Elucidating the mechanisms of charge (pH-induced) and temperature (plasmon-induced) modulated ionic/molecular transport in nanochannels

Yu Zhao[1], Chenyong Li[2] and Guigen Zhang[1]

[1] F. Joseph Halcomb III, M.D. Department of Biomedical Engineering, University of Kentucky

[2] School of chemistry and environment
Guangdong Ocean University, China

University of Kentucky

COMSOL CONFERENCE
2018 BOSTON

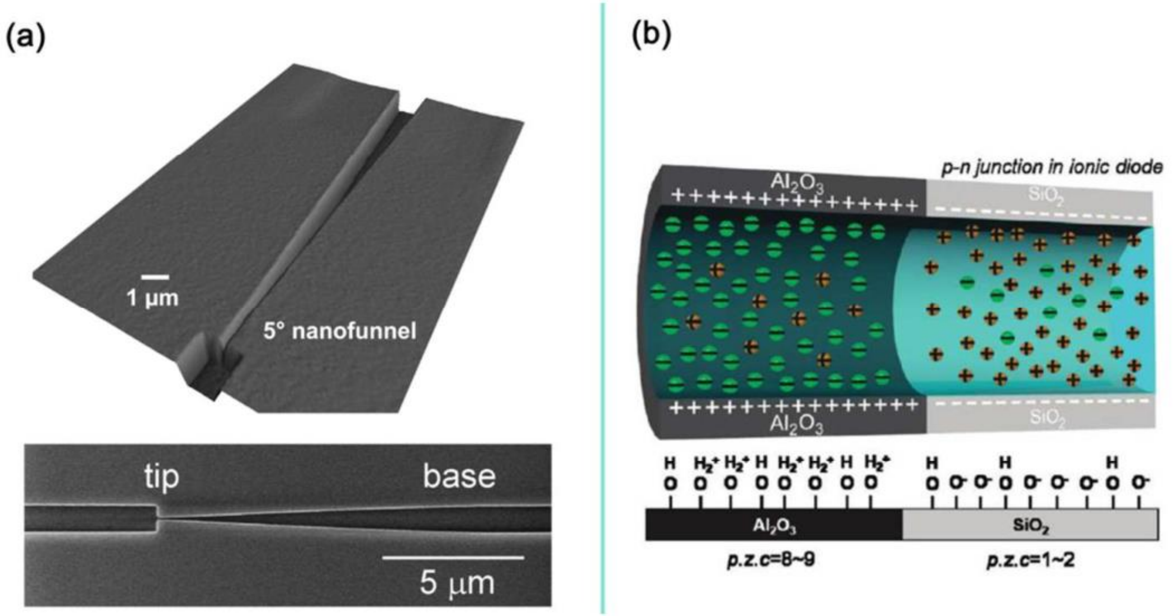
Objective

- Elucidation of the mechanisms underlying the modulation of ionic/molecular transport through nanochannels:
  - Charge (pH-induced) modulated rectification of ionic transport
  - Temperature (plasmon-induced) modulated change of molecular flux
- Integrative means: experimentation coupled with multiphysics computational modeling

Charge-modulated nanochannel

Two existing mechanisms cause ICR (Ionic current rectification)

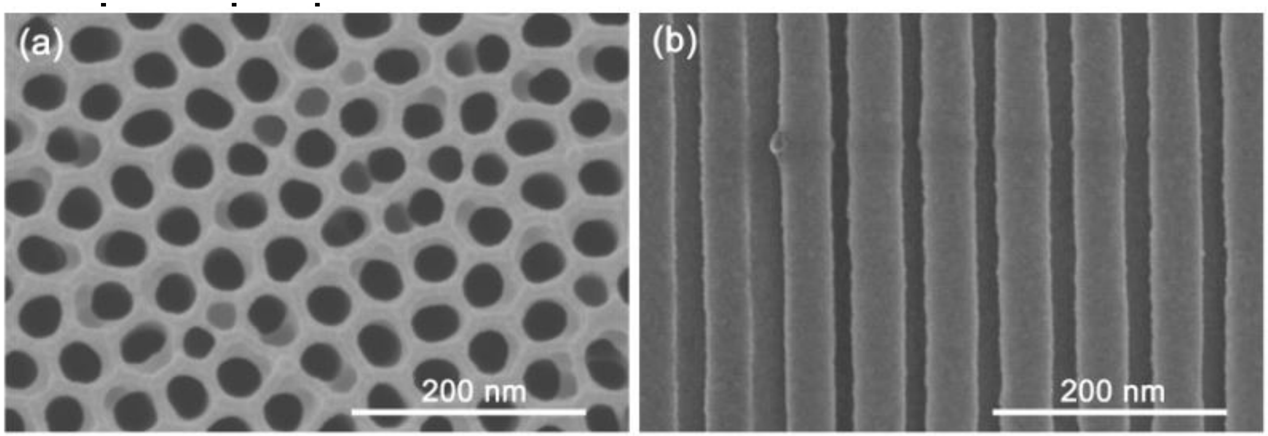
- The natural presence of intrinsic charge distribution in non-prismatic geometry (conical nanopore)
- Non-homogeneous fixed charge distributions in prismatic geometry nanochannels



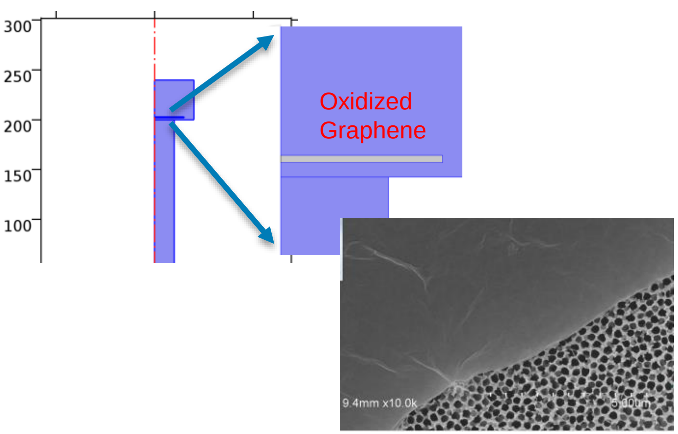
(a) non-prismatic geometry (Anal. Chem. 2011, 84, 267-274)
(b) (b) non-homogeneous charge distributions (Nano Lett. 2009, 9, 3820-3825)

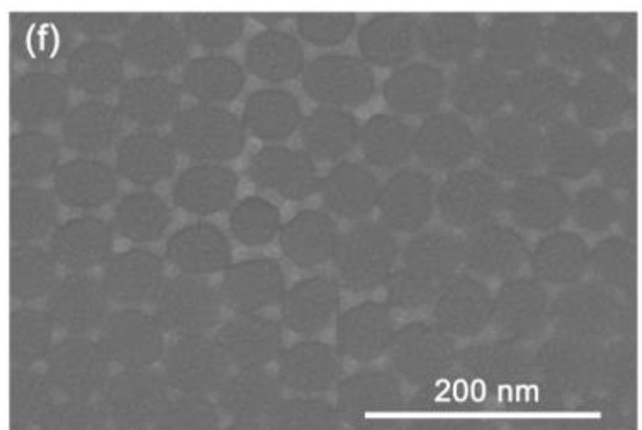
A new charge-modulated interfacial ionic rectification

- A new ionic rectification device is fabricated using PAA (porous anodic alumina) and GO (graphene oxide) via dopamine



(a) Top SEM image of as prepared PAA membrane. (b) Cross-section SEM image of as prepared PAA membrane.



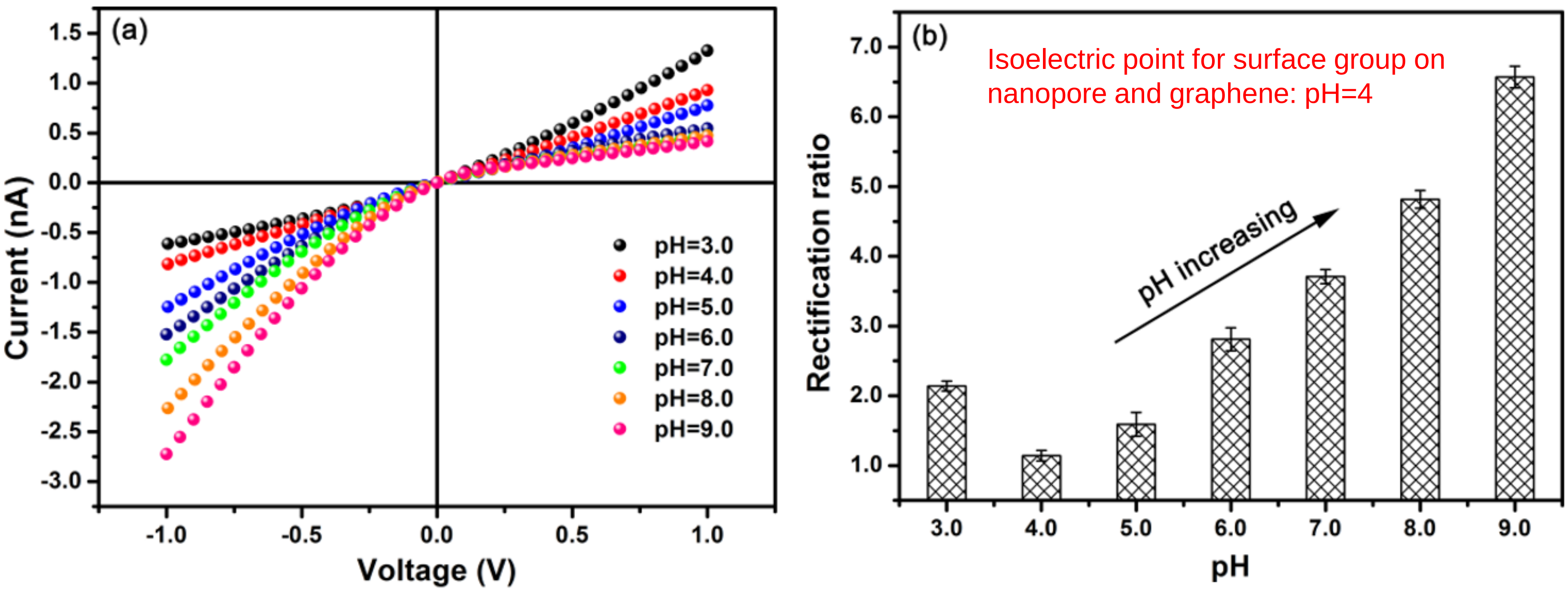


(f) SEM image of PAA/GO composite membrane

Experimental measurements

- Rectification can be represented quantitatively as the rectification ratio, *r*, defined as the absolute value of the current ratio of on-state (representing higher current) to off-state (representing lower current) current measured at ± 1 V applied potential as:

$$r = \frac{|I_{on}|}{|I_{off}|}$$



(a) Rectification curves measured in 1 mM KCl with different pH values.
(b) ICR ratio calculated from rectification curves.

Computational modeling: governing equations

- The creep flow physics is governed by Navier-Stokes equation

$$\rho \frac{\partial \boldsymbol{u}}{\partial t} = \nabla \cdot \left[-p\mathbf{I} + \eta \left(\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T \right) \right] + \boldsymbol{f} \qquad \boldsymbol{f} = \mathrm{F}(\mathrm{c}_K - \mathrm{c}_{Cl})\boldsymbol{E}$$

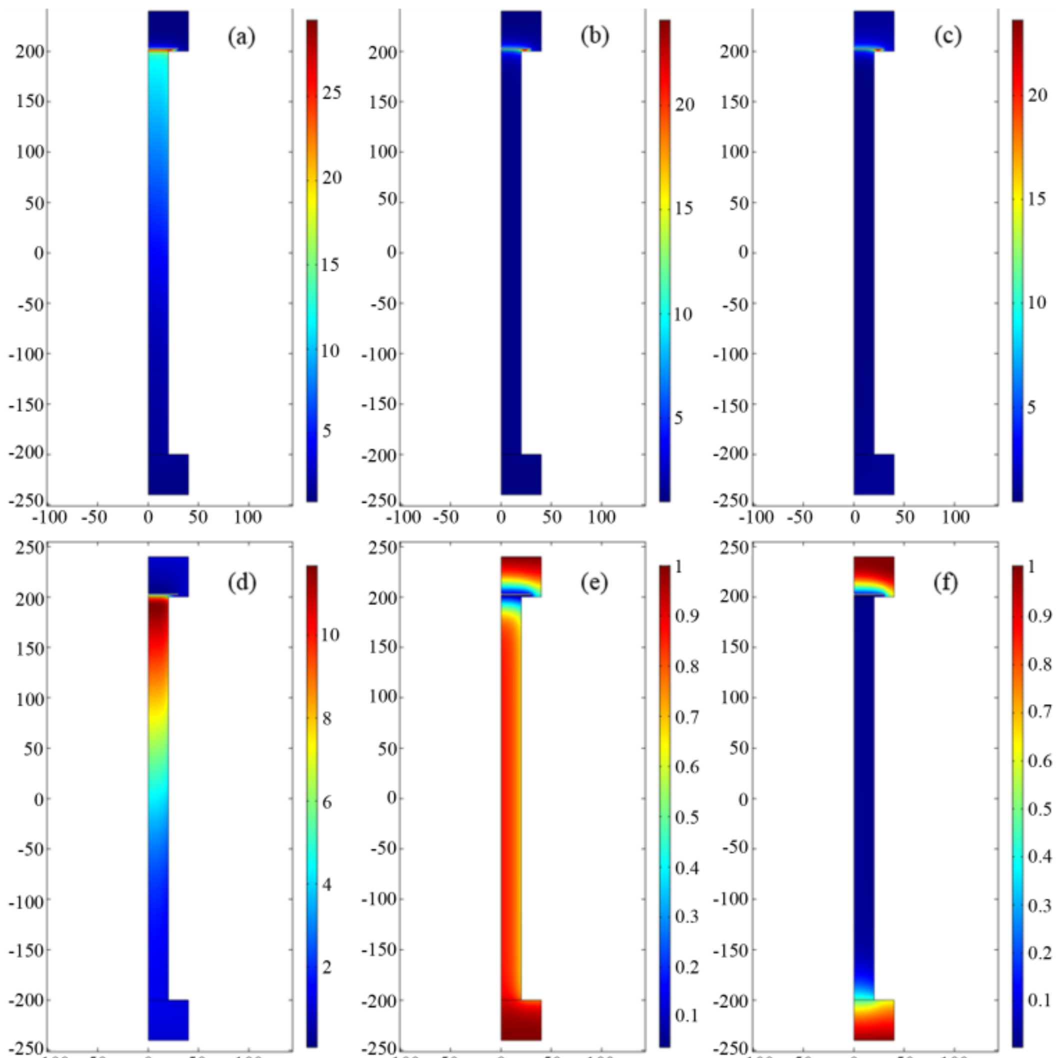
- The electric field is determined by solving Poisson Equation

$$-\nabla^2 \phi = \frac{\mathrm{F}(\mathrm{c}_K - \mathrm{c}_{Cl})}{\varepsilon} \qquad \boldsymbol{E} = -\nabla \phi$$

- The transport of ions is controlled by diffusion, convection and migration as governed by the following Nernst-Planck Equation

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i \mu_i \mathrm{F} c_i \nabla \phi) + \boldsymbol{u} \cdot \nabla c_i = 0$$

Modeling results: Ion distribution

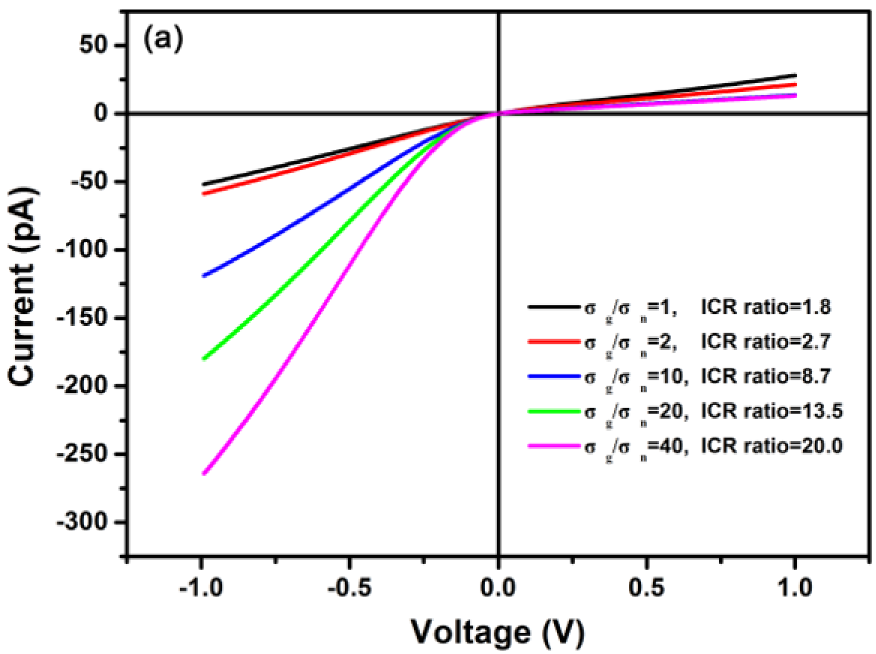


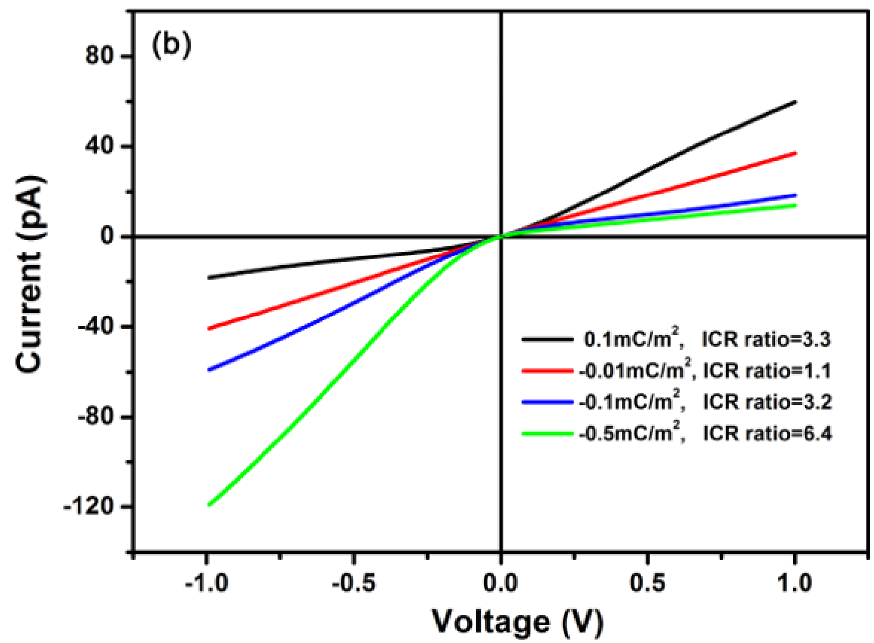
Ion distribution inside the nanochannel at different biasing potentials. (a) K^+: -1V; (b) K^+: 0V; (c) K^+: +1V; (d) Cl^-: -1V; (e) Cl^-: 0V; (f) Cl^-: +1V.

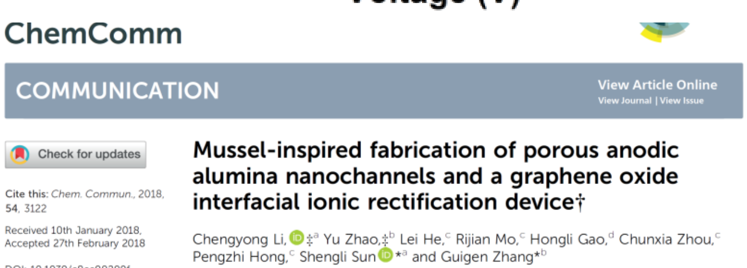
Different profiles of ion distribution are caused by the abrupt change of interfacial surface charge.

Modeling results: ICR behavior

- The rectification ratio is determined by the surface-charge-density ratio between GO sheet and nanochannel and the net surface charge density, which can be controlled by varying pH







ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.*, 2018, 54, 3122

Received 10th January 2018, Accepted 27th February 2018

DOI: 10.1039/c8cc00209f

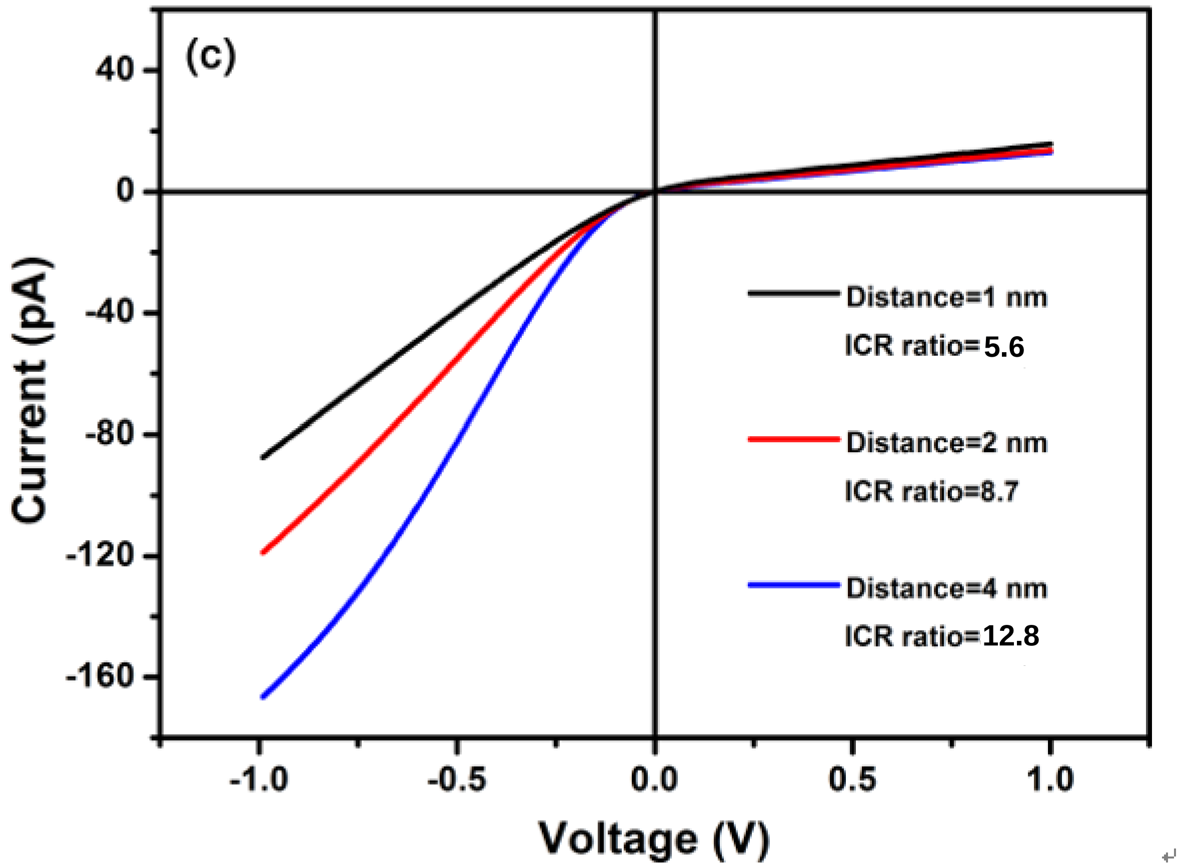
Mussel-inspired fabrication of porous anodic alumina nanochannels and a graphene oxide interfacial ionic rectification device†

Chengyong Li,‡[a] Yu Zhao,‡[b] Lei He,[c] Rijian Mo,[c] Hongli Gao,[d] Chunxia Zhou,[c] Pengzhi Hong,[c] Shengli Sun*[a] and Guigen Zhang*[b]

Chem Comm 2018, 54, 3122.

Beyond charge-modulation

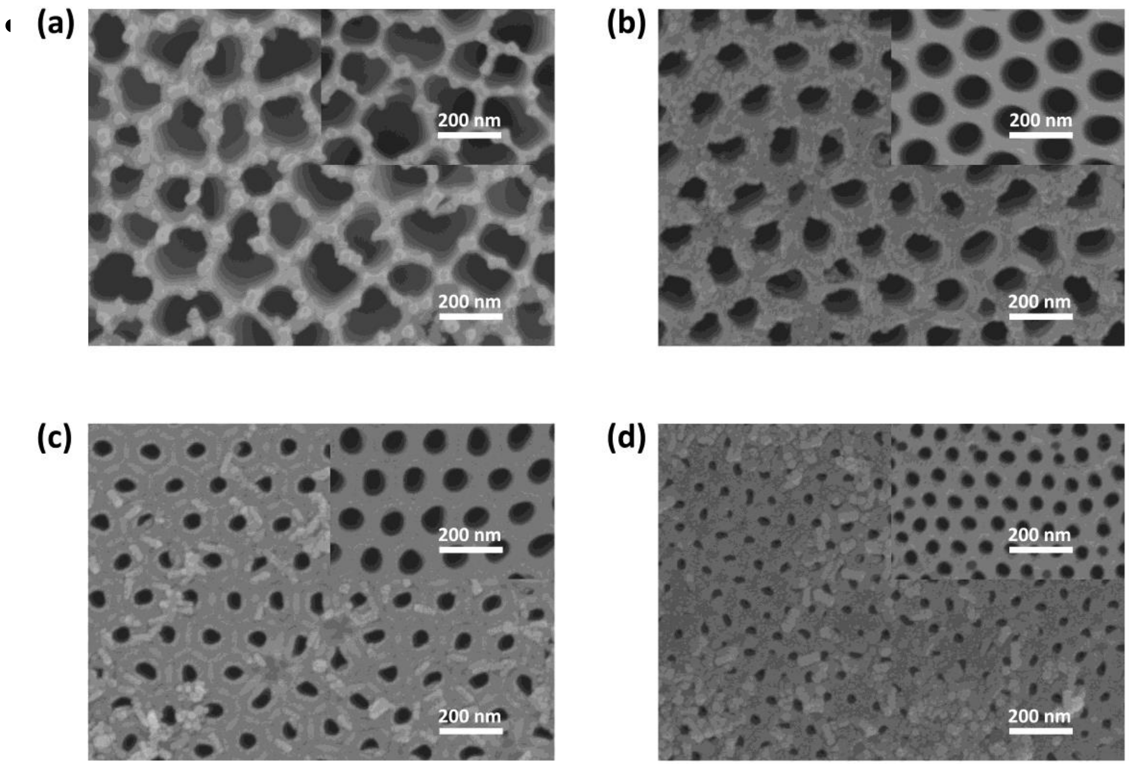
- The interfacial distance between GO sheet and nanochannel will strongly affect the rectification ratio (distar



Plasmon-induced temperature modulated nanochannels

- Temperature control is achieved with plasmon-induced heating to generate molecule transport through a solid-state plasmonic nanopore

h gold nanorods



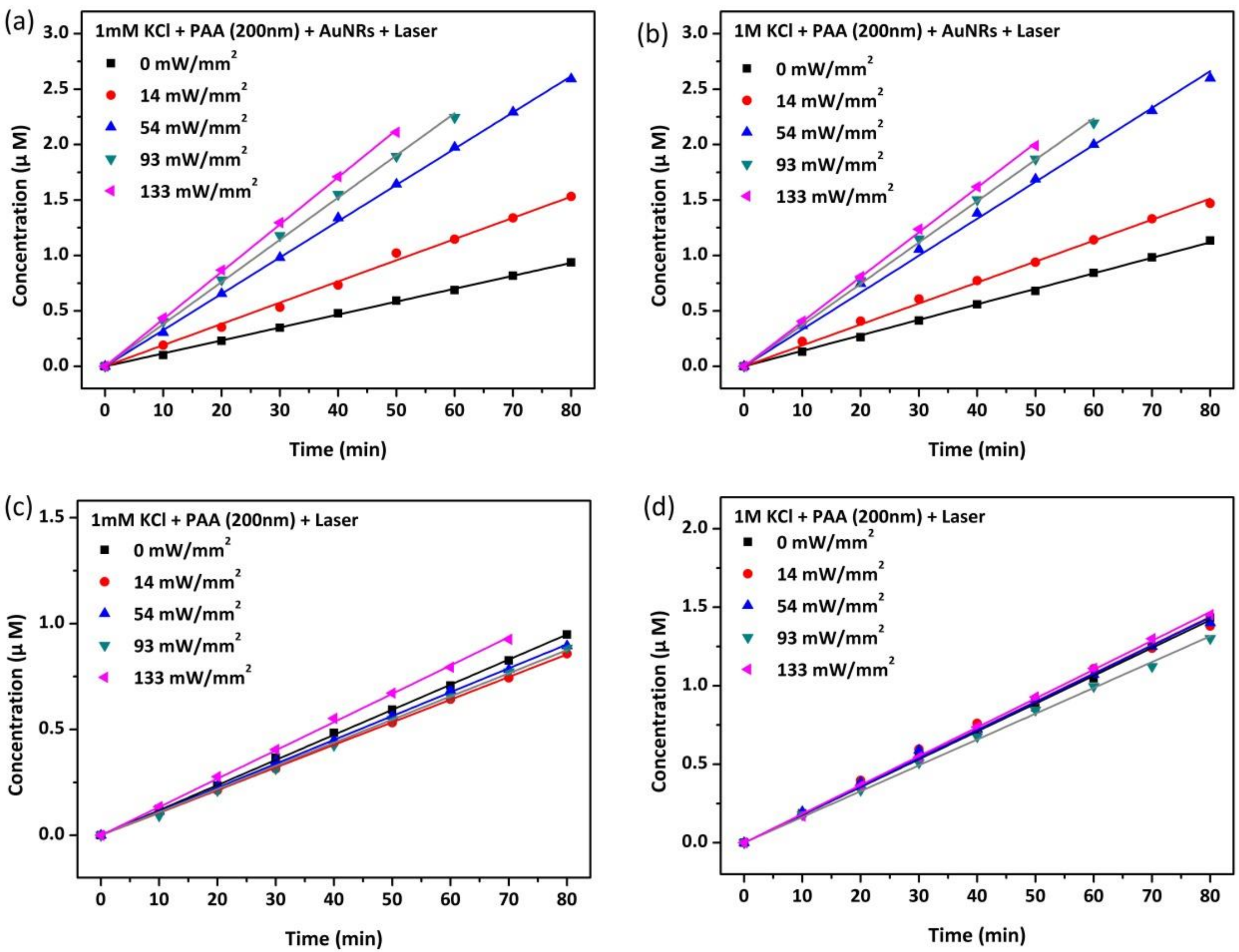
SEM top views of the PAA membranes before and after modification with AuNRs. The pore diameters of PAA membranes are (a) 200 nm, (b) 90 nm, (c) 50 nm, (d) 20 nm, respectively.

Experimental consideration

- Laser illumination on AuNRs generates LSPR (Localized surface plasmon resonance), which induces heating at the PAA membrane surface
- Increasing temperature accelerates the diffusion process by increasing the diffusivity of molecule and affecting the EDL (electric double layer) structure
- Modulation can be achieved by tuning the power of illuminating laser and changing the electrolyte strength of medium

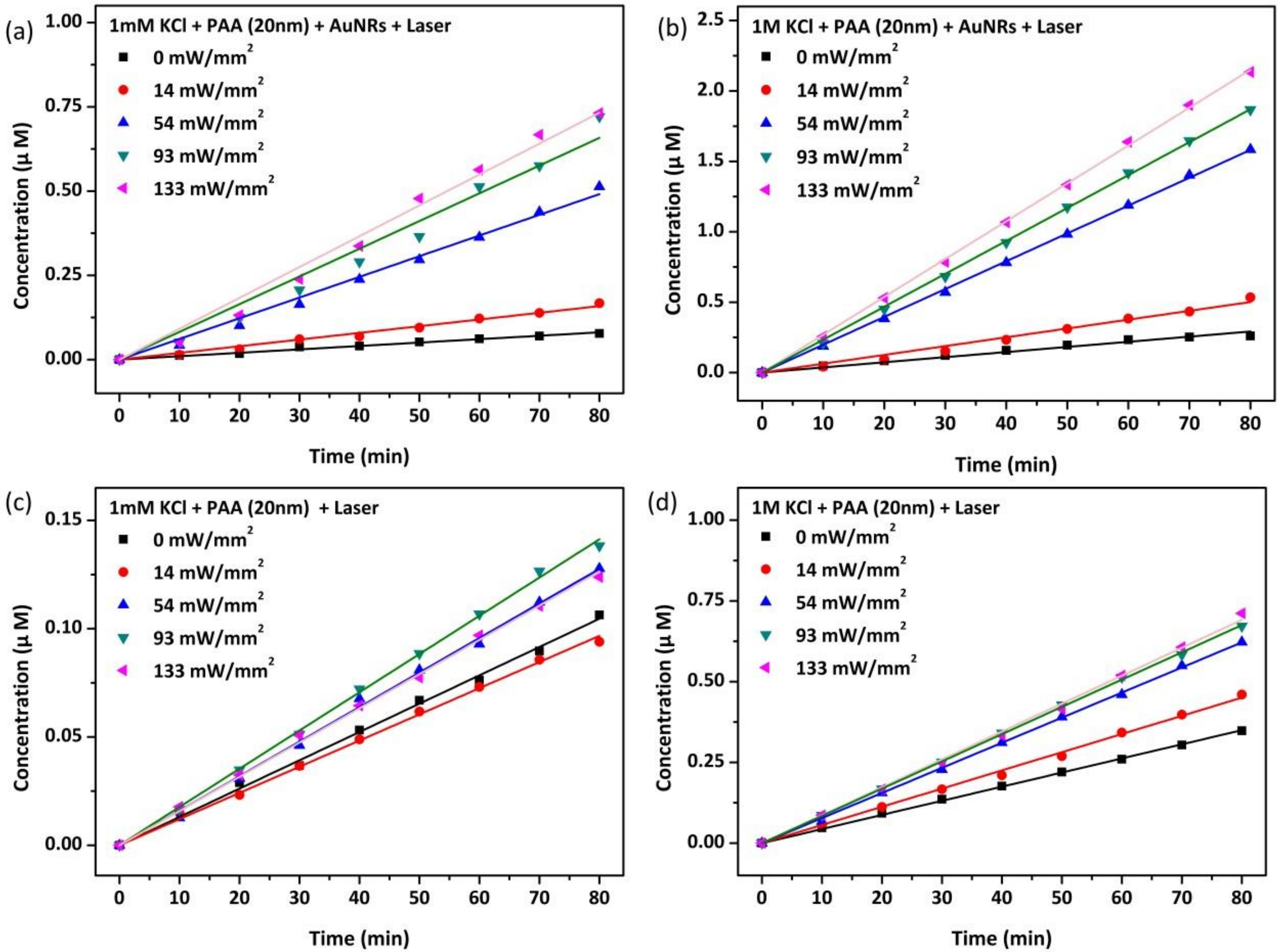
Experimental measurements: enhanced molecular diffusion

Pore size: 200 nm



Concentration of $Ru(bpy)_3Cl_2$ measured across the nanochannels in time in 1mM and 1M KCl solutions

Experimental measurements: enhanced molecular diffusion

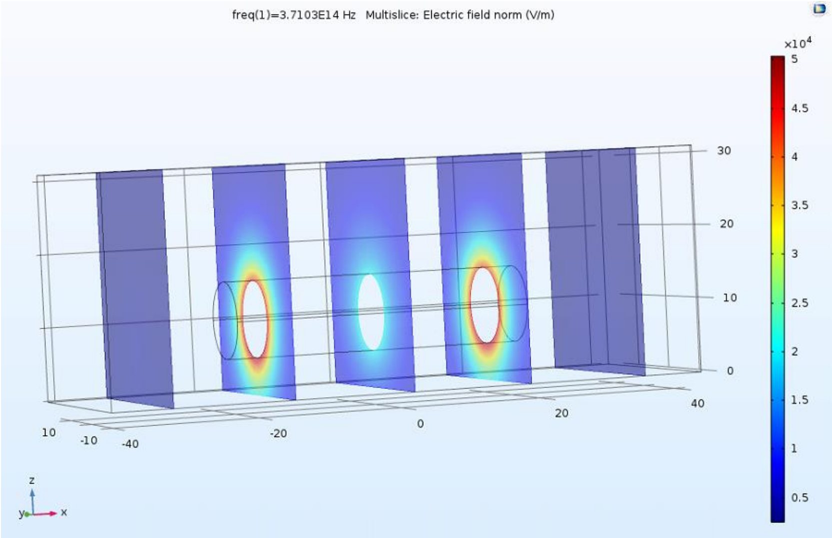


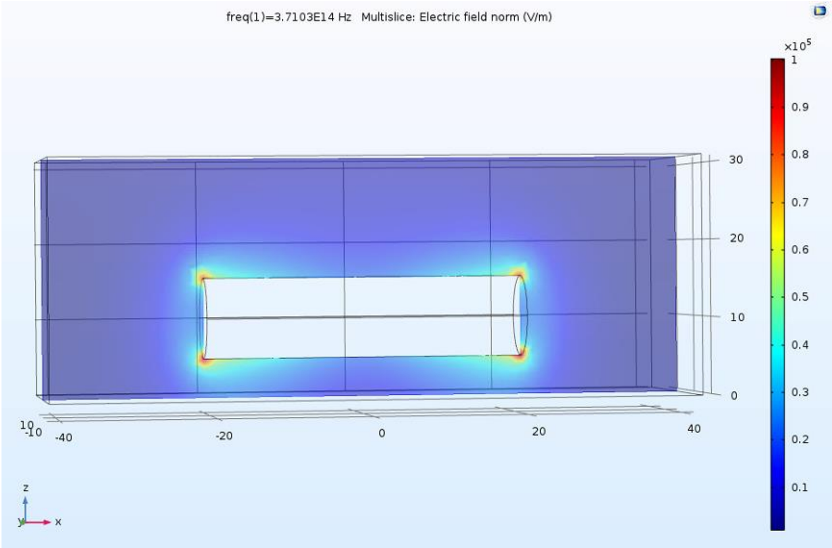
Pore size: 20 nm

Concentration of $Ru(bpy)_3Cl_2$ measured across the nanochannels in time in 1mM and 1M KCl solutions

Modeling of LSPR-induced temperature modulation

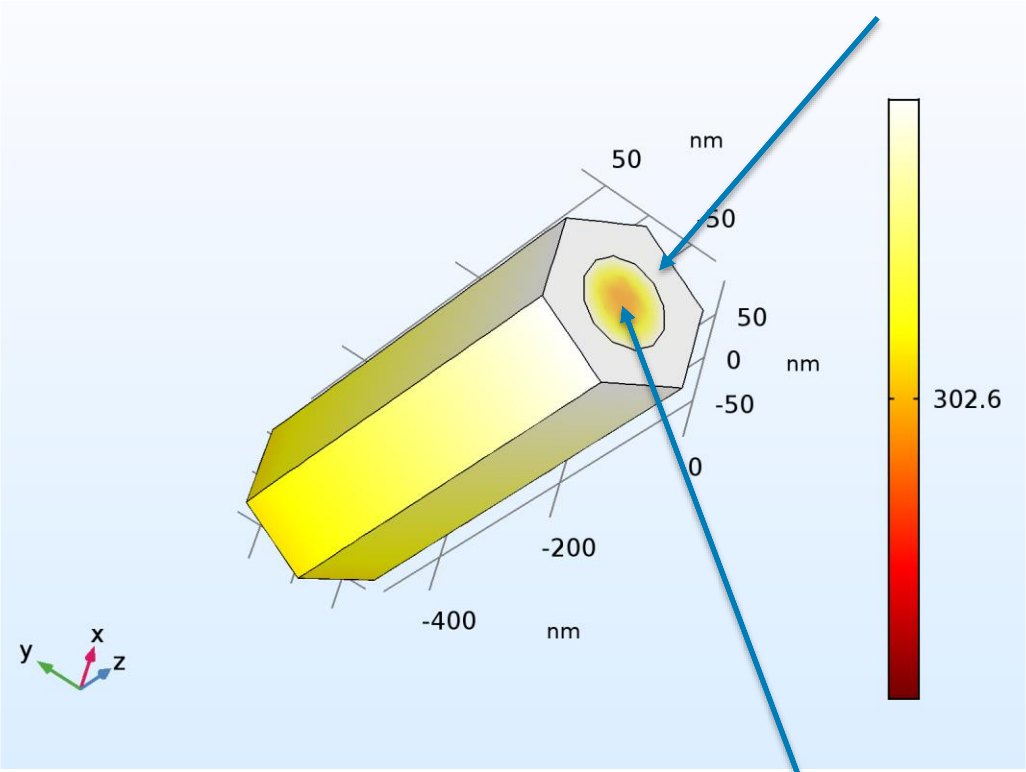
- Enhanced electric field at the surface of AuNR





Temperature profile in nanopore

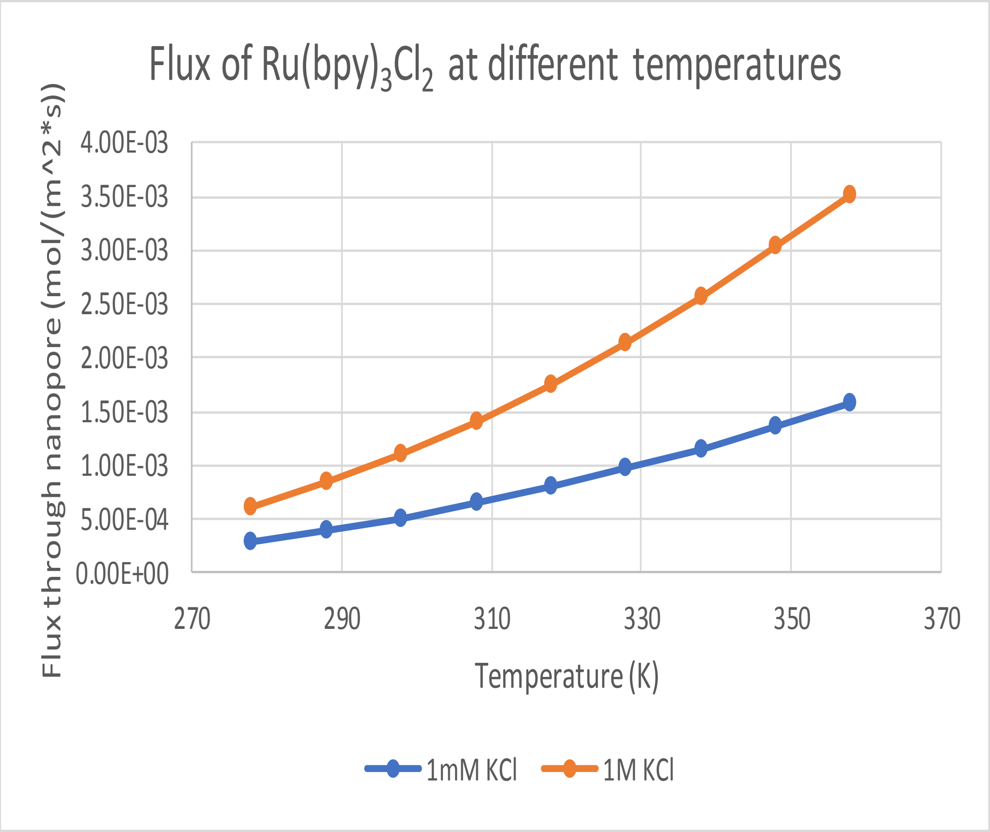
AuNR coated PAA surface

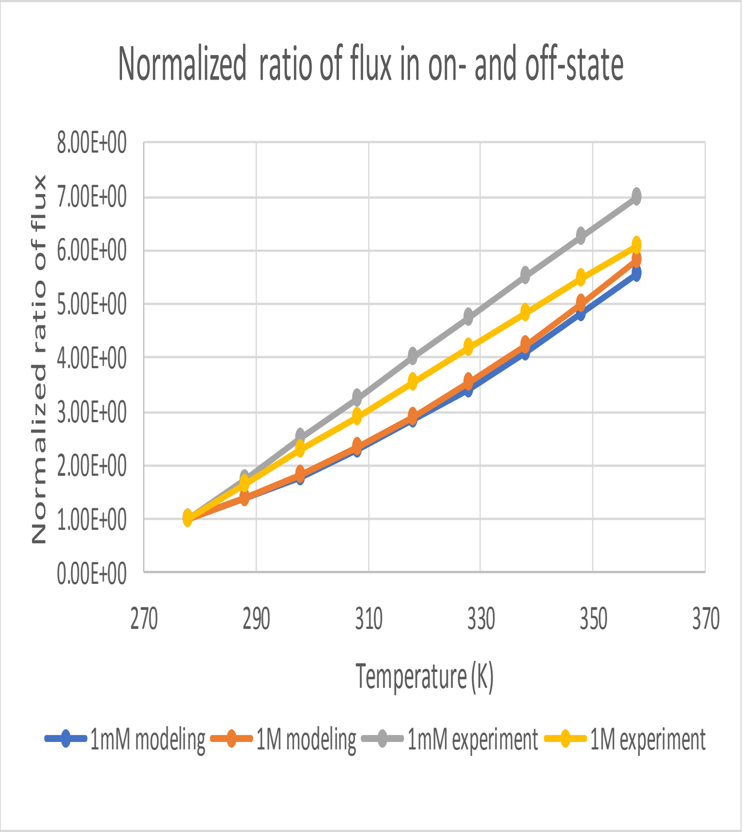


Medium in nanopore

Modeling results: enhanced flux

- Modeling results match experiment measurement in ratio of flux in on- and off-state (J/J_0) and magnitude difference ($J_{1M} > J_{1mM}$)





Conclusions

- We explored using an integrative approach two types of nanochannel devices that make use of surface charge density and temperature to modulate ion/molecule transport process.
- Computational modeling, built upon principles of physics and thermodynamics via finite element simulation in COMSOL Multiphysics, provided valuable insight into the underlying mechanisms.
- Integrative means of exploration is crucial to elucidating complex phenomena and finding novel application for these simple devices in areas such as biosensing and ion transport in confined environments.