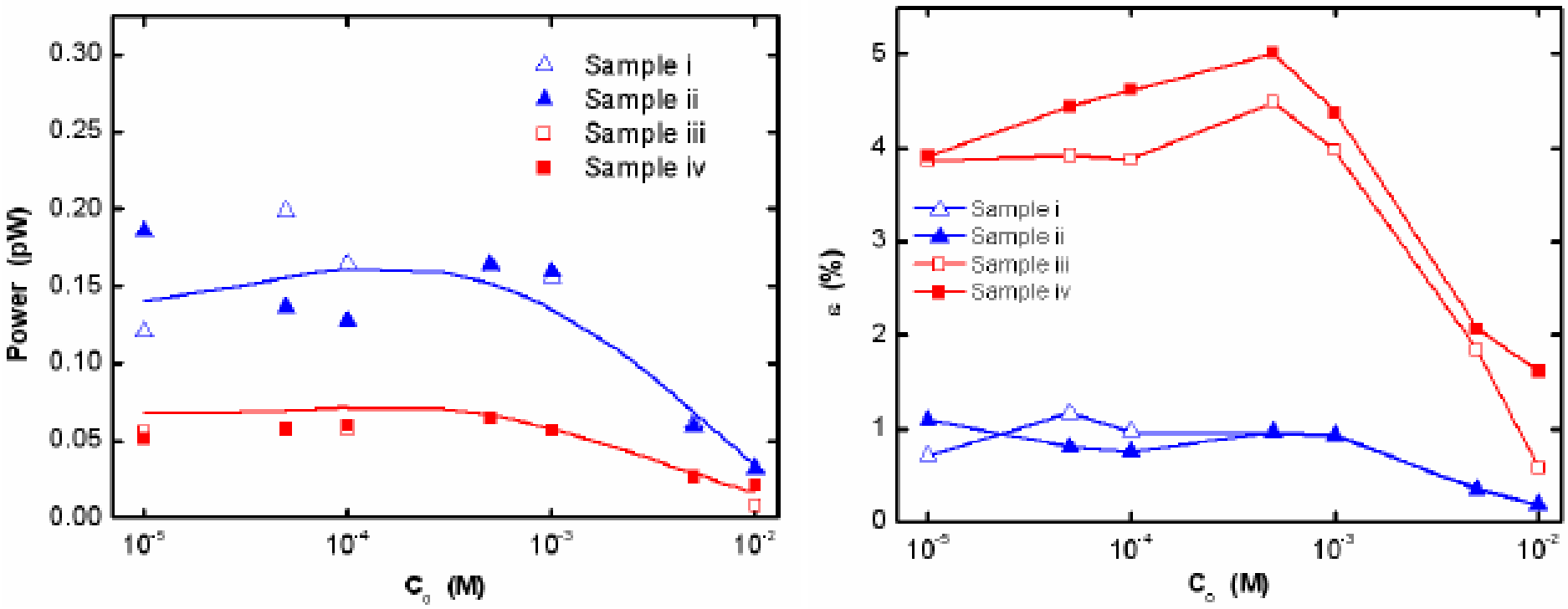
- Following figure shows a linear current-potential characteristic at different KCl concentrations, so the nanopores can be treated as a battery of an ideal current source plus an internal resistance
- I_{str} drops down as the KCl concentration (c_0) decreases





Fabrication and Investigation of Single Nanopore

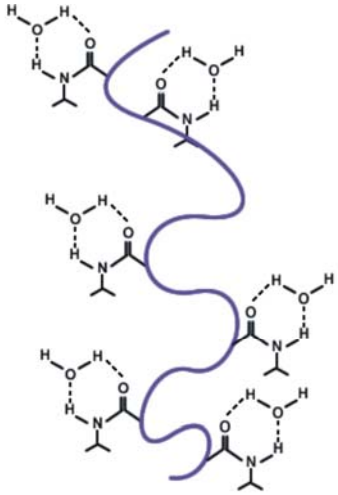
- A larger radius means a larger output power; a smaller radius means higher efficiency of energy conversion.
- Highest energy-conversion efficiency around 4-5% was achieved with this single conical nanopore.
- The track-etched nanopore method is very suitable for practical nanofluidic energy conversion devices.



Fabrication and Investigation of Single Nanopore

Thermal Responsive Nanochannels

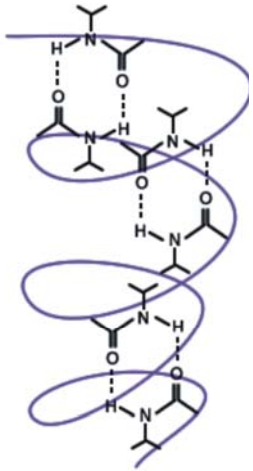
Poly(*N*-isopropylacrylamide), Mn=19,000



T < LCST

T > LCST

PNIPAM

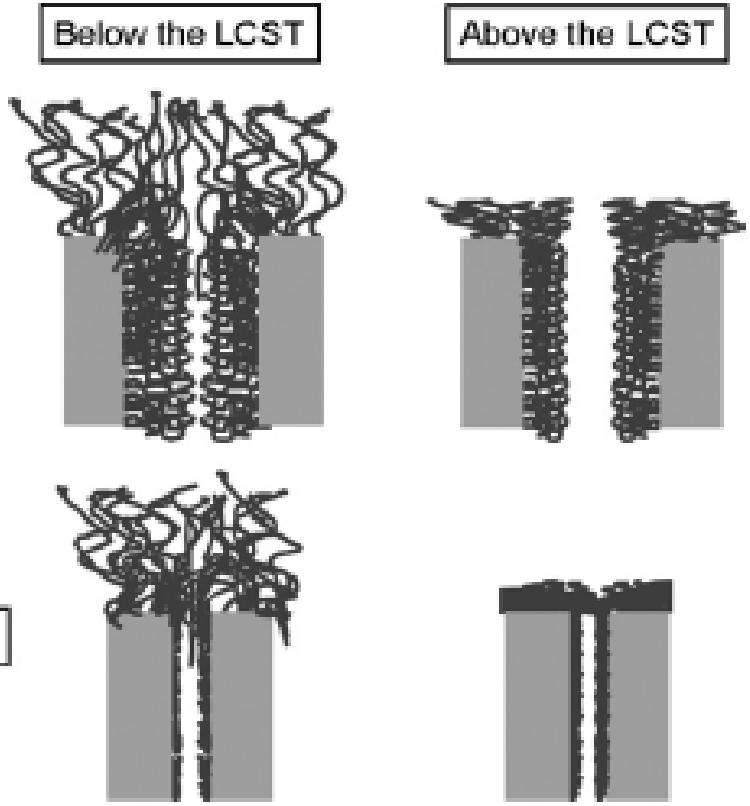


Swollen State

Collapsed State

Larger pores

Smaller pores



LCST: Lower Critical Solution Temperature

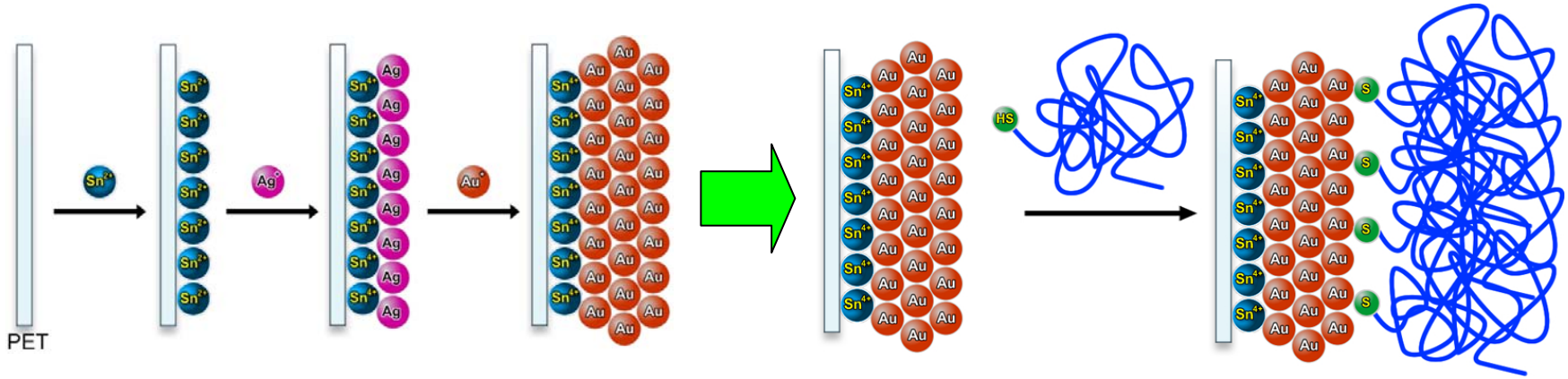
Journal of Membrane Science 308 (2008) 75–86

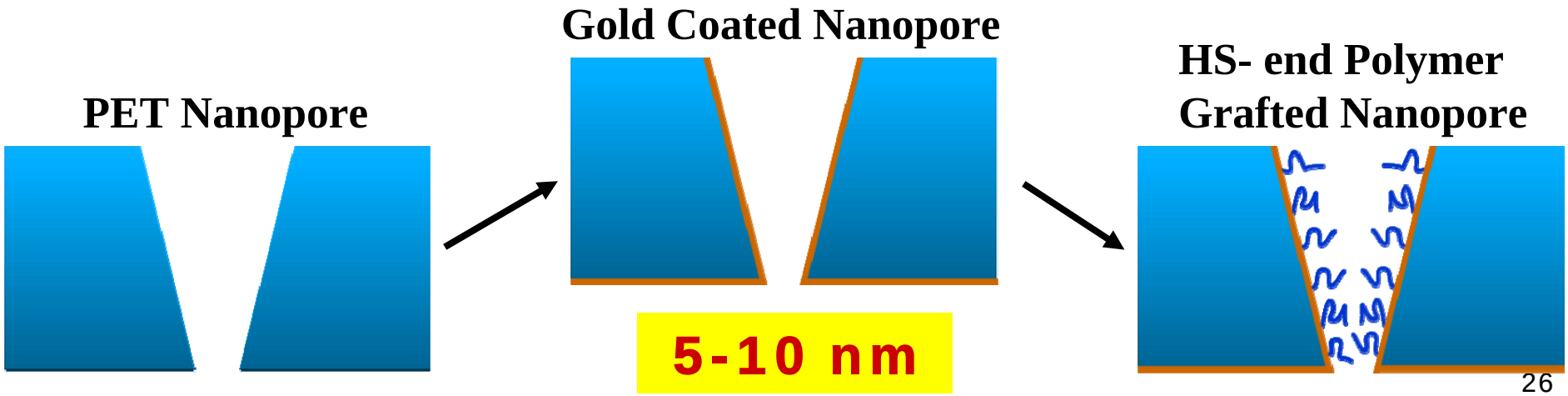
Fabrication and Investigation of Single Nanopore

$$Sn^{2+} + 2Ag^{+} \rightarrow Sn^{4+} + 2Ag$$

$$Au^{+} + Ag \rightarrow Au + Ag^{+}$$

$$2Au^{+} + HCHO + 3OH^{-} \rightarrow HCOO^{-} + 2H_2O + 2Au$$





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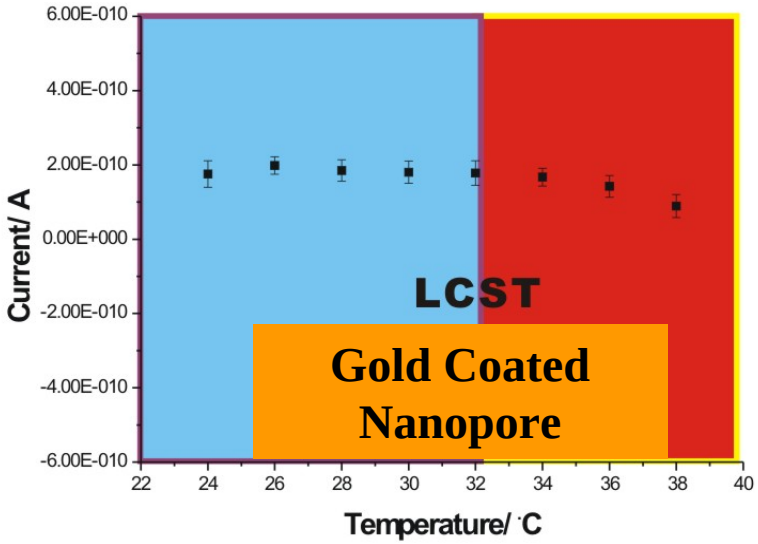
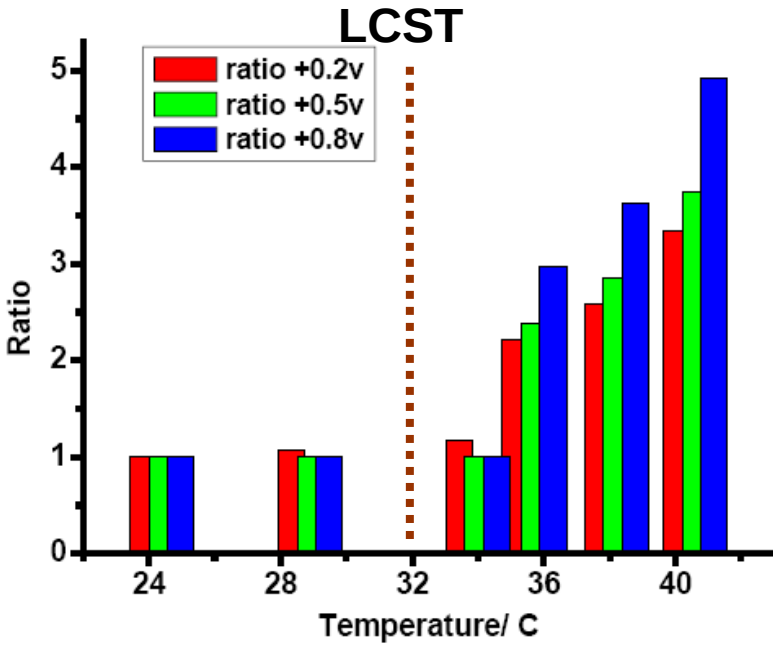
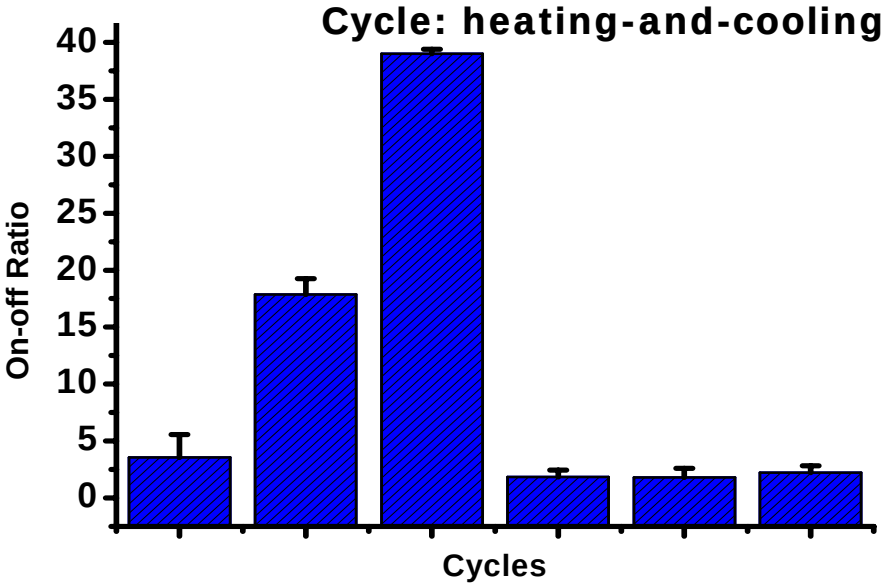
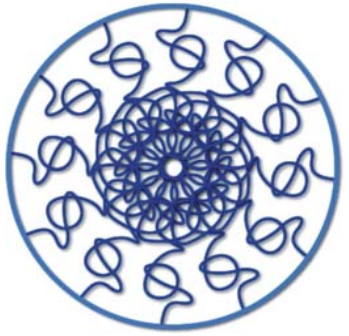






Off: at 24.4 ℃

On: at 38.2 ℃



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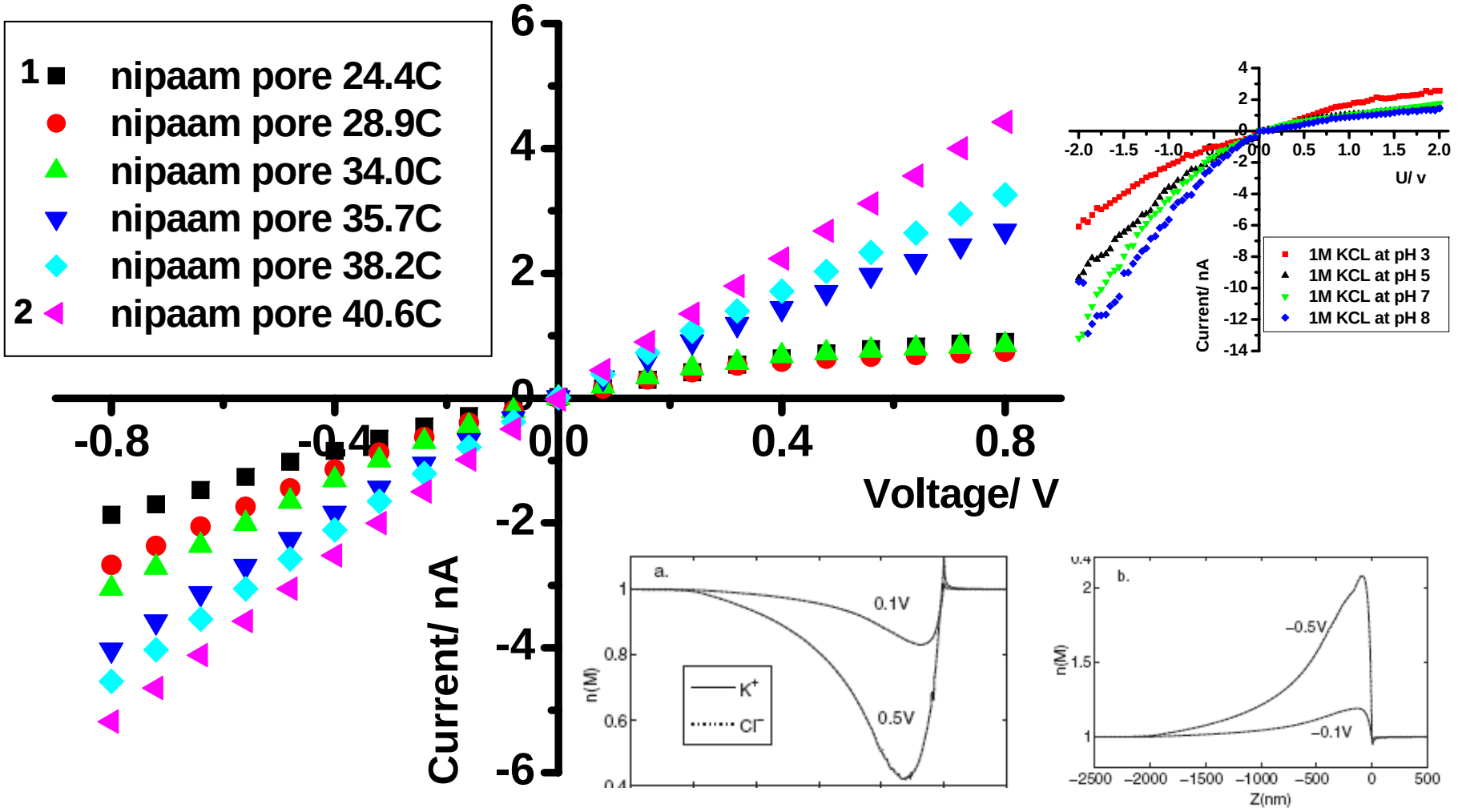
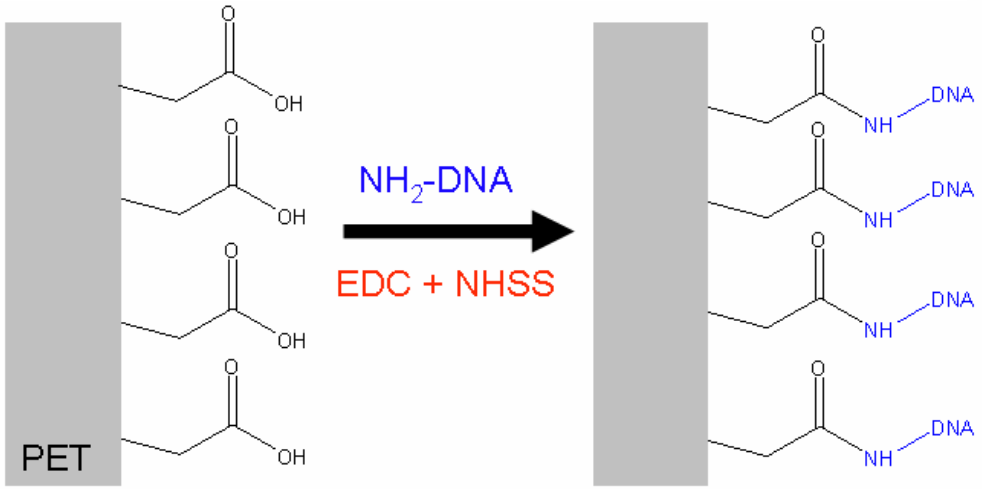


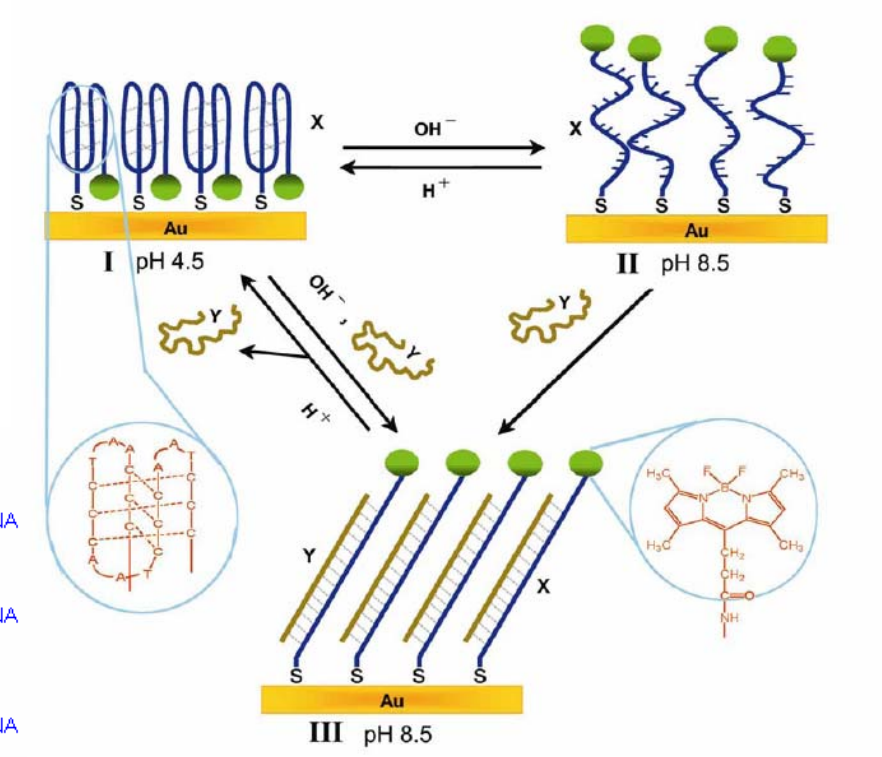
1 → Enrichment ↑ → Depletion ↓ → 2

Fabrication and Investigation of Single Nanopore

Fabrication of synthetic nanopore-C4 DNA

C-quadruplex
（C4）
DNA





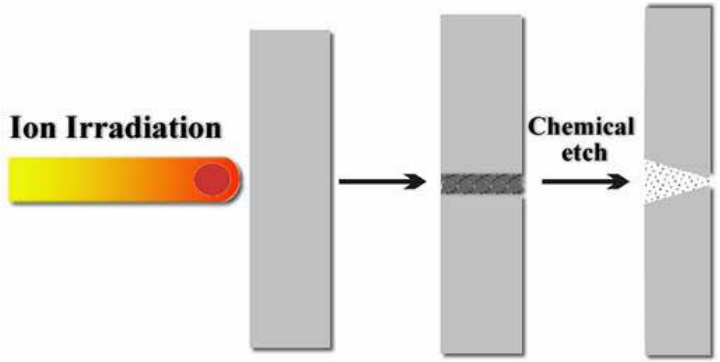
S. Wang and L. Jiang, et al., Angew. Chem. Int. Ed. 2007, 46, 3915.

5’ -(NH_2)-$(CH_2)_6$-AAAAAAAAAA CCC TAA CCC TAA CCC TAA CCC (Bodipy493/503)-3’

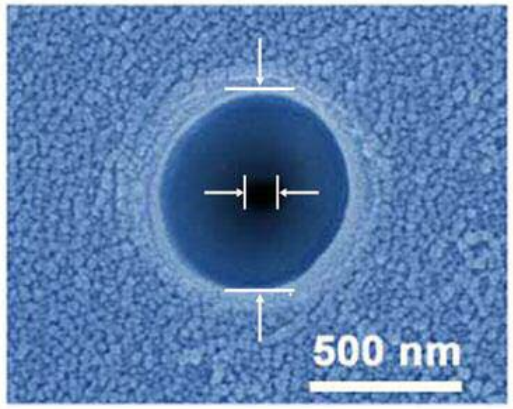
Fabrication and Investigation of Single Nanopore

Fabrication of synthetic nanopore-C4 DNA

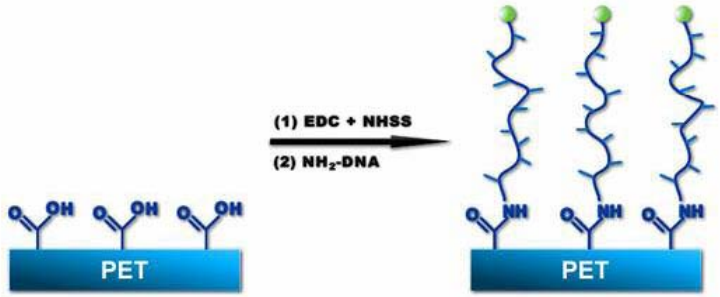
A. Nanopore fabrication by ion-track technique



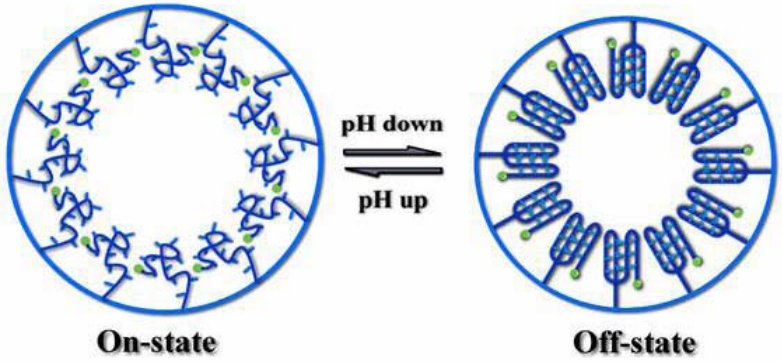
B. SEM image of the nanopore



C. Grafting DNA onto PET by a two-step chemical reaction.

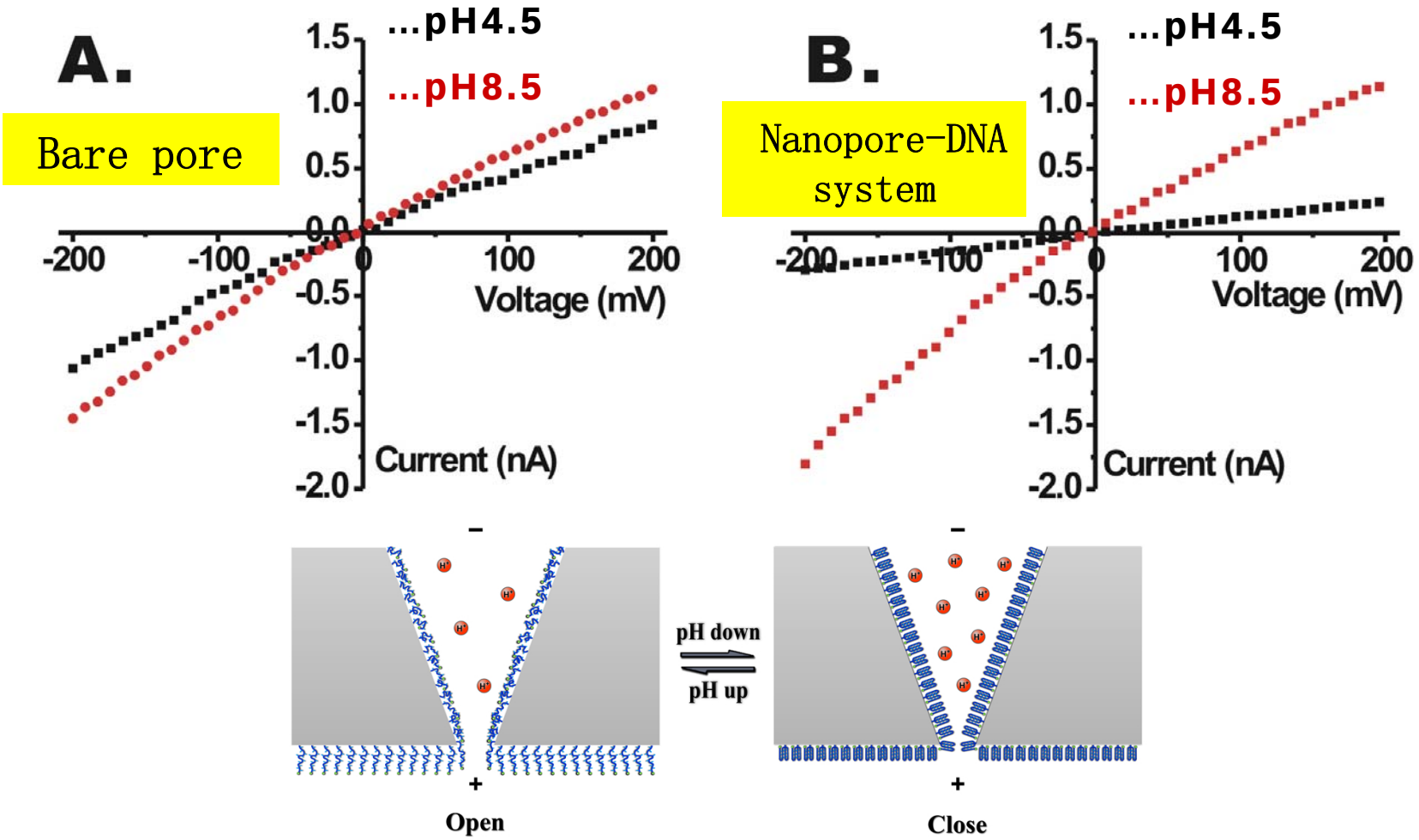


D. The attached DNA motor is responsive to pH



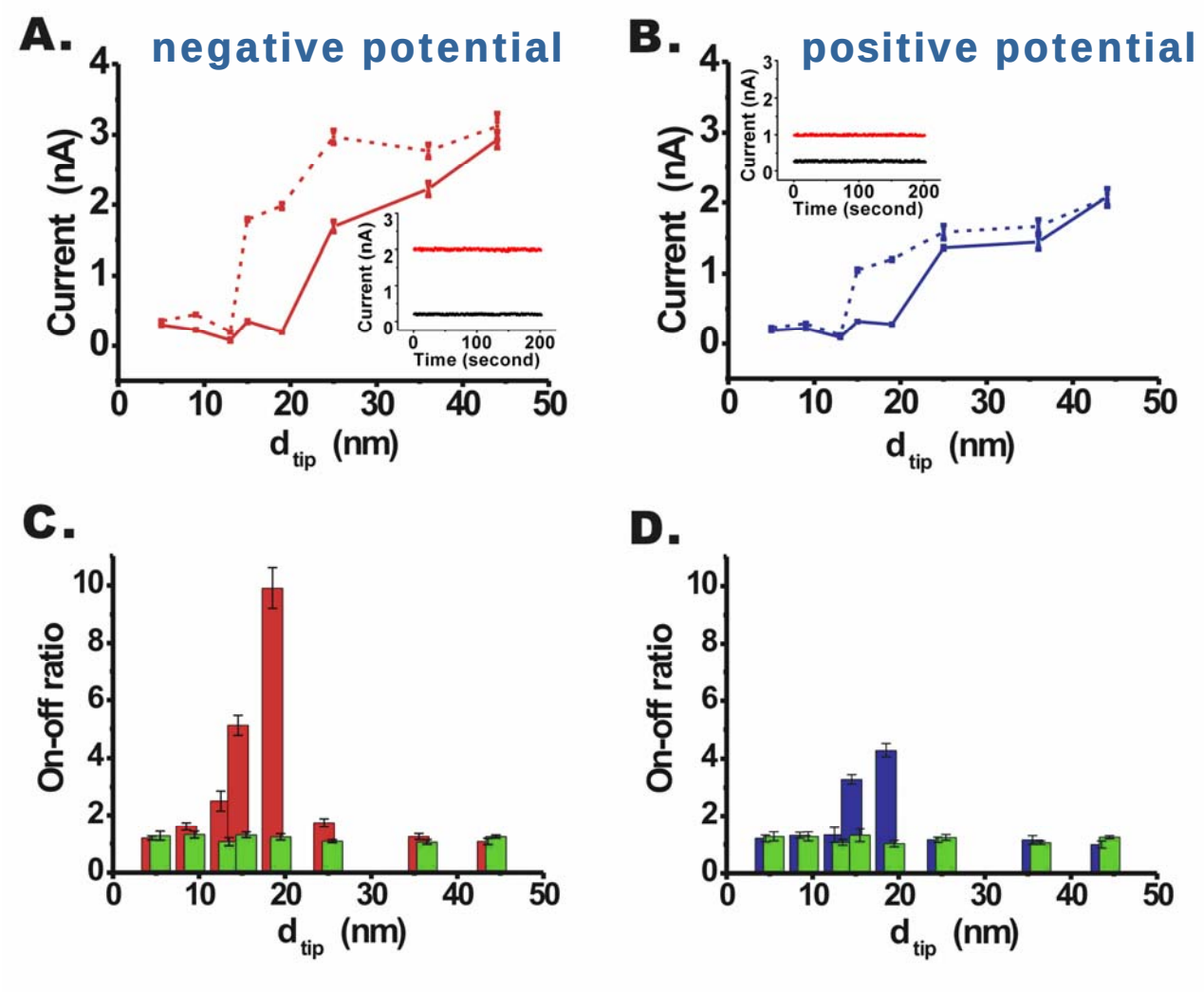
Fabrication and Investigation of Single Nanopore

- I-V curve of single nanopore before and after decoration of DNA



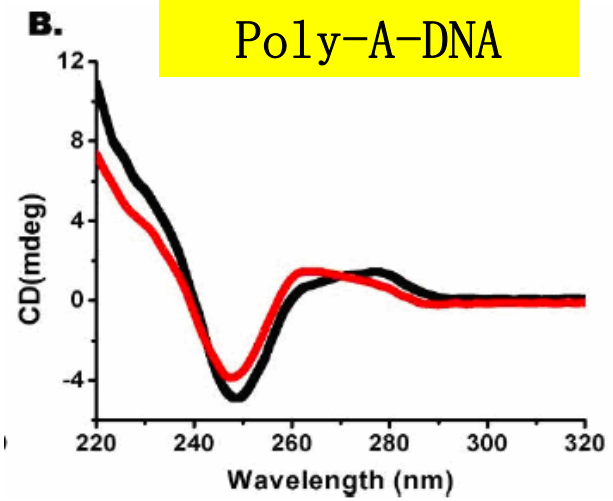
Fabrication and Investigation of Single Nanopore

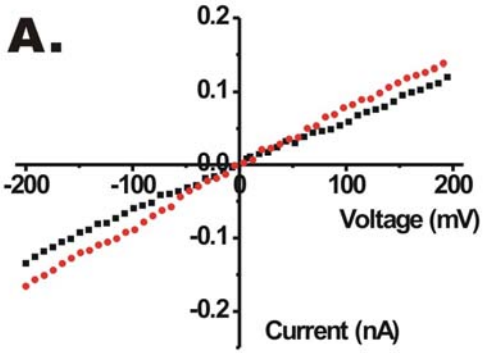
- Performance of nanopore-DNA in switching the "gate"

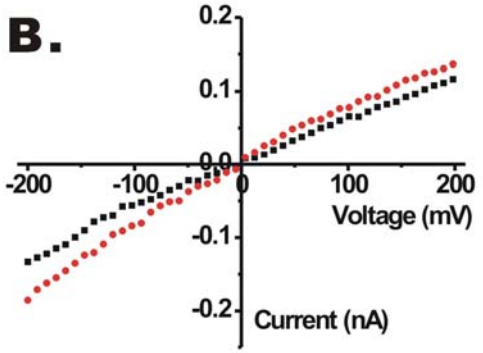


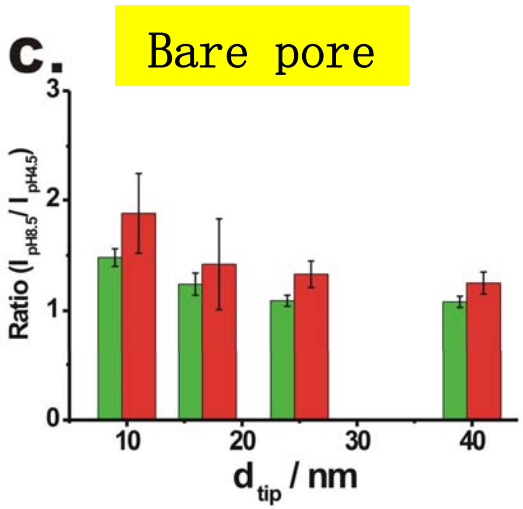
Fabrication and Investigation of Single Nanopore

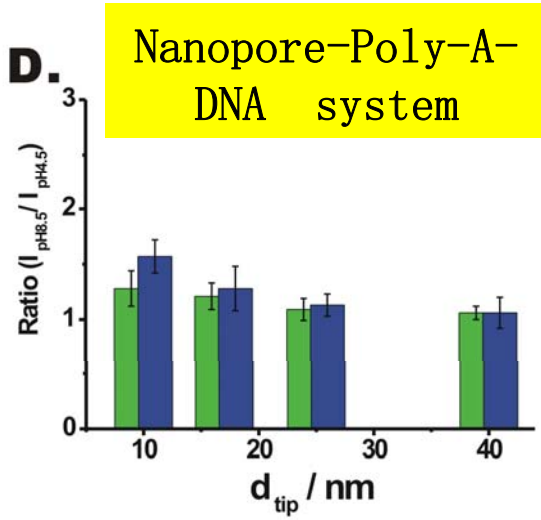
- I-V curve and switching performance of a Poly-A nanopore system







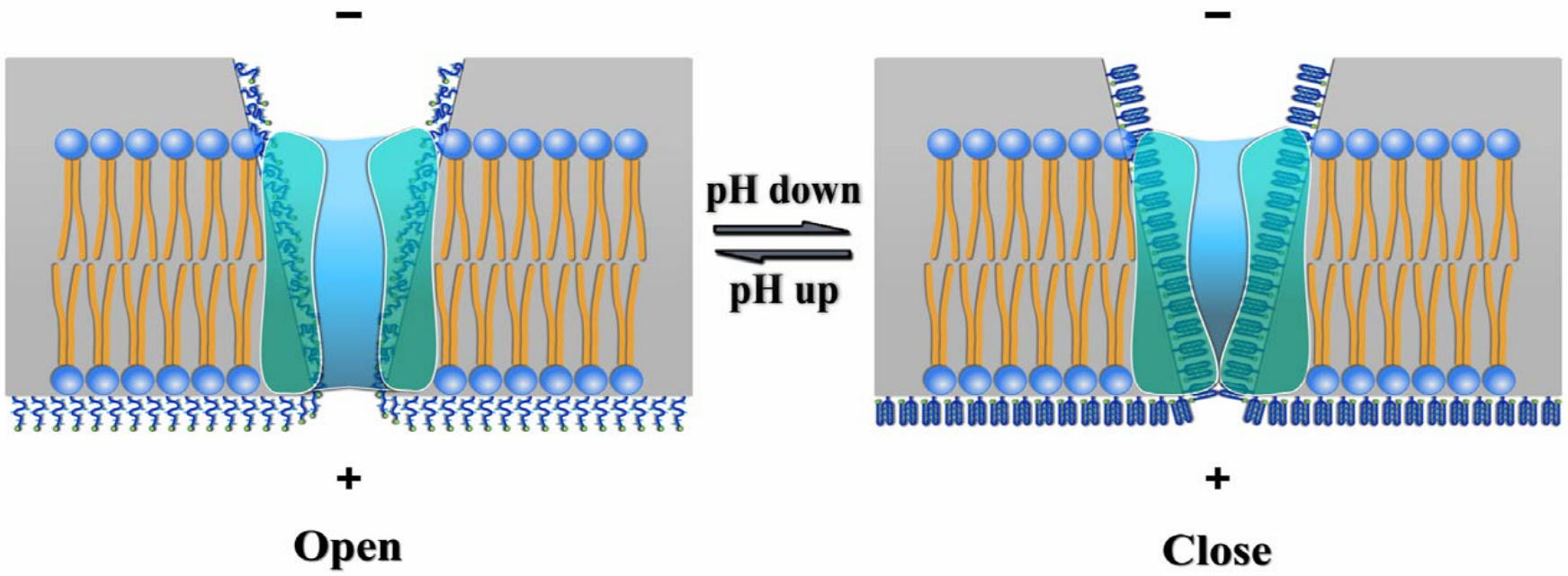




5’ -(NH_2)-$(CH_2)_6$-AAAAAAAAAA AAA AAA AAA AAA AAA AAA AAA (Bodipy493/503)-3’

Fabrication and Investigation of Single Nanopore

- Synthetic nanopores were gated by the conformational change of DNA molecules.
- The pH-responsive nanopore-DNA system was inspired by biological ion channel in nature.



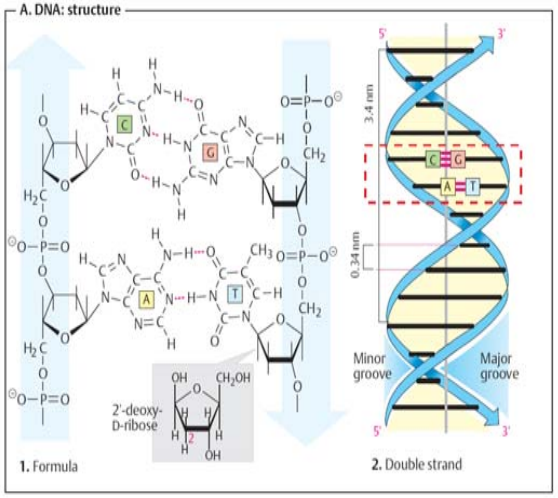
JACS, 2008

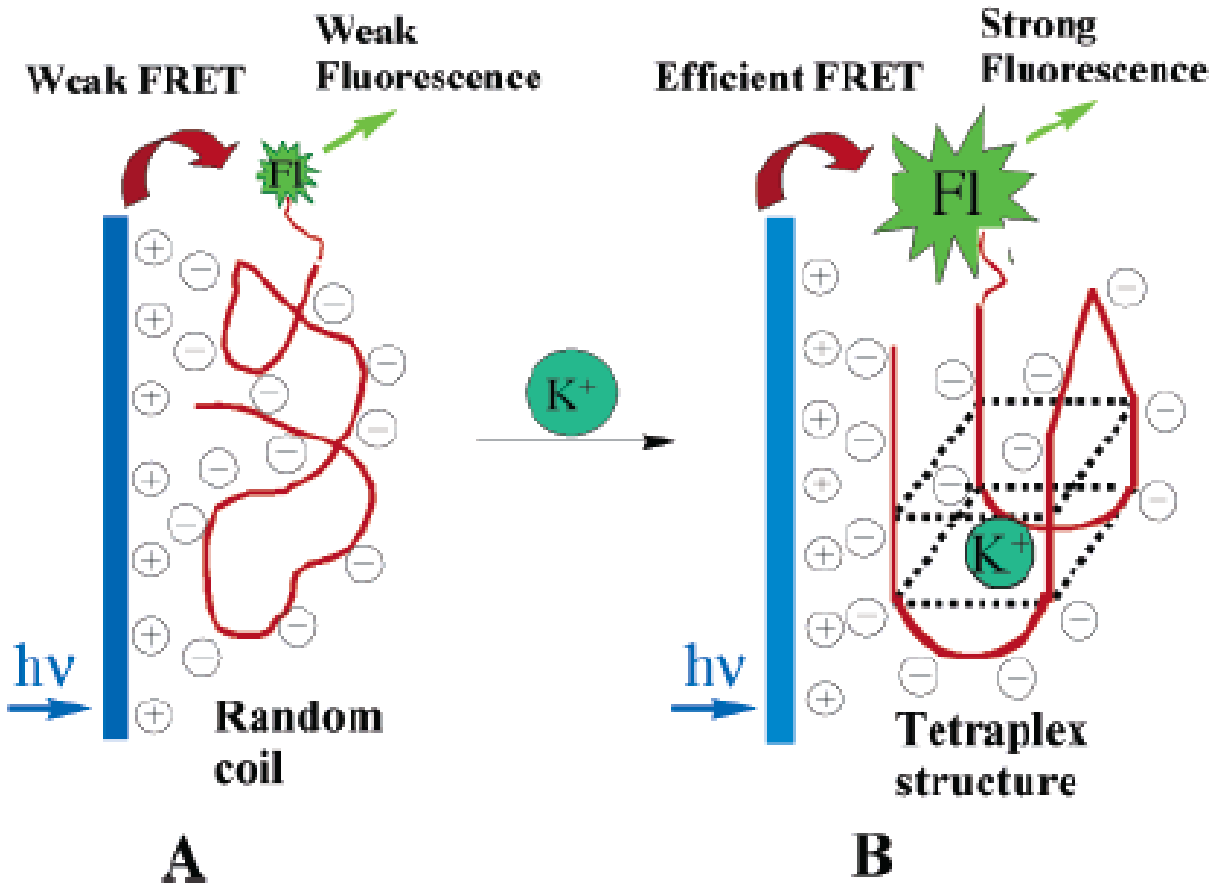
Fabrication and Investigation of Single Nanopore

Nanopore-G4 DNA System

- G4 DNA changes its configuration with alkali metal ions (sensitivity: $K^+ >> Na^+ > Rb^+ > NH_4^+ > Cs^+ >> Li^+$)

G-quadruplex（G4）DNA





Fabrication and Investigation of Single Nanopore

- Nanopre-G4 DNA can be gated by K^+ ions at very low concentration

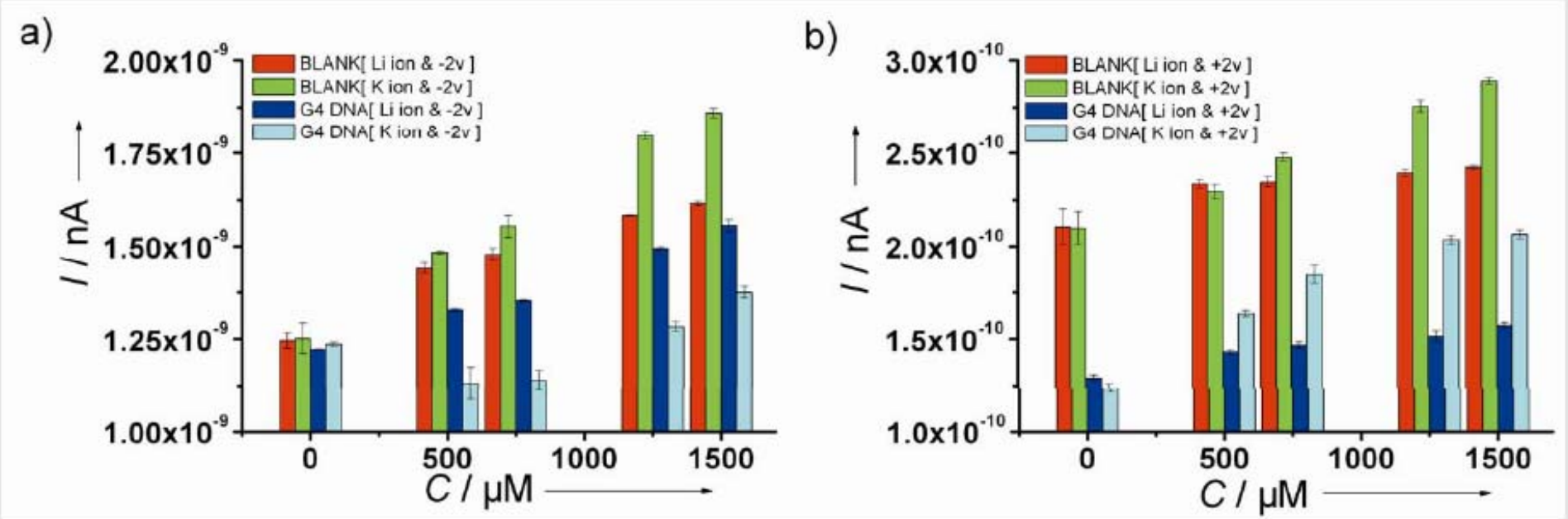
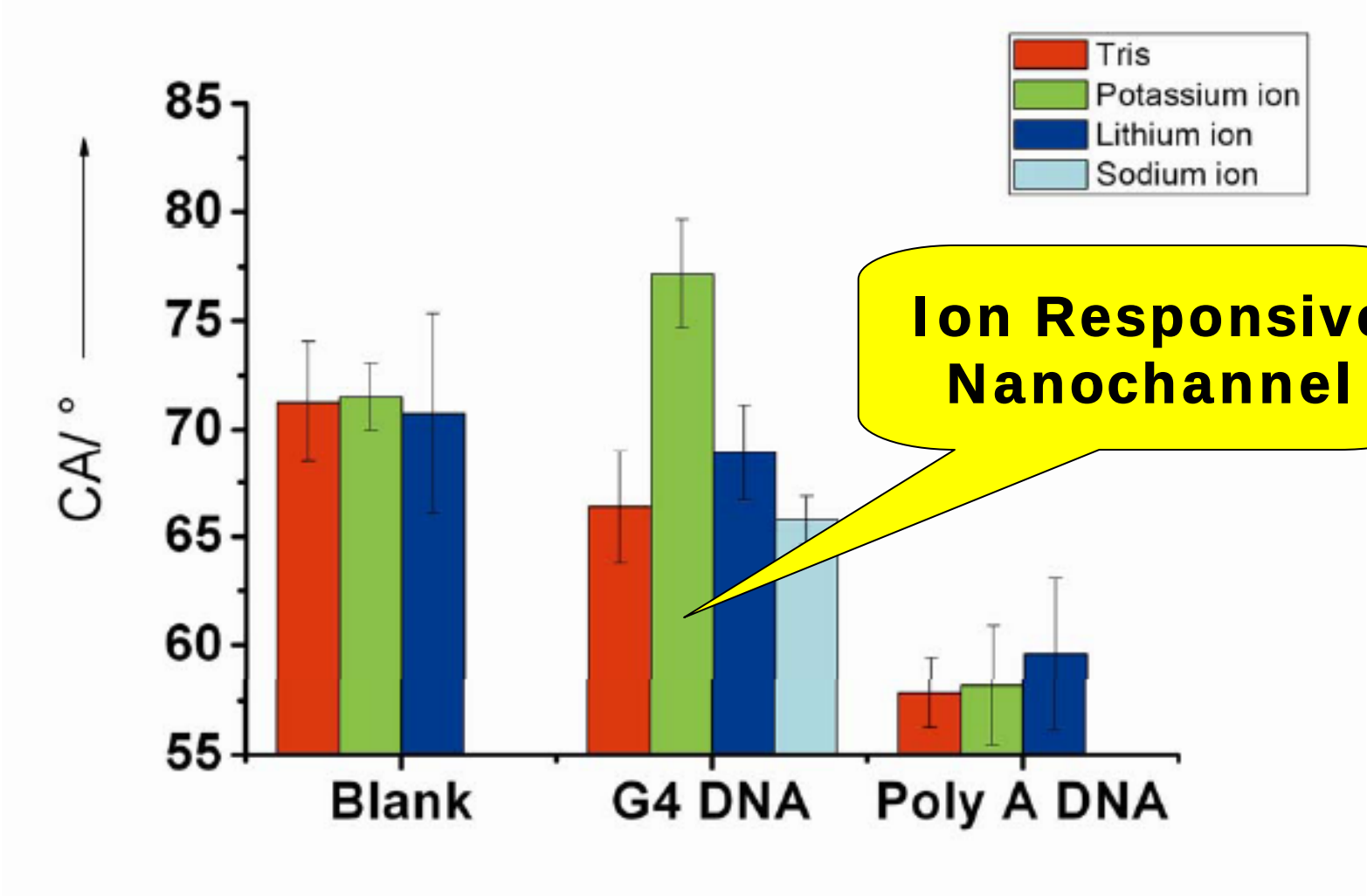


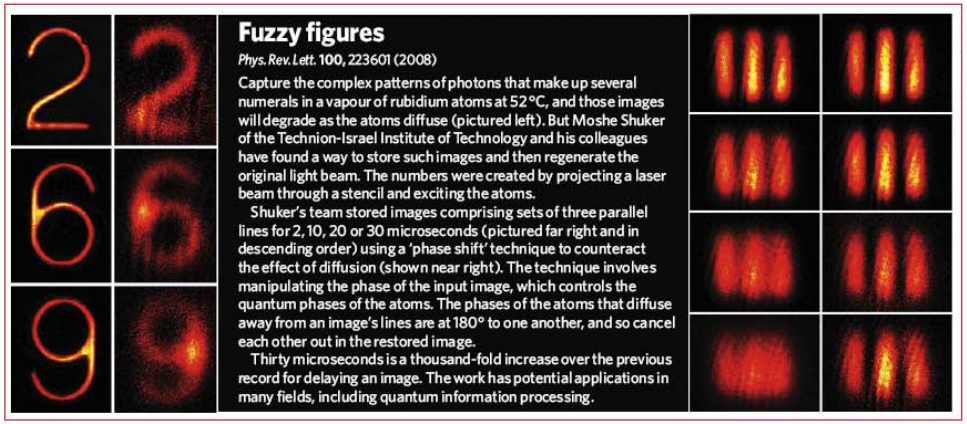
Figure 2. Current-concentration *(I-C)* properties of a single nanopore (Sample 1) embedded in a PET membrane before and after G4 DNA molecules attachment onto the inner pore wall in Tris-HCl(5 mM, pH 7.2 at 296 K). *I-C* curves recorded under symmetric electrolyte conditions at different concentration of alkali metal ions. a) at -2 V (anode facing the tip of nanopore, Scheme S1) , b) at +2v. Before modification, the diameters of the tip and base are about 19 nm and 420nm, respectively.

Fabrication and Investigation of Single Nanopore



Only Potasium ion can switch the nanopore-G4 DNA system

RESEARCH HIGHLIGHTS



M. SHUKER ET AL.

Fuzzy figures

Phys. Rev. Lett. **100**, 223601 (2008)

Capture the complex patterns of photons that make up several numerals in a vapour of rubidium atoms at 52 °C, and those images will degrade as the atoms diffuse (pictured left). But Moshe Shuker of the Technion-Israel Institute of Technology and his colleagues have found a way to store such images and then regenerate the original light beam. The numbers were created by projecting a laser beam through a stencil and exciting the atoms.

Shuker's team stored images comprising sets of three parallel lines for 2, 10, 20 or 30 microseconds (pictured far right and in descending order) using a 'phase shift' technique to counteract the effect of diffusion (shown near right). The technique involves manipulating the phase of the input image, which controls the quantum phases of the atoms. The phases of the atoms that diffuse away from an image's lines are at 180° to one another, and so cancel each other out in the restored image.

Thirty microseconds is a thousand-fold increase over the previous record for delaying an image. The work has potential applications in many fields, including quantum information processing.

CHEMICAL NANOTECHNOLOGY

Close the gate

J. Am. Chem. Soc. doi:10.1021/ja800266[illegible] (2008)

Nanoscale synthetic channels that are o[illegible]d and closed by a DNA 'switch' have been constructed by a team in China. Such channels could form part of a selective membrane for filtering and purifying water or for mimicking the changeable permeability of biological ion channels.

Yugang Wang of Peking University and his colleagues etched funnel-shaped holes, 5–44 nanometres wide at the narrowest point, into polymer membranes and lined the pores' mouths with single strands of DNA. The DNA in the pore is tightly folded in acidic conditions but unravels into loose chains at pH 8.5. This alters the diameter of the hole and therefore the flux of ions through it.

MOLECULAR BIOLOGY

Sod it

Genes Dev. **22**, 1451–1464 (2008)

Mutations in the *SOD1* gene cause motor neurons to die in amyotrophic lateral sclerosis, also known as Lou Gehrig's disease. Hidenori Ichijo of the University of Tokyo and his co-workers have pinned down why.

The key lies in the system of intracellular membranes called the endoplasmic reticulum (ER). Mutations in *SOD1* seem to affect the system that degrades worn-out pieces of ER, and a surfeit of ER containing misfolded proteins activates a genetic programme that kills the cell.

Ichijo's team found that they could mitigate motor-neuron death and extend the lifespan of *SOD1*-mutant mice by deleting a gene (*ASK1*) that turns on the cell-death programme.

ANIMAL BEHAVIOUR

[illegible]ken symbolism

PLoS ONE **3**, [illegible]2008)

Apes use and un[illegible]d symbols but they are not unique in this re[illegible]nchin monkeys (*Cebus apella*; below) can[illegible]s to tokens that represent different items.

Elsa Addessi of the CNR, Italy's nation[illegible] research council, and her colleagues trained five monkeys to associate a particular token — such as a green chip, black plastic tube or a brass hook — with one of three specific types of food. They then gave the monkeys a series of choices, each time between different amounts of two food items or between two types of token.

The value the monkeys assigned to a token was very similar to the value they gave to the food it represented, which suggests that the animals weighed up both real and symbolic options in an equivalent manner.

ASTROPHYSICS

Cosmic tiara

Astrophys. J. **680**, 295–311 (2008)

A halo of stars surrounds the Milky Way, but researchers disagree how it got there. One theory proposes that it formed from the same cloud of gas as the galaxy itself; the other says the halo is the remains of several 'dwarf galaxies' that were originally separate from but close to the Milky Way proper. A survey of about three million halo stars weighs [illegible] in favour of the latter hypothesis.

[illegible]he Max Planck Institute for Astron[illegible]ny, Germany, and his colleagues ca[illegible] the Sloan Digital Sky Survey [illegible]. The halo's structure, they say, [illegible] remains of several smaller galaxi[illegible] subsumed into the Milky Way after it h[illegible]

ECOLOGY

Dotty diets

Nature Nanotech. doi:10.1038/nnano.2008.110 (2008)

Those who worry about nanotechnology do so partly because of its potential environmental impact. So David Holbrook and a team from the US National Institute of Standards and Technology, in Gaithersburg, Maryland, have tested whether quantum dots (tiny blobs of semiconducting material) accumulate in a simple invertebrate food web.

Over a series of experiments, they put bacteria (*Escherichia coli*), rotifers (*Brachionus calyciflorus*) and ciliates (*Tetrahymena pyriformis*) in flasks with carboxylated and biotinylated quantum dots, which may find a use in computing and solar cells.

E. VIGALBERGHI

CHEMICAL NANOTECHNOLOGY

Close the gate

J. Am. Chem. Soc. doi:10.1021/ja800266p (2008)

Nanoscale synthetic channels that are opened and closed by a DNA 'switch' have been constructed by a team in China. Such channels could form part of a selective membrane for filtering and purifying water or for mimicking the changeable permeability of biological ion channels.

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The work on nanopore-DNA was highlighted by Nature recently

Fabrication and Investigation of Single Nanopore

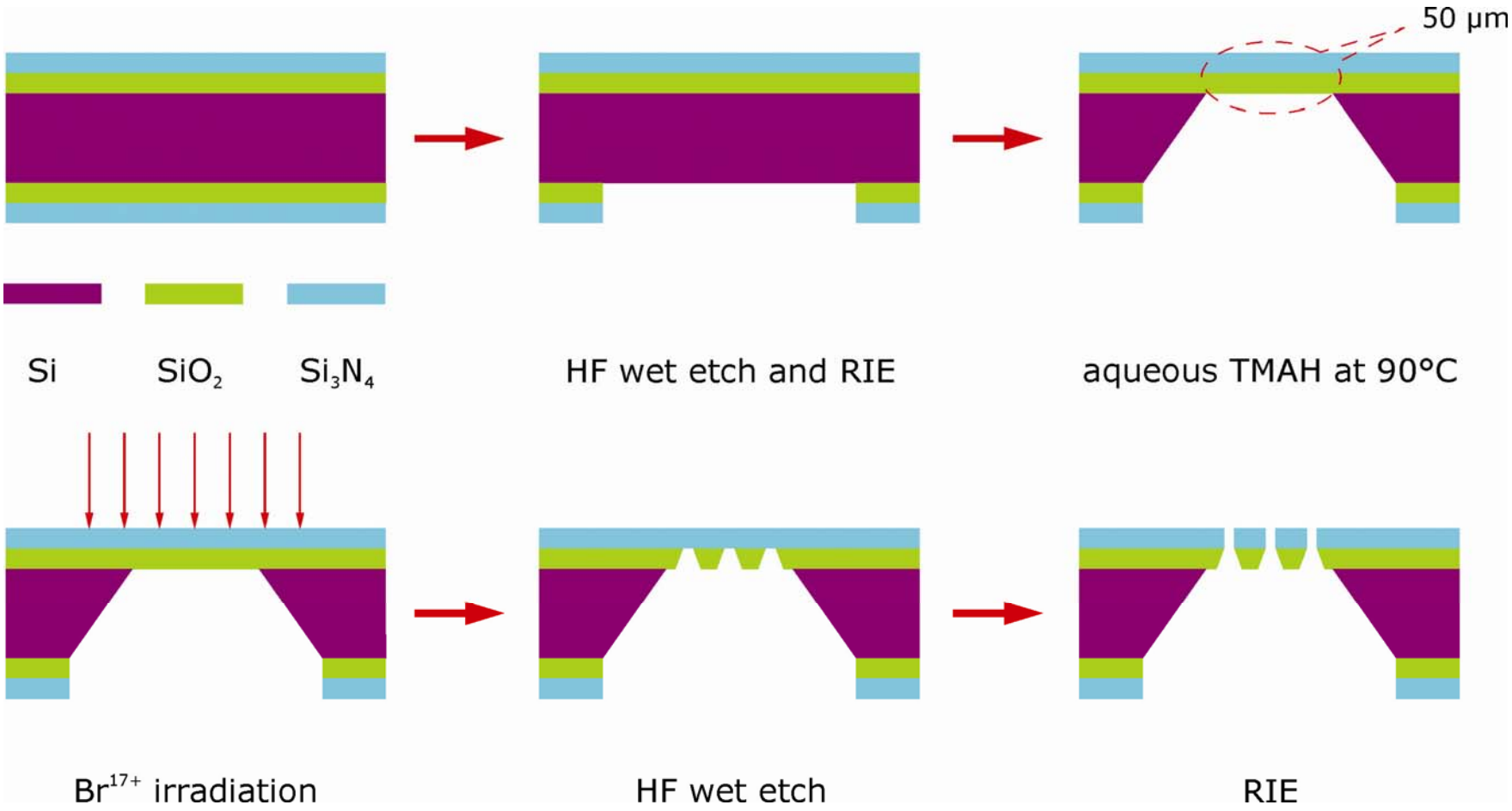
- Advantages
  - Gating of protein channel can only work in the environment of the lipid membrane.
  - Our nanopore-DNA system is live-like but solid as well.
- Potential Applications
  - Mimicking the changeable permeability of the biological ion channels and serve as sensor.
  - Study of the dynamics conformational transition of bio-molecular in a confined environment.
  - Open a way that many well-studied functional molecules can be applied to the hybrid nanopore system to construct functional nanomachinery.

Fabrication and Investigation of Single Nanopore

- **Nanopore in Si-based films**
  - Si_3N_4/SiO_2 membrane were irradiated by Br^{17+} ions at Peking University, with a total energy of 90MeV
  - Ion tracks in SiO_2 were etched out as window for RIE (reactive ion etching) process on Si_3N_4
  - Nanoporous membrane of Si_3N_4/SiO_2 with pores diameter of tens of nanometer was obtained
  - Controllable shrinking and shaping of silicon nitride nanopores under electron irradiation

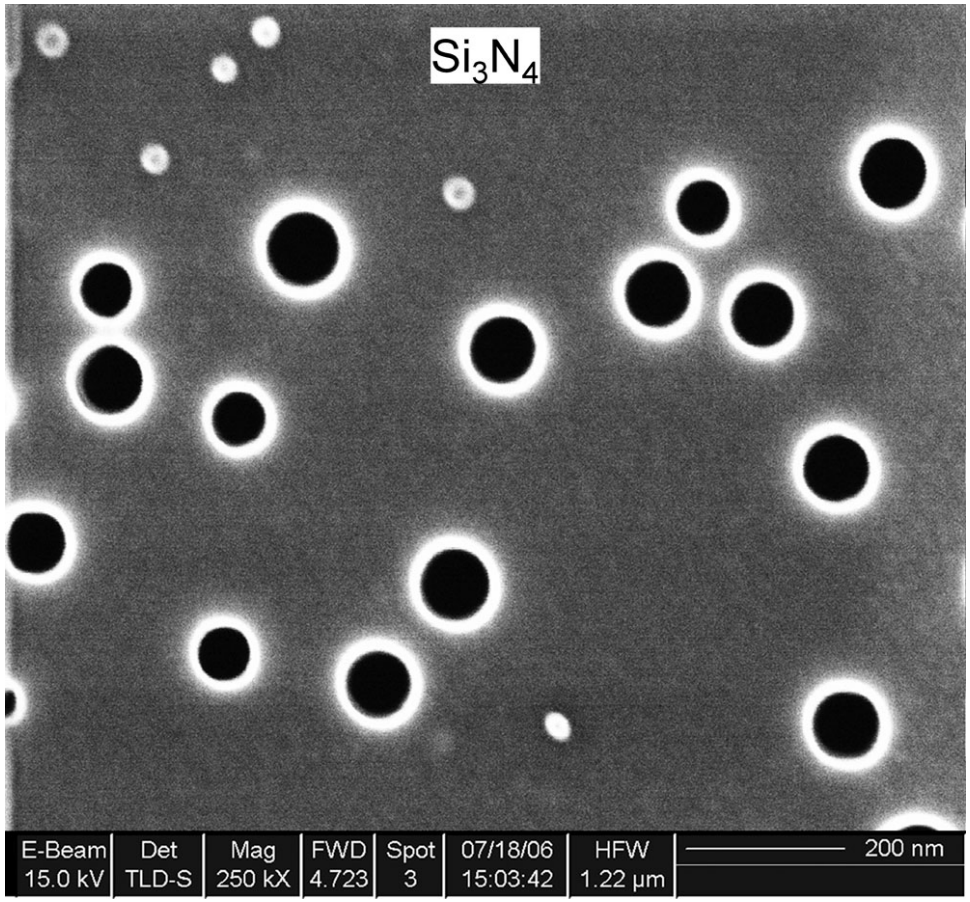
Fabrication and Investigation of Single Nanopore

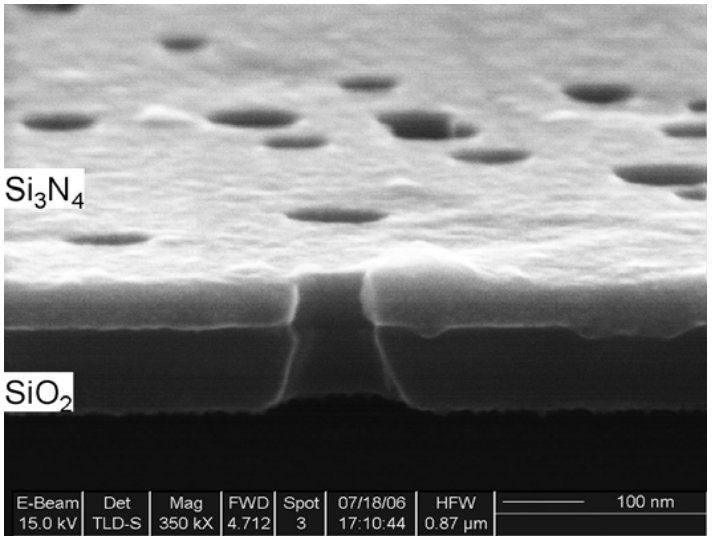
❑ Processing steps

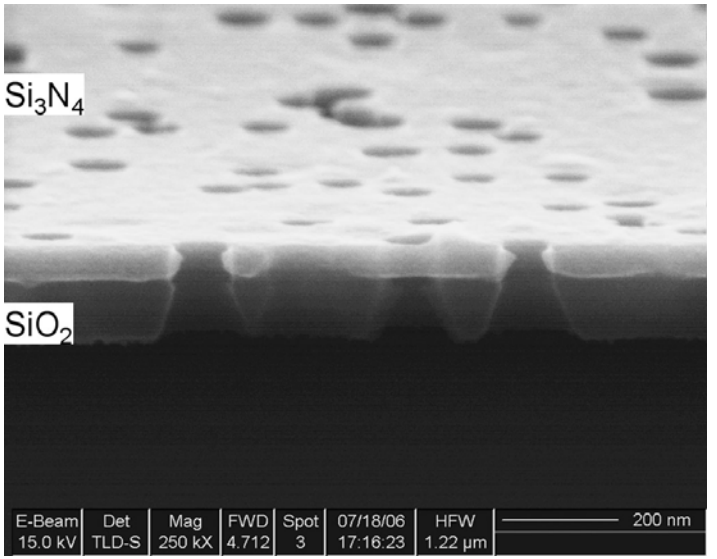


Fabrication and Investigation of Single Nanopore

- SEM images of nanoporous membranes

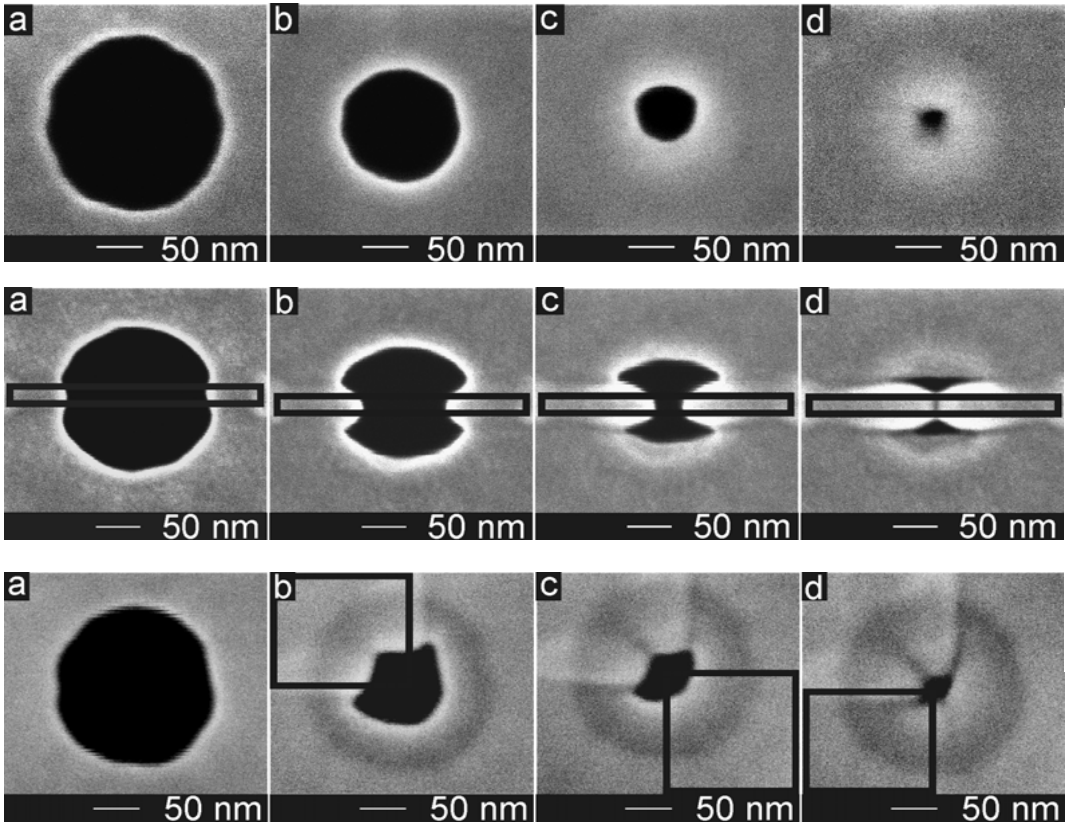


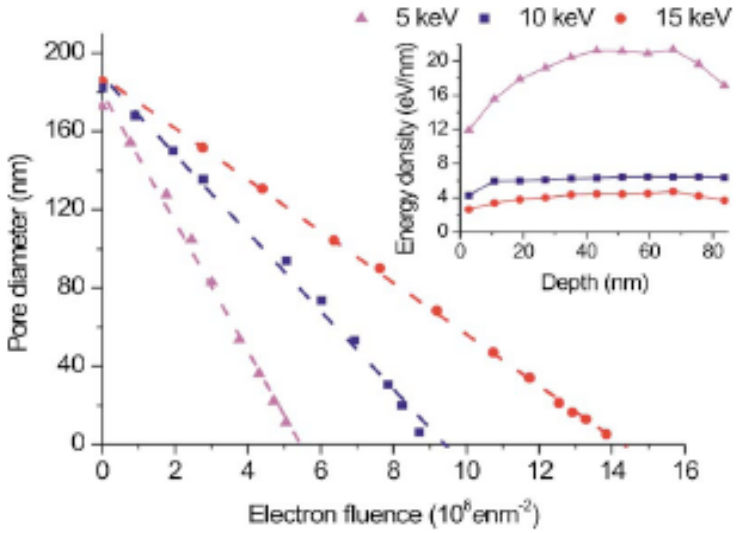




Fabrication and Investigation of Single Nanopore

- **Controllable shrinking and shaping of silicon nitride nanopores under electron irradiation**

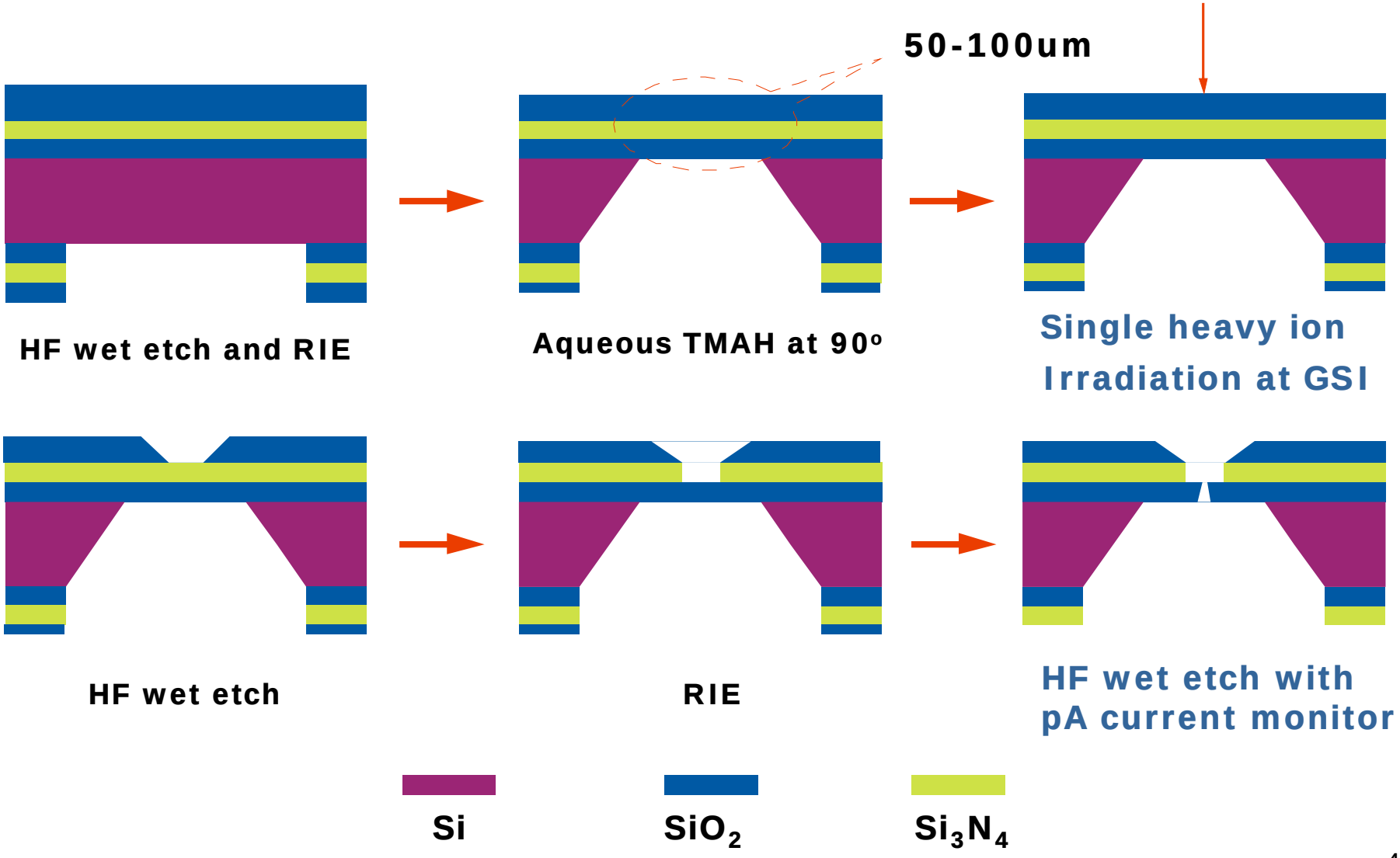




Appl. Phys. Lett., 2007

Fabrication and Investigation of Single Nanopore

- Single nanopore in SiO_2 based on ion track ?



Open Questions

- Could the tip diameter and its inner profile be identified or measured directly?
- Based on track-etching technique, could we fabricate multipore (10^7-10^8/cm^2) nanopre-membrane with uniform tip diameter at nm scale in polymer and in Si-based materials?
- Could the synthetic and hybrid nanopre system be used for some practical applications?

Do-it-yourself nanostructures are possible with simple equipment--***R. Spohr***

Many thanks to my cooperators:

GSI: Prof. R. Neumann, Dr. C. Trautmann

Professors: Qi Ouyang, Lei Jiang, Hang Ji, Jianming Xue

Many thanks to my students:

Weiming Zhang, Wei Guo, Fan Xia, Qi Liu, Lin Wang, Liuxuan Cao, Xinwei Wang, Yanbo Xie, ...


Thanks for your attention !
ygwang@pku.edu.cn
THE REALM OF THE NANOPORE