New Concepts in Mass and Energy Transport using Graphene and Carbon Nanotubes

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Carbon Nanotubes and Graphene

Graphene (2D)

Graphite (3D)

Nanotube (1D)

Electrons restricted to single dimension
Diameter ~1 nm

Synthesis (now > 1000 tons/year)
Stratis V. Sotirchos: electric arc synthesis
Over metal (Fe, Co, Mo) nanoparticle

C$_2$H$_2$ → C$_2$ + H$_2$

Semiconductor
Semimetal
Metal

Length can range from 10 nm to 1 cm

Diversity of Electronic Structure

Metal
- Conduction Band
- Valence Band

Semi-conductor
- Conduction Band
- Valence Band

Insulator
- Conduction Band

Rolling into cylinder constrains electrons to 1-D

Metallic Nodes

Semiconducting gap

E - E_F [eV]

π

π*

E_F

Rolling into cylinder


⇒ semimetallic

www.photon.t.u-tokyo.ac.jp
The Chirality Vector \((n,m)\)

- \((n,m)\) where \(n = m\)
  - “armchair” nanotube, 1-D metal if \((n - m)/3 = \text{integer}\) then metallic
  - Energy (eV)

- Chiral nanotube, 1-D metal or semiconductor if \((n - m)/3 \neq \text{integer}\)
  - Energy (eV)
Construction of Nanotubes from a Graphene Sheet

Armchair
Zigzag
Chiral angle

Red – Metallic Carbon Nanotubes
Black – Semi-conducting Carbon Nanotubes
“Face it, Fred—you’re lost!”
Applications of Graphene and Carbon Nanotubes

Ideal Molecular Wires and Films

High current density $10^9$ A/cm$^2$ or 30 $\mu$A per nanotube
High electron mobility 20,000 cm$^2$/V/s

V. Perebeinos, J. Tersoff, and Ph. Avouris,

Unique Field Effect Transistors

Graphene bilayers – tunable bands

Near Infrared Absorption/Emission

Tissue implantable SWNT glucose sensors
Yoon, H. and Strano, M. S. Angewandte Chemie 50, 8 (2011) 1828

Structural Applications

High elastic modulus 1 TPa
Highest strength to weight ratio

Applications of Graphene and Carbon Nanotubes

**Ideal Molecular Wires and Films**

- High current density: \(10^9 \text{ A/cm}^2\) or \(30 \mu\text{A}\) per nanotube
- High electron mobility: \(20,000 \text{ cm}^2/\text{V/s}\)


**Unique Field Effect Transistors**

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- Tissue implantable SWNT glucose sensors

Yoon, H. and Strano, M. S. *Angewandte Chemie* 50, 8 (2011) 1828

**Structural Applications**

- High elastic modulus: \(1 \text{ TPa}\)
- Highest strength to weight ratio

Applications of Graphene and Carbon Nanotubes

Insulin patch

Wireless glucose sensor

Adhesive patch

Dual glucose monitor and insulin injection

Wireless transmitter

Excitation source

Glucose-sensor tattoo embedded in subcutaneous layer

IR sensor

nIR fluorescence from carbon nanotubes

Alginate microparticles with carbon nanotubes

Optical

nIR Fluorescence
**Applications of Graphene and Carbon Nanotubes**

**Ideal Molecular Wires and Films**
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**Unique Field Effect Transistors**
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**Structural Applications**
- High elastic modulus \(1 \text{ TPa}\)
- Highest strength to weight ratio

**New Concepts in Mass and Energy Transport using Graphene and Carbon Nanotubes**

- Coherence resonance in molecular transport through a single walled carbon nanotube nanopore
- Energy storage and generation using thermopower waves
- Near infrared fluorescent sensors with single molecule sensitivity for studying biological signaling fluxes: reactive oxygen and nitric oxide signaling in Epidermal Growth Factor Receptor (EGFR)
New Concepts in Mass and Energy Transport within Carbon Nanotubes

- Coherence resonance in molecular transport through a single walled carbon nanotube nanopore

- Energy storage and generation using thermopower waves

- Near infrared fluorescent sensors with single molecule sensitivity for studying biological signaling fluxes: reactive oxygen and nitric oxide signaling in Epidermal Growth Factor Receptor (EGFR)
Molecular Transport through a Single Nanotube

Substantial interest in understanding molecular transport within nanotubes

Most studies have been computational;

Many applications
- Fuel cells membranes
- Energy storage
- DNA sequencing
- Water desalination

Molecular dynamics & nanotube transport

Published Items in Each Year

scitizen.com/.../slippery-nanopipes_a-5-131.html

physics.illinois.edu/people/aksimentiev/
Creating and Characterizing SWNT Ion Channels

Choi, W., Shimizu, S., Strano, M.S. in preparation

Won Joon Choi
Chang Young Lee
Ion Transport in the Nanotube Interior

Majority (unblocked) current carrier: protons ($\text{H}_3\text{O}^+$)

Minority (blocker) primarily cations ($\text{Na}^+$, $\text{Li}^+$, $\text{K}^+$)

Electro-osmosis

CNT (open)

CNT (blocked)

Ag/AgCl wires

Ionic Solution

Epoxy Barrier

Nanotube

2 sec

60 pA

Pure Water (without electrolyte, 1000 mV)

KCl 3M (with electrolyte, 1000 mV)

Stochastic Pore Transport: the Coulter Effect

Wallace H. Coulter (1913-1998)

Blocker

Charge carriers

Analyte at different concentration

Ion channels from peptide nanotubes

DNA sequencing by nanopore

1M NaCl, 300 mV
1M LiCl, 600 mV
1M LiCl, 600 mV
1M LiCl, 3 V
1M KCl, 600 mV
3M KCl, 700 mV

Unblocked Current is Carried by Protons

Measured $\Delta G_{H2O}/ \Delta G_{D2O} = 2.5$

From acid/base titrations in bulk water (diffusion limited) = 1.6
(Pillings and Seakins, Reaction Kinetics, Oxford Science Press)

pH influences pore conductance $\Delta G$

Cations block the nanotube

Cations are the Blocking Species

No blocking events with tetramethylammonium chloride or hydrogen chloride

Note: only **cations** appear to block the pore

Hypothesis: plasma etch leaves residual carboxylic acid groups at pore ends (negative zeta potential)

Threshold potential observed for cation pore blocking

Theory: Molecular Transport in Nanotubes

Important theoretical/computational predictions (300+ since 2000)
Enhanced water permeation flux through carbon nanotubes


Large proton fluxes through water filled carbon nanotubes


Ice-like water phase in carbon nanotube interior


High ion rejection rates from nanotube interior


Experimental: success with nanotube membranes

J. K. Holt et al., Science 312, 1034 (May 19, 2006).
Ion Translocation Follows Expected Nanopore Physics

• Current fluctuations for Ca$^{2+}$ demonstrated trends expected for stochastic pore blocking

Dwell time follows simple scaling of a single ion moving through the nanotube:

$$\tau_{\text{dwell, ion}} = \frac{L^2}{\mu_{\text{ion}} \cdot (V - V_{\text{threshold}})} \propto \frac{1}{V}$$

$$\tau_{\text{dwell, ion}} = \text{Dwell Time of Ion (s)}$$

$$L = \text{length of barrier (nanotube) (m)}$$

$$V = \text{applied voltage (V)}$$

$$\mu_{\text{ion}} = \text{ion mobility inside nanotube (m}^2/\text{V-s)}$$

Pore blocking current scales linearly with applied voltage:

$$I_{\text{blocking}} = \frac{q}{\tau_{H^+}} = \frac{q \cdot \mu_{H^+} \cdot (V - V_{\text{threshold}})}{L^2} \propto V$$

$$I_{\text{blocking}} = \text{pore blocking current (pA)}$$

$$q = \text{charge on H}^+ \ (\text{C})$$

$$\tau_{H^+} = \text{average residence time of H}^+ \text{ inside the nanotube (s)}$$

$$\mu_{H^+} = \text{H}^+ \text{ mobility inside nanotube (m}^2/\text{V-s)}$$

$$V_{\text{threshold}} = \text{threshold voltage at which pore blocking observed (V)}$$
Proton conductivity is unusually large x $10^4$ compared with sputtered Si ion channels.

Blocking current $\sim 100$ pA = $6.25 \times 10^8$ protons/s gramicidin (biological) proton channel = $2.2 \times 10^9$ protons/s (at low pH).

Highly efficient conduction mechanism – “hop-and-turn” Grotthuss mechanism along the water chain.


Divide by linear water density in tube 33/nm yields hopping velocity of 0.02 m/s and mobility of $2 \times 10^{-5}$ m$^2$/V/s at $E = 10^3$ V/m or x 100 bulk water.

Blockade Current and Dwell Time Dependence on Ion Type

Dwell time: $\text{Na}^+ > \text{Cs}^+ > \text{K}^+ > \text{Li}^+$
Blockade Current: $\text{K}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$

Summary
Hydrogen bond dynamics and microscopic structure of confined water inside carbon nanotubes

Itsuo Hanasaki and Akihiro Nakatani
Department of Adaptive Machine Systems, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
(Received 28 September 2005; accepted 16 March 2006; published online 5 May 2006)

Blockade Current vs Diameter Shows Maximum

Water density increases strongly with decreasing diameter
Coordinated Molecular Transport

- Under some conditions, electro-osmotic current can become synchronized for a duration of up to several minutes.
- Never previously reported for any synthetic nanopore system
- Clearly arises from a single nanotube
- FFT of output current displays unique coherence of transport 46 mHz to 8.1 Hz, ion dependent
Resonant, Synchronized Transport

1 M KCl, 500 mV

Stochastic Simulation Explains the Oscillation

Mechanism can be simulated via 6 stochastic differential equations:

1) \( H_{np} + T \xrightarrow{k_1} H_{tube} \) (proton in)
2) \( I_{np} + T \xrightarrow{k_2} I_{tube} \) (ion in)
3) \( H_{tube} \xrightarrow{k_{1d}} \) (proton out)
4) \( I_{tube} \xrightarrow{k_{2d}} \) (ion out)
5) \( H_{bulk} \xrightarrow{k_s} H_{np} \) (proton exchange)
6) \( H_{np} \xrightarrow{k_{sd}} H_{bulk} \)

\( T = \) open nanopore state

Summary and Future Work – Ion Transport

- Carbon nanotube: new experimental conduit to manipulate single molecules in a nano-confined channel; test computational predictions

- Coherence resonance – dramatically increases the throughput of a nanopore sensor (x 100)

- Confined reactions and reactors, molecular synthesis and catalysis one molecule at a time

- Trace ion detection and ion separation in aqueous phases
Coherence resonance in molecular transport through a single walled carbon nanotube nanopore

Energy storage and generation using thermopower waves

Near infrared fluorescent sensors with single molecule sensitivity for studying biological signaling fluxes such as reactive oxygen and nitric oxide signaling in Epidermal Growth Factor Receptor (EGFR)

Won Joon Choi

Joel Abrahamson
Chemical Energy Densities are Much Larger than Electrochemical for Battery Applications

<table>
<thead>
<tr>
<th>Electrochemical</th>
<th>Energy Density (MJ/L)</th>
</tr>
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<tbody>
<tr>
<td>Li-ion</td>
<td>1.44</td>
</tr>
<tr>
<td>NiCd</td>
<td>0.72</td>
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<tr>
<td>NiMH</td>
<td>1.08</td>
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</table>

<table>
<thead>
<tr>
<th>Chemical</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>21.2</td>
</tr>
<tr>
<td>Glucose</td>
<td>24.0</td>
</tr>
<tr>
<td>Methane</td>
<td>22.2</td>
</tr>
</tbody>
</table>

Efficient, direct conversion of chemical to electrical energy is an unresolved problem.
Nanomaterials can demonstrate large anisotropic thermal conductivities

Quantum confinement suppresses phonon scattering mechanisms

Graphene
2D confined material
Thermal conductivities 3080 to 5150 W/m/K in plane

A. A. Balandin et al. Nano Lett. 2008, 8

Single Walled Carbon Nanotube
1D confined material
Thermal conductivities 2,500 to 10,000 W/m/K axial


Graphite
3D bulk material
Thermal conductivities 5.7 (⊥) to 1950 W/m/K (||)

Handbook of Chem. and Phys., 2010
Thermopower wave: reaction wave pushes electrons

Heat transfer from nanowire to fuel

Fuel

Self-propagating thermal wave

Enthalpy of reaction

Molar density of fuel (1st order decomposition)

Energy balance for fuel

Interfacial conductivity

Molar weight

Thermal conductivity

Energy balance for thermal conduit

\[
\frac{\rho C_p}{M_w} \frac{\partial T}{\partial t} = \chi \frac{\partial^2 T}{\partial x^2} + Q \left( \frac{\partial y}{\partial t} \right) - G(T - T_2)
\]

\[
\frac{\rho_2 C_{p,2}}{M_{w_2}} \frac{\partial T_2}{\partial t} = \chi_2 \frac{\partial^2 T_2}{\partial x^2} + G(T - T_2)
\]
Chemically driven thermal waves along CNT

CNT: 0.3 to 10 kW/m/K

$\Delta C_3N_6O_6 \rightarrow$ more $\Delta$

Thermopower Waves in Carbon Yarns

Carbon nanotubes can be spun into yarns, and coated with organic fuel (trinitroamine)
1D thermal wave is accelerated x10000

Mass ratio

TNA/MWNT = 10.35

TNA/MWNT = 5.5

Alignment of MWNT

Scale bar : 2mm

Position of flame propagation (mm)

Time (ms)

Bulk TNA x 1000

Reaction induces an electrical pulse: \textit{thermopower wave – a first demonstration}

Electrons entrained in the thermal wave drive a current along nanotube

Potential for exceeding traditional thermoelectric figures of merit

Thermal gradient is preserved at the reaction front

Thermopower electrical pulse follows thermal wave propagation

Slow Wave Velocities Yield Conventional Thermopower

Conventional thermopower (a slow wave) yields a sinusoidal voltage profile as the reaction zone traverses the nanotube.

\[ V = \kappa (T_{rxn} - T_{ambient}) + f(v) \]

Thermopower Wave Research at MIT

Courtesy: The Discovery Channel
The carbon **survives** the high temperature and can be used again!
Theoretical Calculations Predict Oscillating Thermal Wavefronts: AC Batteries


\[
\beta = \frac{C_p E_a}{-QR}
\]
Coherence resonance in molecular transport through a single walled carbon nanotube nanopore

Energy storage and generation using thermopower waves

Near infrared fluorescent sensors with single molecule sensitivity for studying biological signaling fluxes: reactive oxygen and nitric oxide signaling in Epidermal Growth Factor Receptor (EGFR)
Semiconducting carbon nanotubes fluoresce in the near infrared.

Optical Properties: Near Infrared Band Gap

Semiconducting Carbon Nanotubes Fluoresce

SWNT are non-photo-bleaching, no blinking at high fluence
Near infrared emission is uniquely situated in the *tissue transparency window*; no auto-fluorescence from biomaterials

No surface states, environmentally sensitive (two types):

- **Solvatochromism** (emission wavelength changes)
- **Charge transfer, quenching** (intensity variation)
Single Molecule Detection using SWNT Fluorescence

1D confined exciton can detect stochastic adsorption of single molecules

Exciton excursion distance = 90 nm  

In diffraction limited spot, as many as 900 nm / 90 nm ~ 10 emission states (3 shown above)

Quenching molecules (NO, H₂O₂, H⁺, Fe(CN)₆³⁻) extinguish emission of state stochastically  
Single Molecule Detection In-Vivo using a Collagen Platform

Collagen thin film

SWNT embedded into type 1 collagen film

nIR (>900-1600 nm) detection using 2D InGaAs array

658 nm excitation

Single-step quenching of SWNT via H$_2$O$_2$

Red line: fit to Hidden Markov model


Single Molecule Detection of Hydrogen Peroxide

InGaAs nIR Detector
(0.7 to 1.9 um)

Objective:
1.46 NA (TIR)

Single isolated SWNT in collagen film, 10 uM H$_2$O$_2$

Epidermal Growth Factor Receptor (EGF): extracellular membrane protein; tyrosine kinase; ErbB family of receptors; modulates cell proliferation

EGFR over-expression implicated in many cancers.

Monoclonal antibody inhibitors:

Cetuximab and Panitumumab

> $620 million/year


Massachusetts Institute of Technology
Questions about H$_2$O$_2$ signaling pathway in EGFR

Source of H$_2$O$_2$ generation in response to EGF stimulation
Location within the cell
Relationship to better known phosphorylation pathway

Goal of our work: develop a platform to study ROS signaling at the single cell, single molecule level
Spatial and Temporal Single Molecule Map from Live A431 Human Epidermoid Carcinoma

- SWNT sensors from InGaAs nIR array
- Phase contrast picture from Si CCD camera

One example trace, from a 4 pixel region of interest (ROI) on one single nanotube.

The goal is to examine all the ROIs and map the spatial behavior in real time.
Real Time, Spatially Resolved Single Molecule Detection of H$_2$O$_2$ from a single A431 Cell

Single A431 Cell Plated onto Type I Collagen Film

Molecules of H$_2$O$_2$ Detected per 150 seconds

Time = 0 s
Real Time, Spatially Resolved Single Molecule Detection of H$_2$O$_2$ from a single A431 Cell

Molecules of H$_2$O$_2$ Detected per 150 seconds

Single A431 Cell Plated onto Type I Collagen Film

Time = 2850 s

4 µm

Pixel Number

Pixel Number
Single cell analysis

3T3 – Control Cells

A431

Red = EGFR

EGF Stimulation on 3T3 cells

EGF Stimulation on A431 cells

Red = EGFR
Sensors can distinguish background/membrane generation!

**H₂O₂ raining down randomly**

Simulation: 1,000,000 H₂O₂ randomly falling onto 300 sensors

**Red: H₂O₂ generated locally**

Simulation: 1,000,000 H₂O₂ randomly falling onto 300 sensors

Plus: Local generation

Inverse incomplete gamma function
Counting molecules originating from the membrane

Given any distribution of sensor responses (rank ordered), \( y(x) \), the curve at \( x \to 0 \) specifies the binomial background (gamma function):

\[
y_{\text{membrane}}(x) = y(x) - \Gamma\left(p, \frac{x}{n}\right)
\]

\( \Gamma \): incomplete gamma function (background)

\( p \): mean value of background distribution, obtained from fitting the small number of data points at \( x \to 0 \)

\( n \) = number of sensors

\( \Gamma (p, x/n) \)

Generated at the membrane

Use low rank region to fit \( \Gamma \)

Separating EGFR Effect From Background H₂O₂

Activity increase arises from EGF-EGFR binding
Similar between live and fixed A431 cells
Increase in activity is more evident in A431 than 3T3

Receptor activity:

SWNT arrays measure receptor activity in real time on a single cell!

Singlet Oxygen (\(^1\text{O}_2\)) Oxidation is the H\(_2\text{O}_2\) Source

Add EGF

+ EGF in D\(_2\)O (lifetime of \(^1\text{O}_2\) increases x 16)

Add EGF

Add NaN\(_3\)

+ EGF and NaN\(_3\)

+ NaN\(_3\)

(\(^1\text{O}_2\) quencher)

\[2^1\text{O}_2 + 2\text{H}_2\text{O} \xleftrightarrow{EGF-EGFR} 2\text{H}_2\text{O}_2 + \text{O}_2\]

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