SAND2011-7791 C

SAND2011-7791C

Catalytically Induced Electrokinetics for Motors and Micropumps

Wally Paxton

September 15, 2011

CINT User Conference

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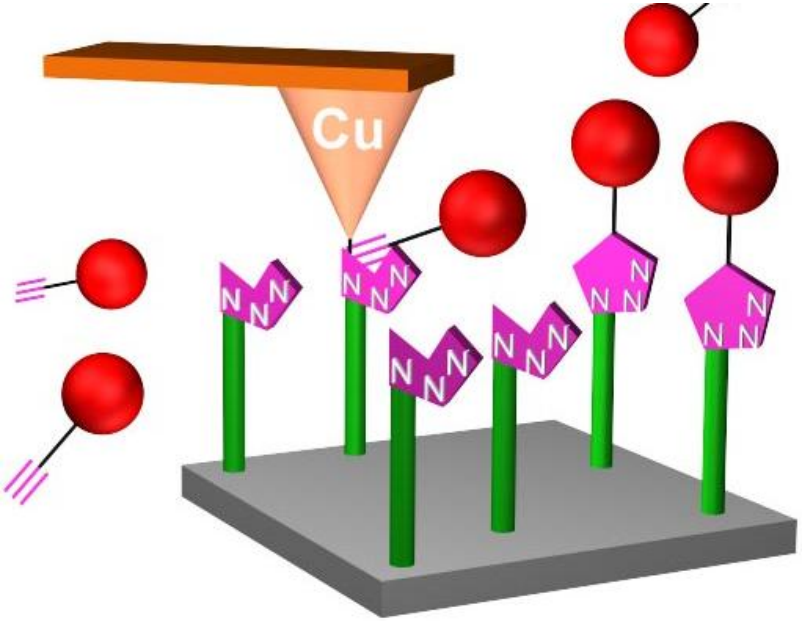
Sandia National Laboratories

New Staff Member: Wally Paxton

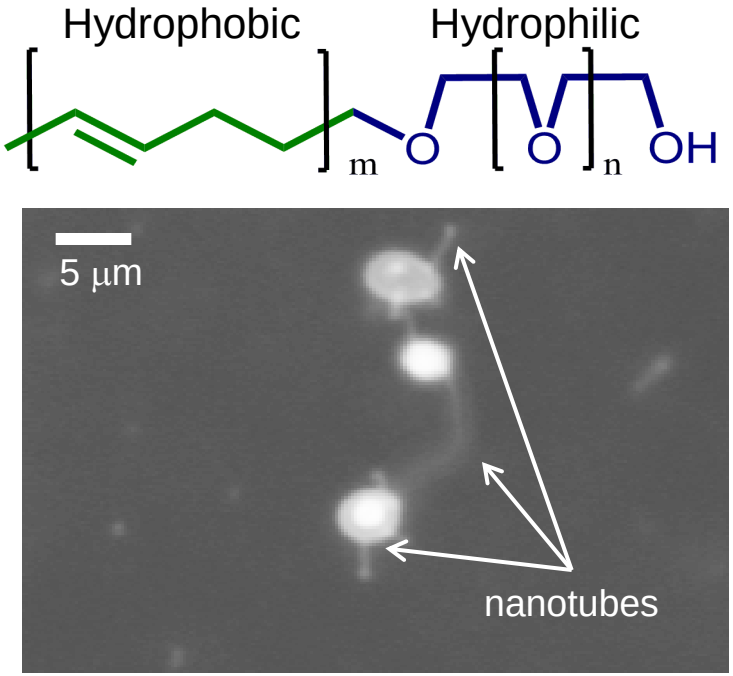
PhD: Penn State
Post-Doc: Northwestern

Soft, Biological, and Composite Nanomaterials Thrust

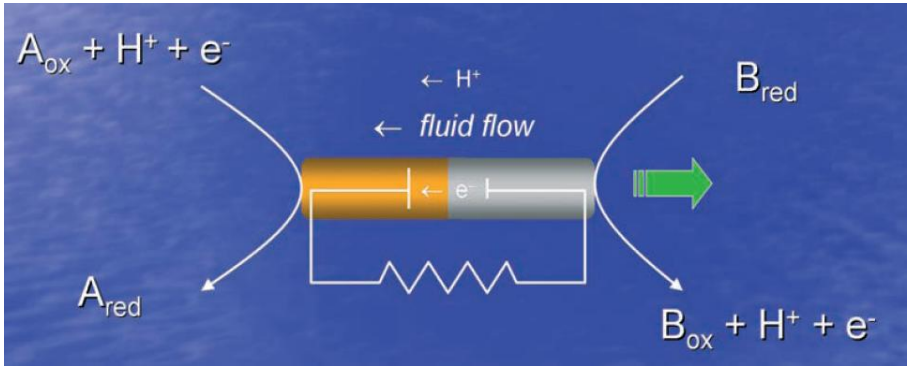
Colloid and Interfacial Chemistry
Electrochemistry / Self-Assembly



Direct-Write Click Chemistry (*J. Am. Chem. Soc.* **2009**)



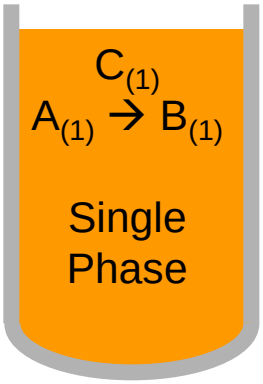
Robust Polymer Vesicles and Nanotubes



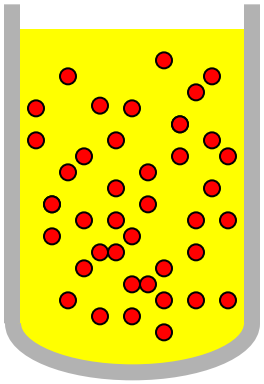
Catalytic Nanomotors (*J. Am. Chem. Soc.* **2004**)

Catalysis in Nanotechnology

Homogeneous Catalysis

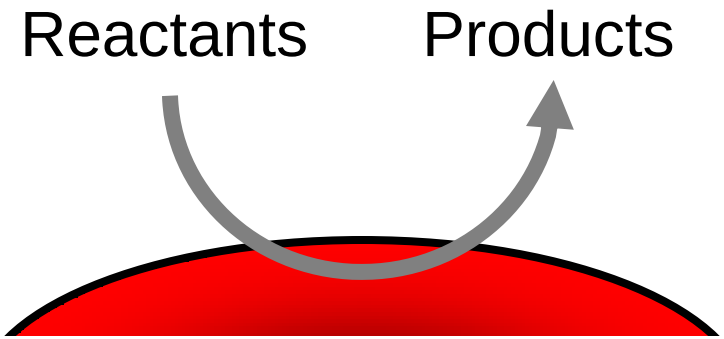


Heterogeneous Catalysis



$C_{(2)}$
$A_{(1)} \rightarrow B_{(1)}$

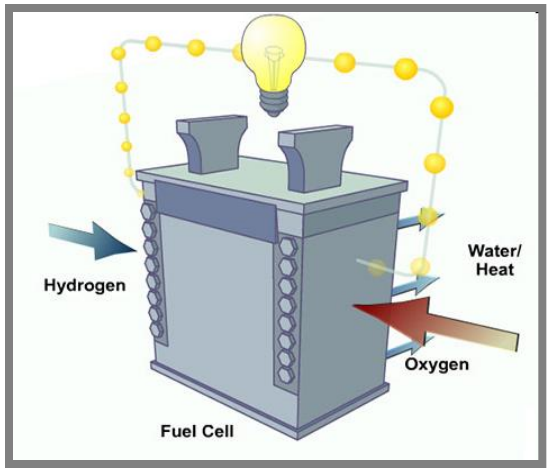
Multiple Phases



Occurs at the Catalyst Surface

→ ***Spatial Control of Reactions***

Efficient / Controllable Chemical Transformations



Electrocatalysts for Fuel Cells

Catalyst Miniaturization

Nanostructures for catalytic applications

Understand size/shape effects on catalytic properties

Consequences of Spatially-Confined Reactions

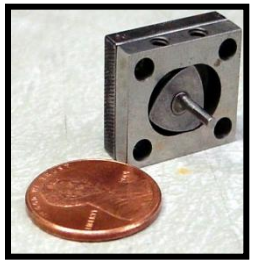
Exploiting those Consequences

Scaling of Chemical Locomotion

Ayusman Sen

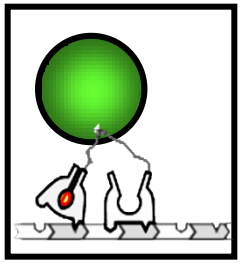
Tom Mallouk

www.porsche.com



www.berkeley.edu

www.fuga.ru



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Macroscale

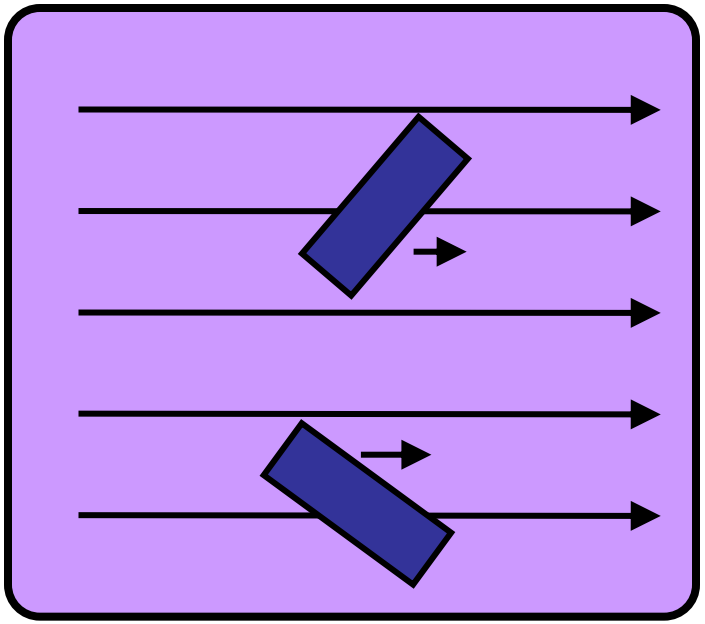
- Inertia important
- Body forces (gravity)

Micro/nanoscale

- Viscosity important
- Interfacial forces
- Brownian motion
- Harvest energy
- Catalysis and Asymmetry

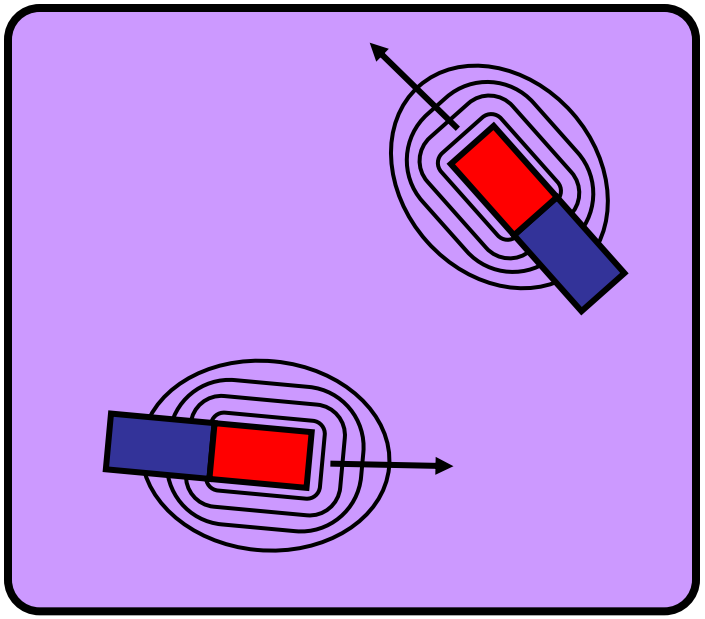
Gradient-Based Motion

External Fields[a]



- Many types of fields:
  (*magnetic, chemical, thermal, electric*)
- Energy applied from external source
- Ensemble behavior of all particles

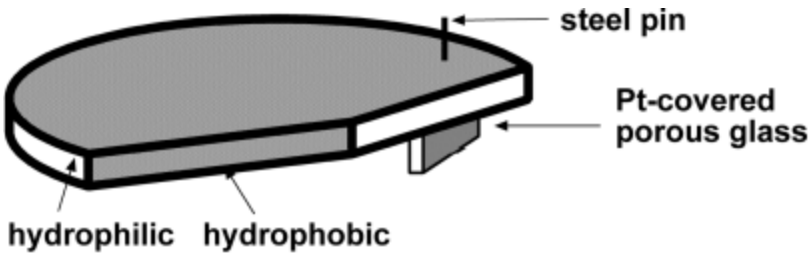
Self-generated Fields[b]



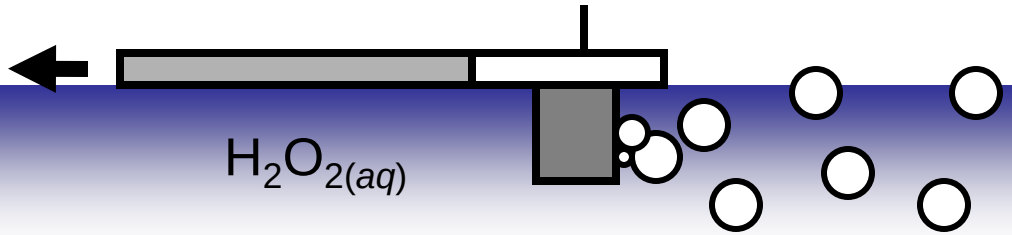
- Catalytically generated fields:
  (*chemical, thermal, electric*)
- Energy harvested locally
- Particles move independently
- Catalysis and asymmetry

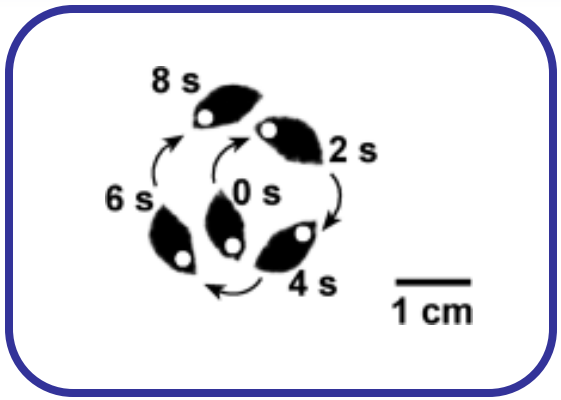
[a] J. L. Anderson, *Ann. Rev. Fluid. Mech.* **1989,** *21,* 61-99. [b] **W. F. Paxton**, T. E. Mallouk, A. Sen, *Chem.—Eur. J.* **2005,** *11,* 6462-6470.

A Catalytic Motor



$$2H_2O_{2(aq)} \xrightarrow{Pt} 2H_2O_{(l)} + O_{2(g)}$$

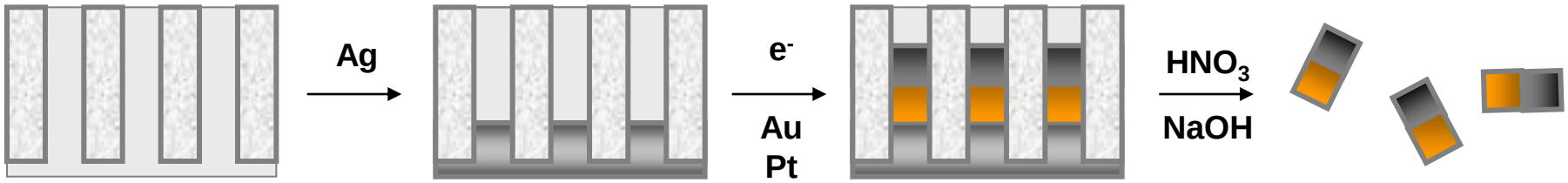




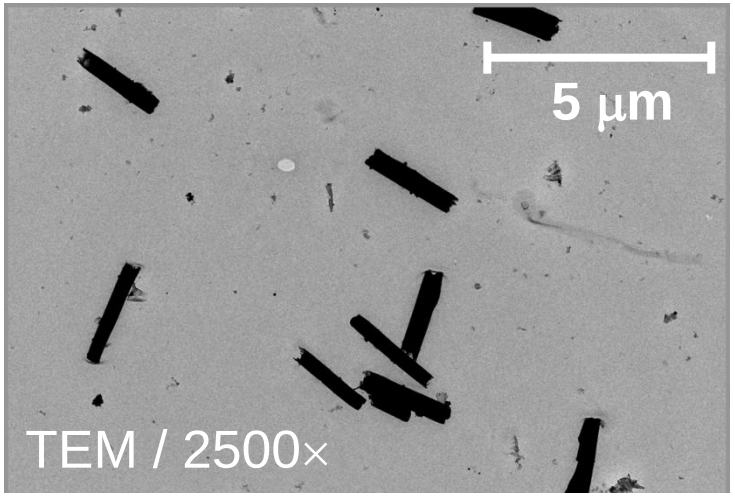
How small can we make these?

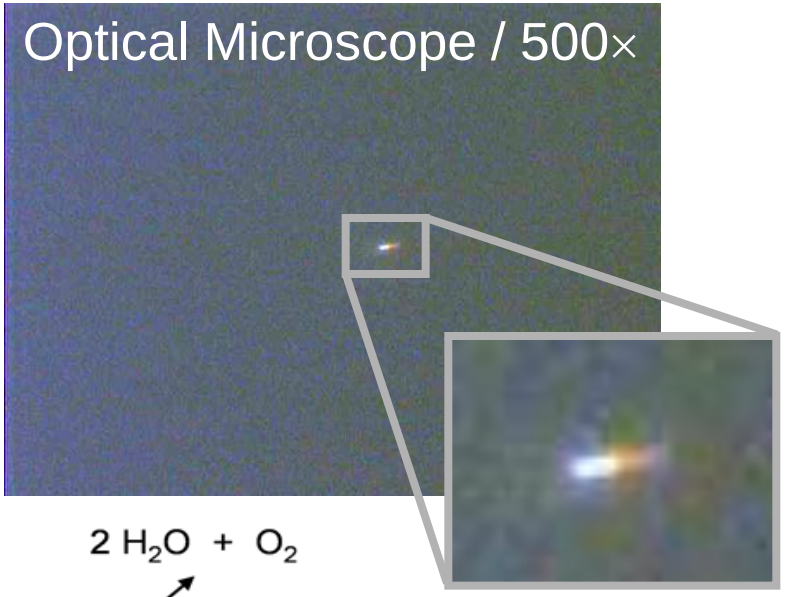
R. F. Ismagilov, A. Schwartz, N. Bowden, G. M. Whitesides, *Angew. Chem. Int. Ed.* **2002,** *114,* 674-676.

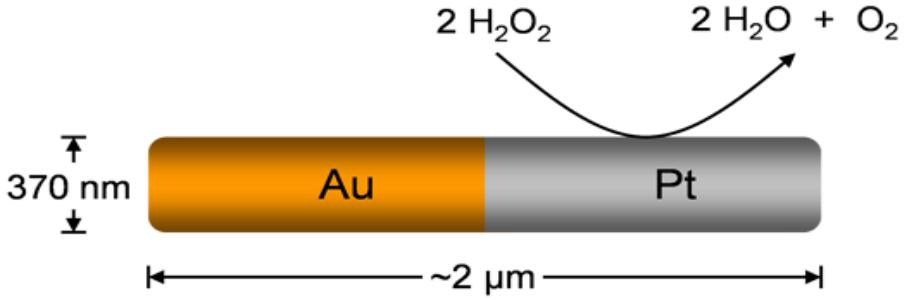
Miniaturizing Catalytic Motors



Aluminum Oxide Membrane | Ag-filled Pores | Au/Pt Nanorods | Free Nanorods

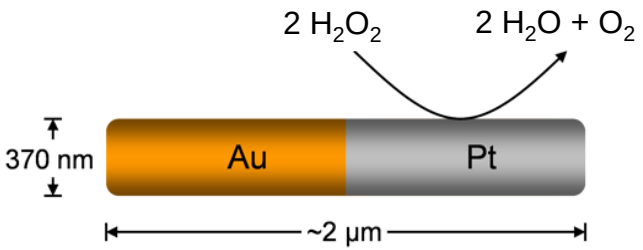


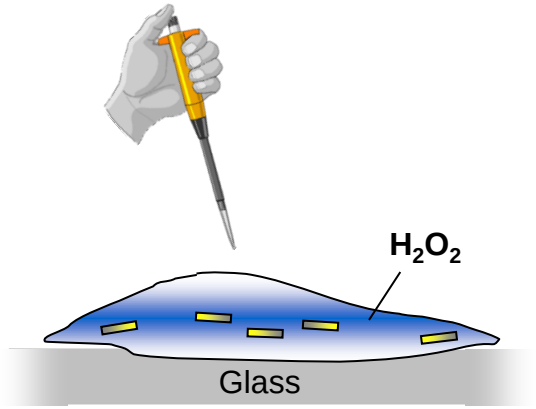




W. F. Paxton, et al. *J. Am. Chem. Soc.* **2004,** *126,* 13424–13431.

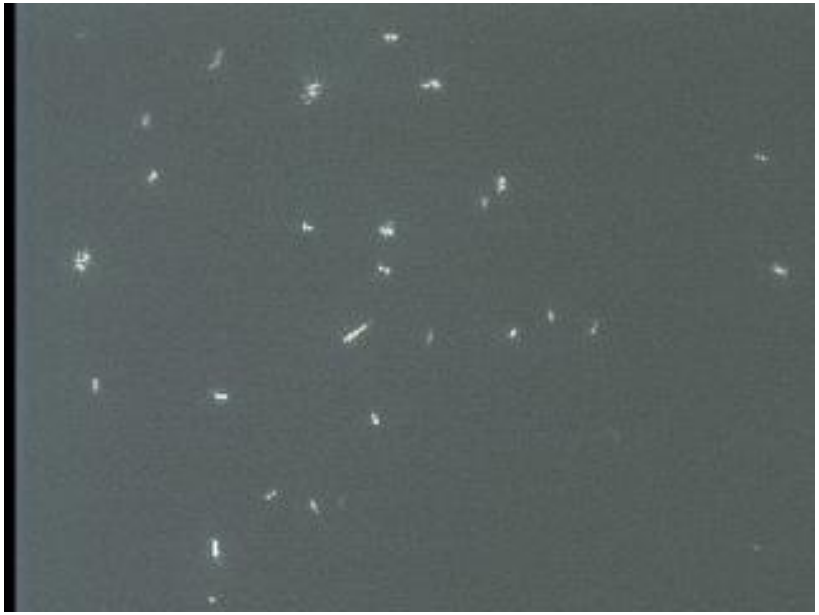
Diffusion vs. Catalytic Motors





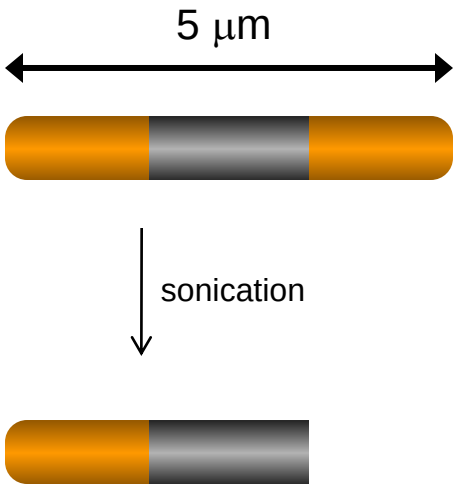
Pt/Au rods in *H_2O (DI)*

Pt/Au rods in *3% H_2O_2*

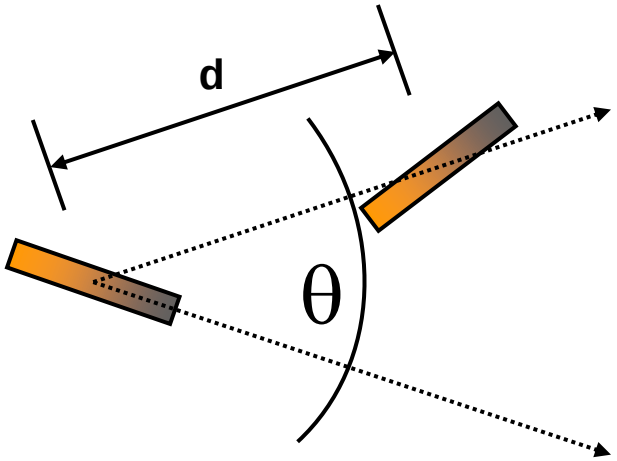


W. F. Paxton, et al. *J. Am. Chem. Soc.* **2004,** *126,* 13424–13431.

Catalysis and Asymmetry



H_2O_2 Concentration Effect

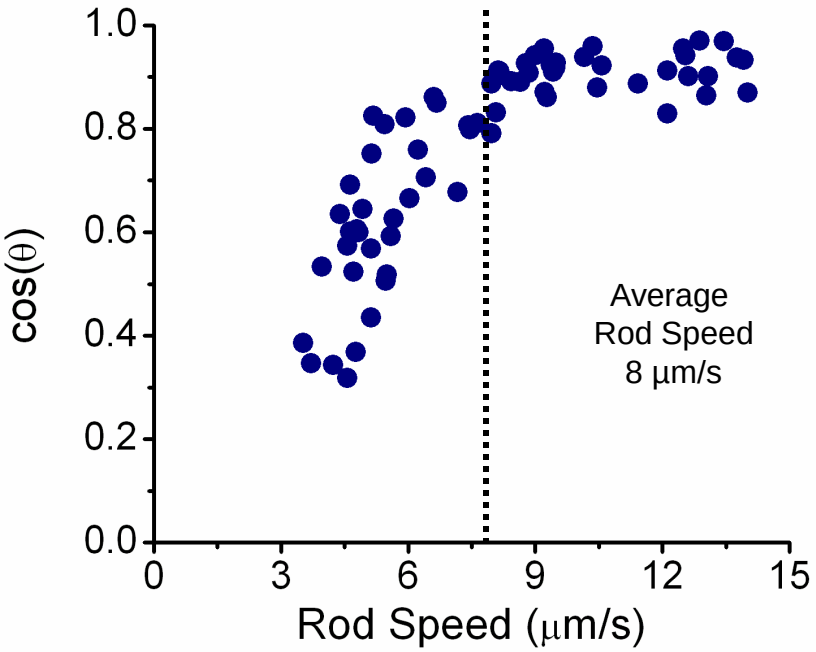


Displacement = d

Directionality = cos(θ)

Axial velocity = cos(θ) × d / t

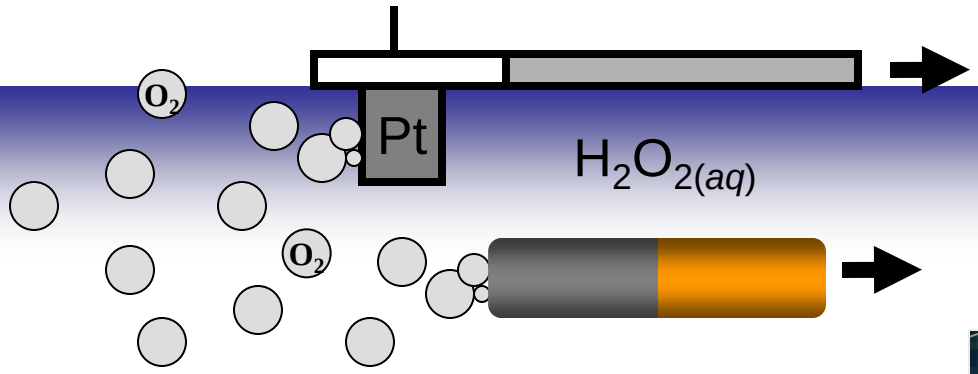
H_2O_2 (%)	Average Speed (μm/s)	cos(θ)	Axial Velocity (μm/s)
5	8	0.8	6.6
3	8	0.8	6.6
1.5	6	0.7	3.8
0.3	5	0.6	3.4
0.03	4	0.2	0.9
0	3	0.01	0.0

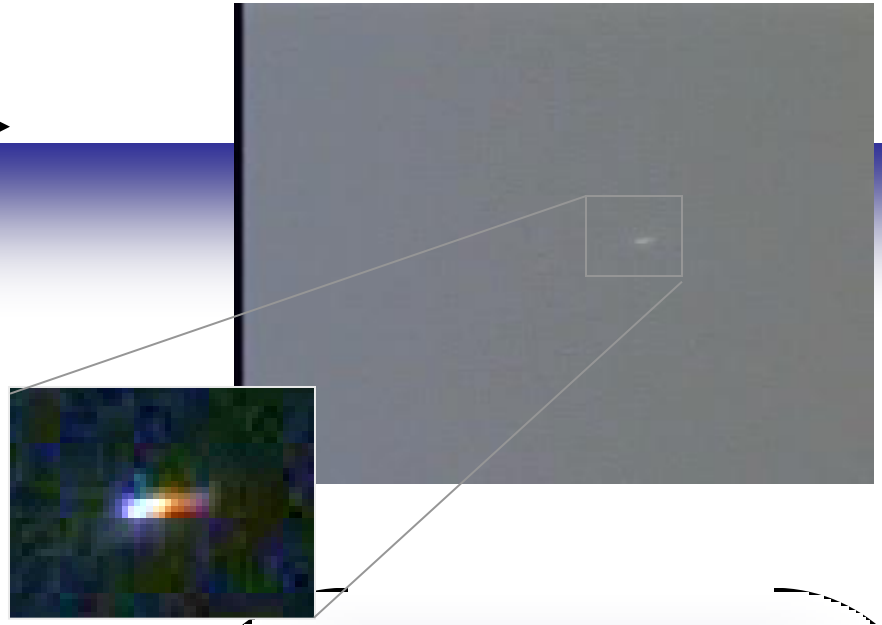


W. F. Paxton, et al. *J. Am. Chem. Soc.* **2004,** *126,* 13424–13431.

Why Do They Swim?

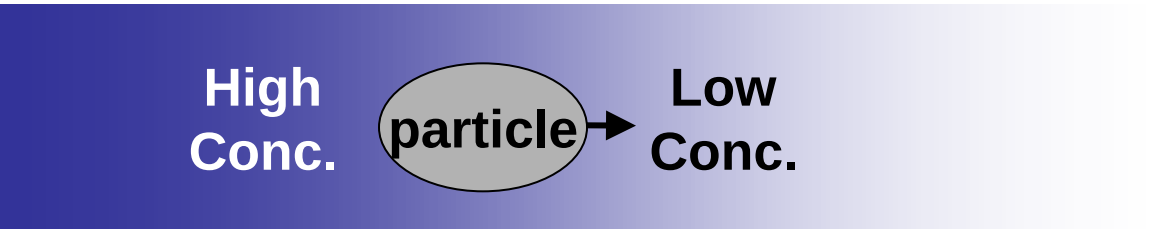
Bubble Propulsion?

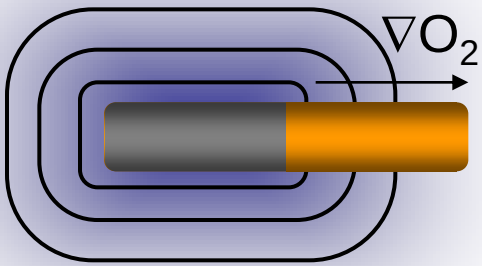




No bubbles near motors
Predicts motion in wrong direction

Diffusiophoresis?[a,b]





Pushes particle to
lower concentration region

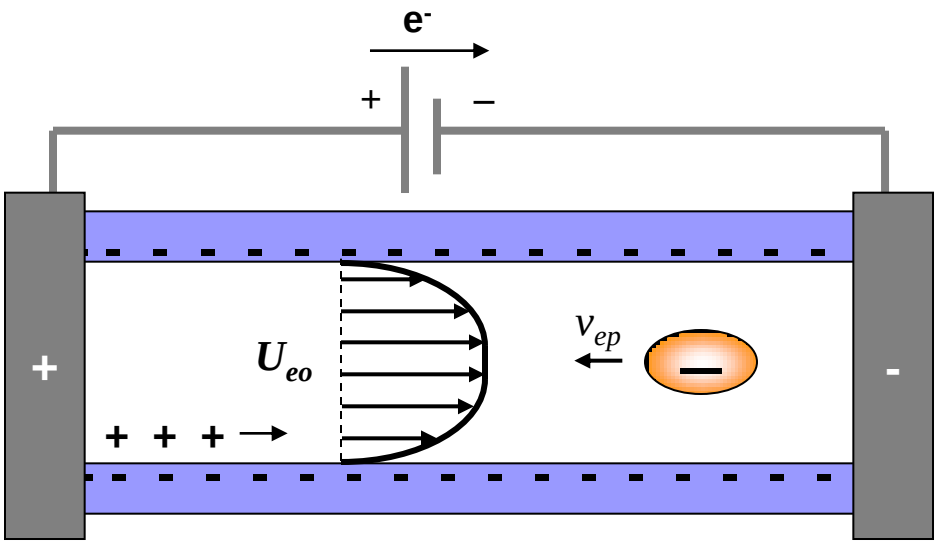
O_2 gradient acts on *gold* end

Predicted motion:

- *toward gold (to low C)*
- *speed <4 nm/s*

[a] M. M. Lin, D. C. Prieve, *J. Colloid Interface Sci.* **1983,** *95,* 327-339.
[b] J. L. Anderson, *Ann. Rev. Fluid. Mech.* **1989,** *21,* 61-99.
[c] **W. F. Paxton**, T. E. Mallouk, A. Sen, *Chem.—Eur. J.* **2005,** *11,* 6462-6470.

Electrokinetic Phenomena



Electroosmosis

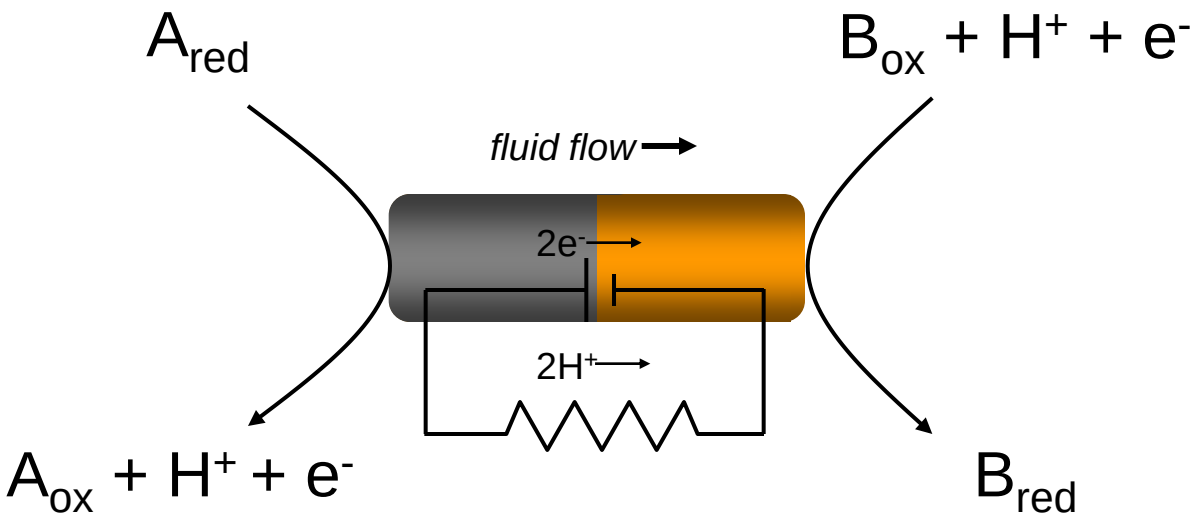
$$U_{eo} = \frac{\zeta_w \varepsilon E_x}{\mu}$$

Electrophoresis

$$v_{ep} = \frac{\zeta_p \varepsilon E_x}{\mu} f$$

Observed velocity

$$v_{obs} = U_{eo} + v_{ep}$$

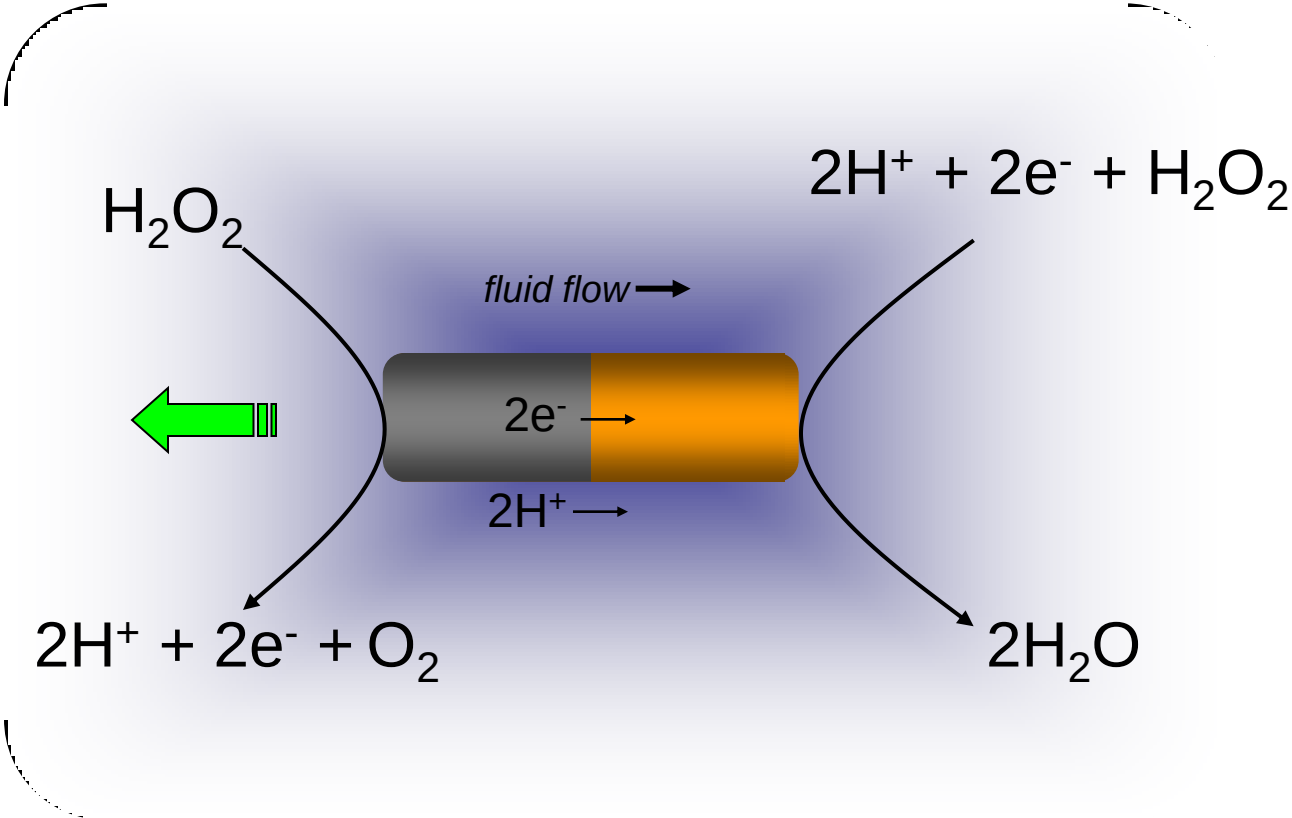


Electrochemical Reaction

Electric Field

W. F. Paxton, T. E. Mallouk, A. Sen, *Chem.—Eur. J.* **2005,** *11,* 6462-6470.

Electrokinetic Mechanism[a,b]



$$i_{e^-} = i_{H^+}$$

$$E = \frac{J_{H^+}}{\sigma}$$

$$v = \frac{\zeta \varepsilon E}{\mu} f$$

On Pt: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

On Au: $H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

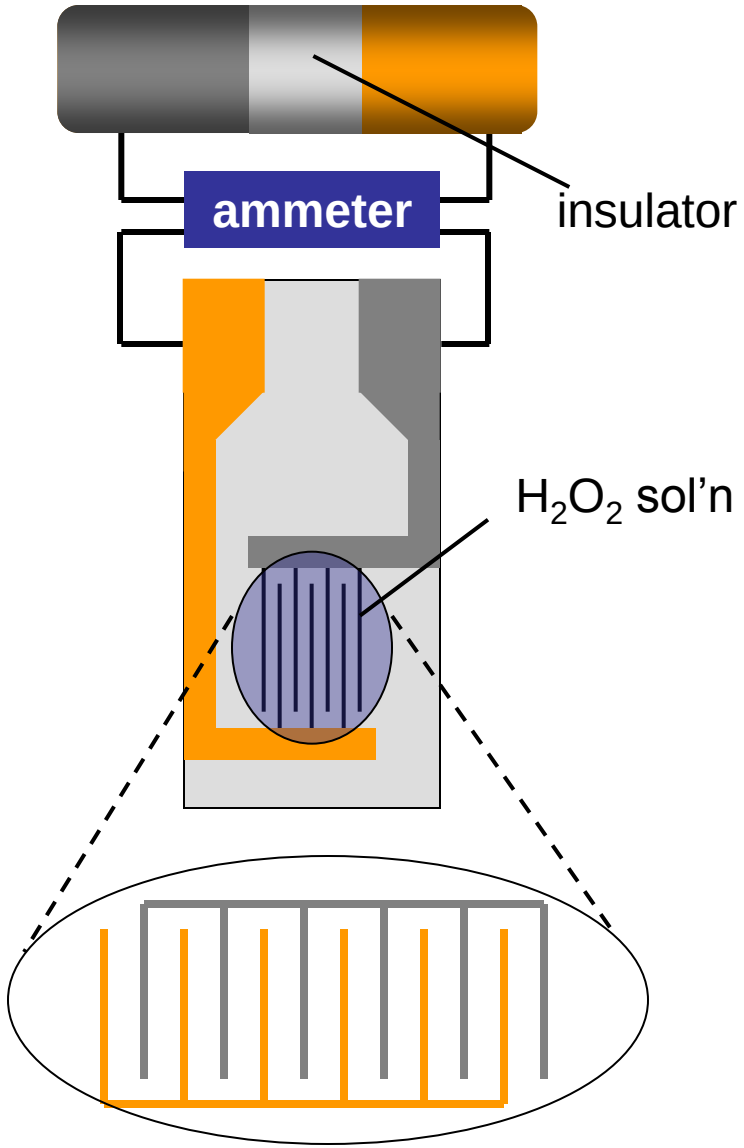
[a] **W. F. Paxton**, T. E. Mallouk, A. Sen, *Chem.—Eur. J.* **2005,** *11,* 6462-6470.
[b] **W. F. Paxton**, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

Measuring Current in Small Systems

- Pt/Au motor

- Interdigitated Array
  - baseline: <0.00001 A/m^2
  - water: ~0.00001 A/m^2
  - 0.6% H_2O_2: 0.27 A/m^2
  - 3% H_2O_2: 0.53 A/m^2

- Predicted Electric Field ($E=J/\sigma$)
  - J = 0.53 A/m^2
  - σ = 4.1 μS/cm
  - **E = 13.1 V/cm**



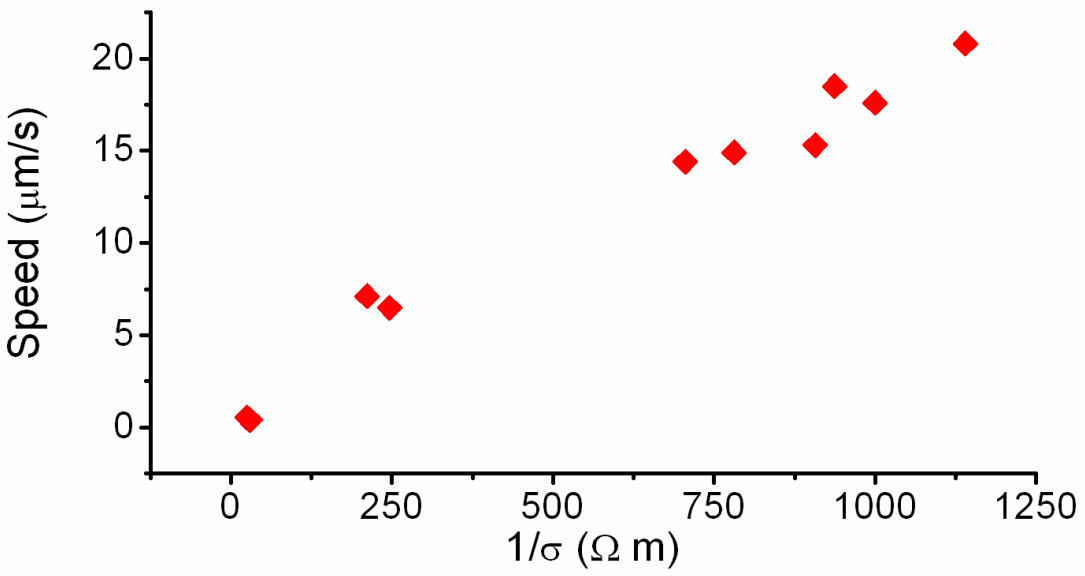
W. F. Paxton, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

Rod Speed vs. Conductivity

$$v = \frac{\zeta \varepsilon E_x}{\mu} f$$

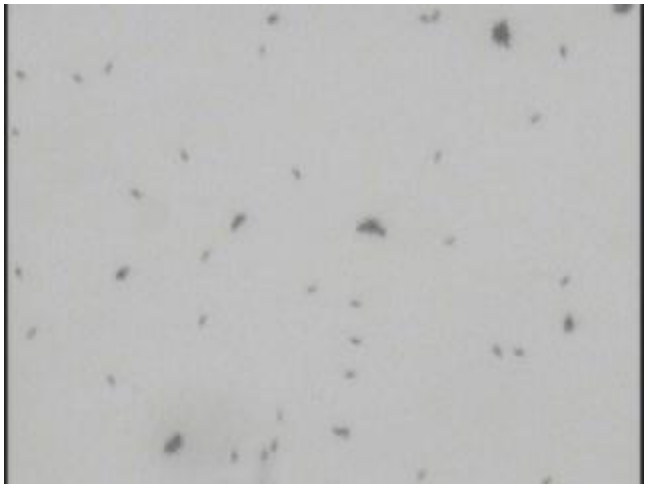
$$v = \frac{\zeta \varepsilon}{\mu} \frac{J}{\sigma} f$$

As conductivity *increases*, velocity should *decrease!*

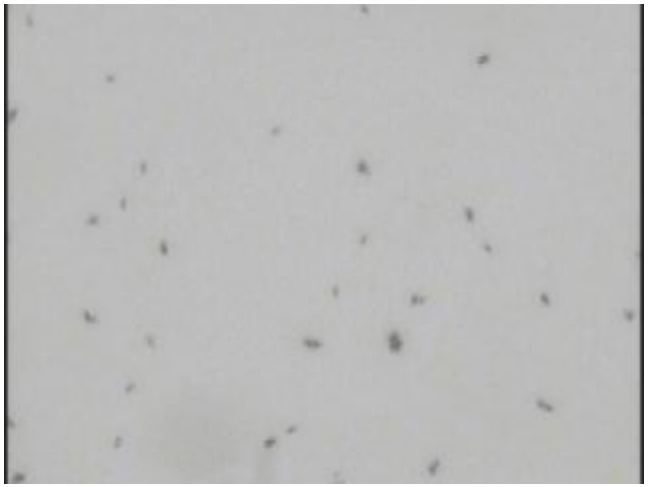


slowing due to increased conductivity

PtAu rods / 3% H_2O_2



PtAu rods / 3% H_2O_2 / 3 mM $NaNO_3$

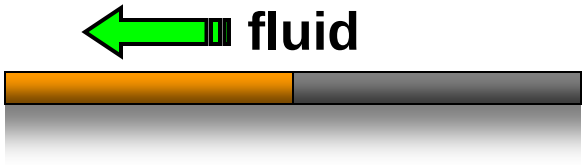


W. F. Paxton, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

From Motors to Micropumps

Motor

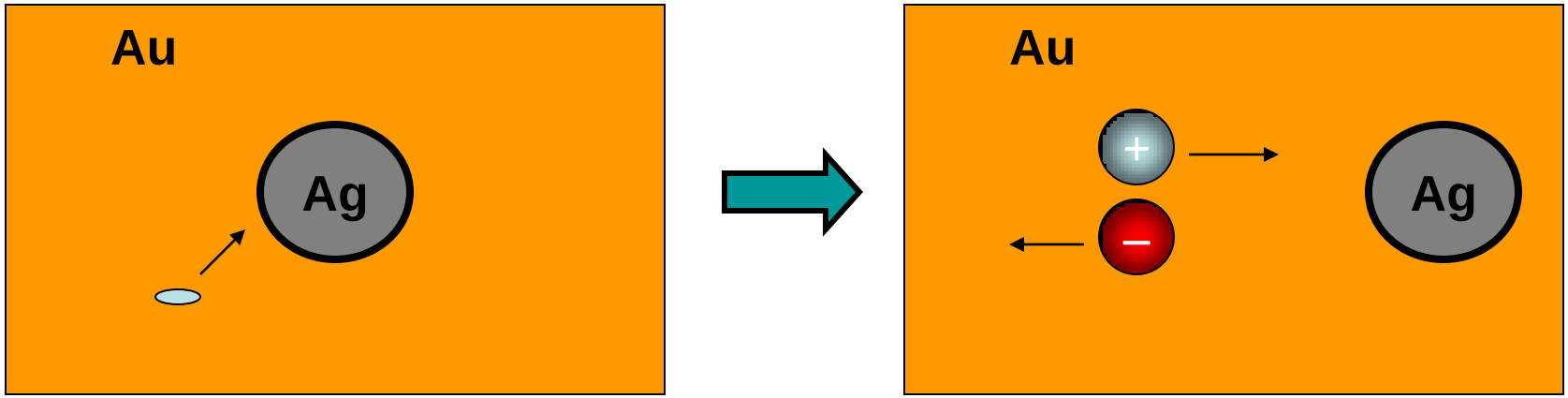
- Suspended motor moves itself.

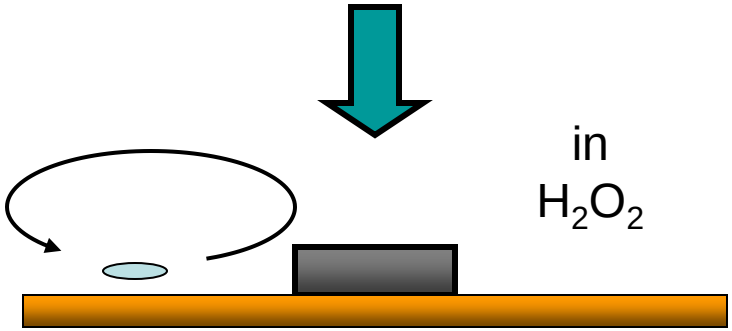


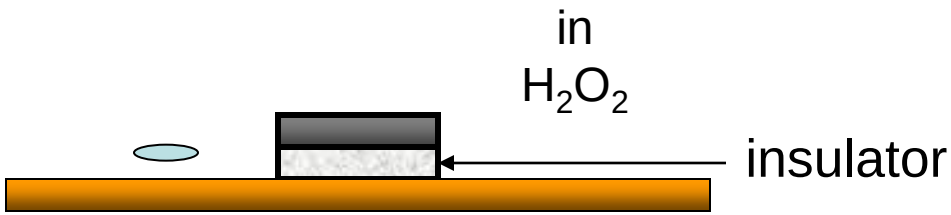
Micropump

- Immobilized motor moves surrounding fluid.

Catalytic Fluid Pumping







- Motion depends on particle charge (ζ)
- Insulator shuts motion “off”

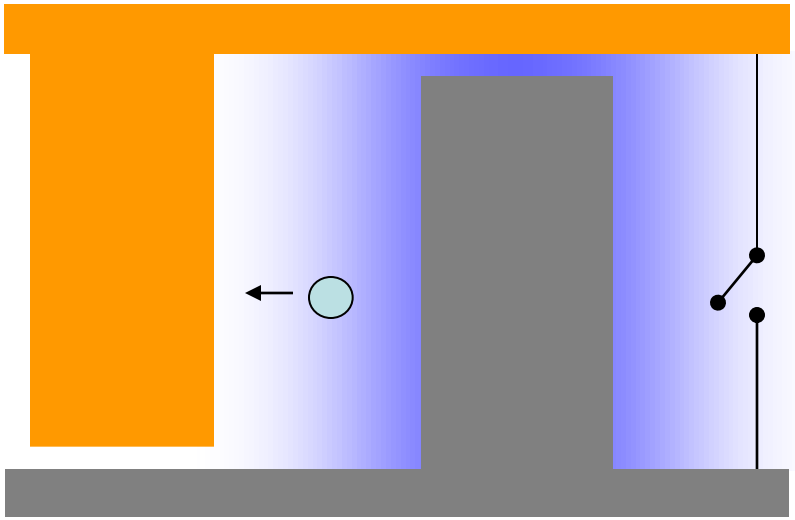
Strongly suggests electrokinetics

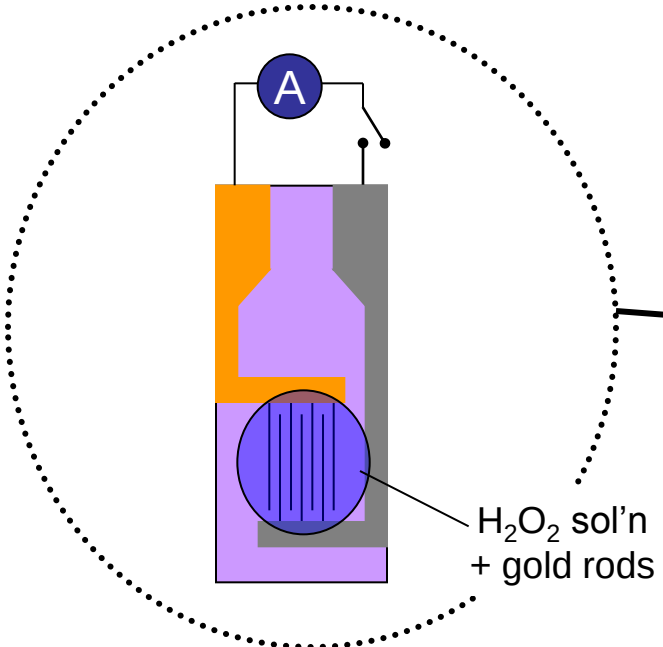
T. R. Kline, **W. F. Paxton**, Y. Wang, D. Velegol, T. E. Mallouk, A. Sen, *J. Am. Chem. Soc.,* **2005,** *127,* 17150 -17151.

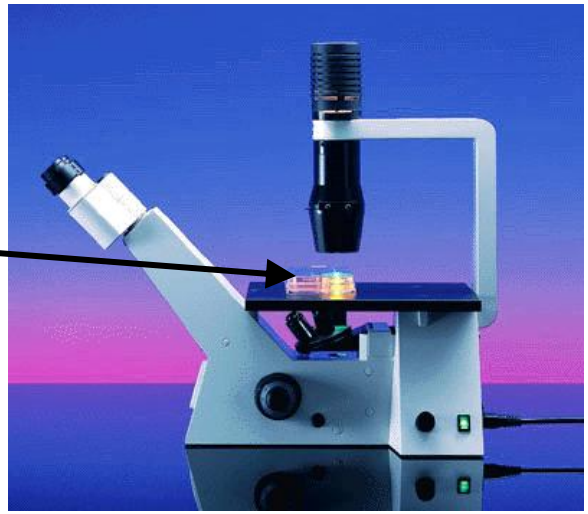
Microelectrode Experiments

- O_2 gradient:
  motion independent of switch.

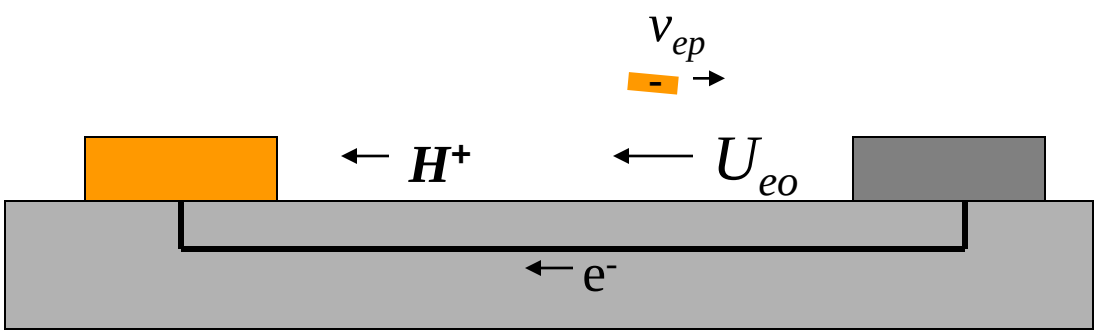
- Electrokinetics:
  “off” = diffusion only
  “on” = linear motion

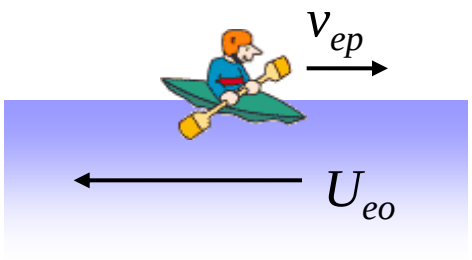






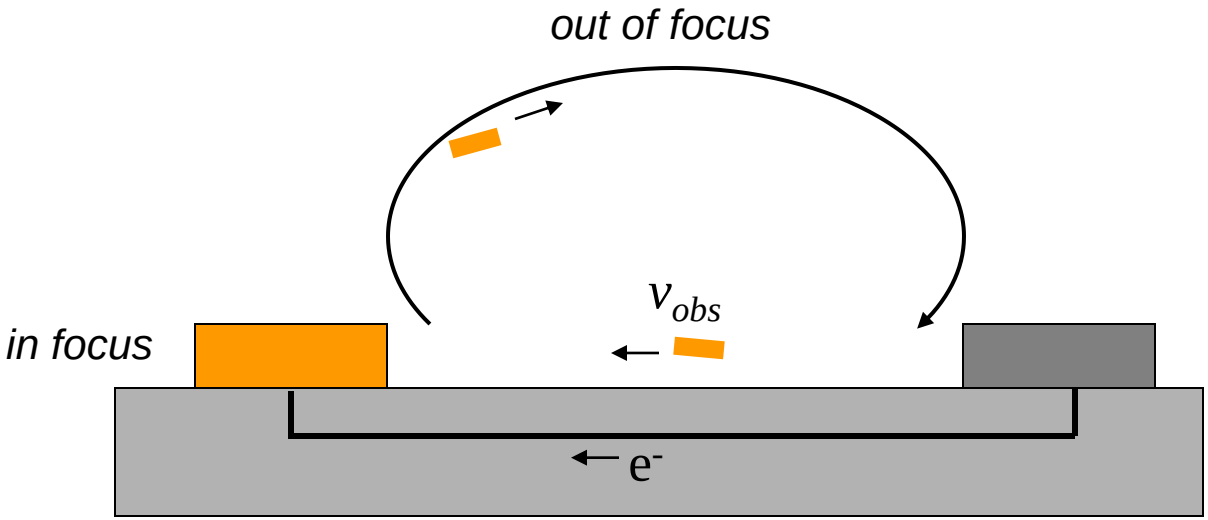
Catalytically Induced Electrokinetics





$$v_{obs} = U_{eo} + v_{ep}$$

$$v_{obs} \sim \left(\zeta_w - \zeta_p\right)$$



Electroosmosis dominates when

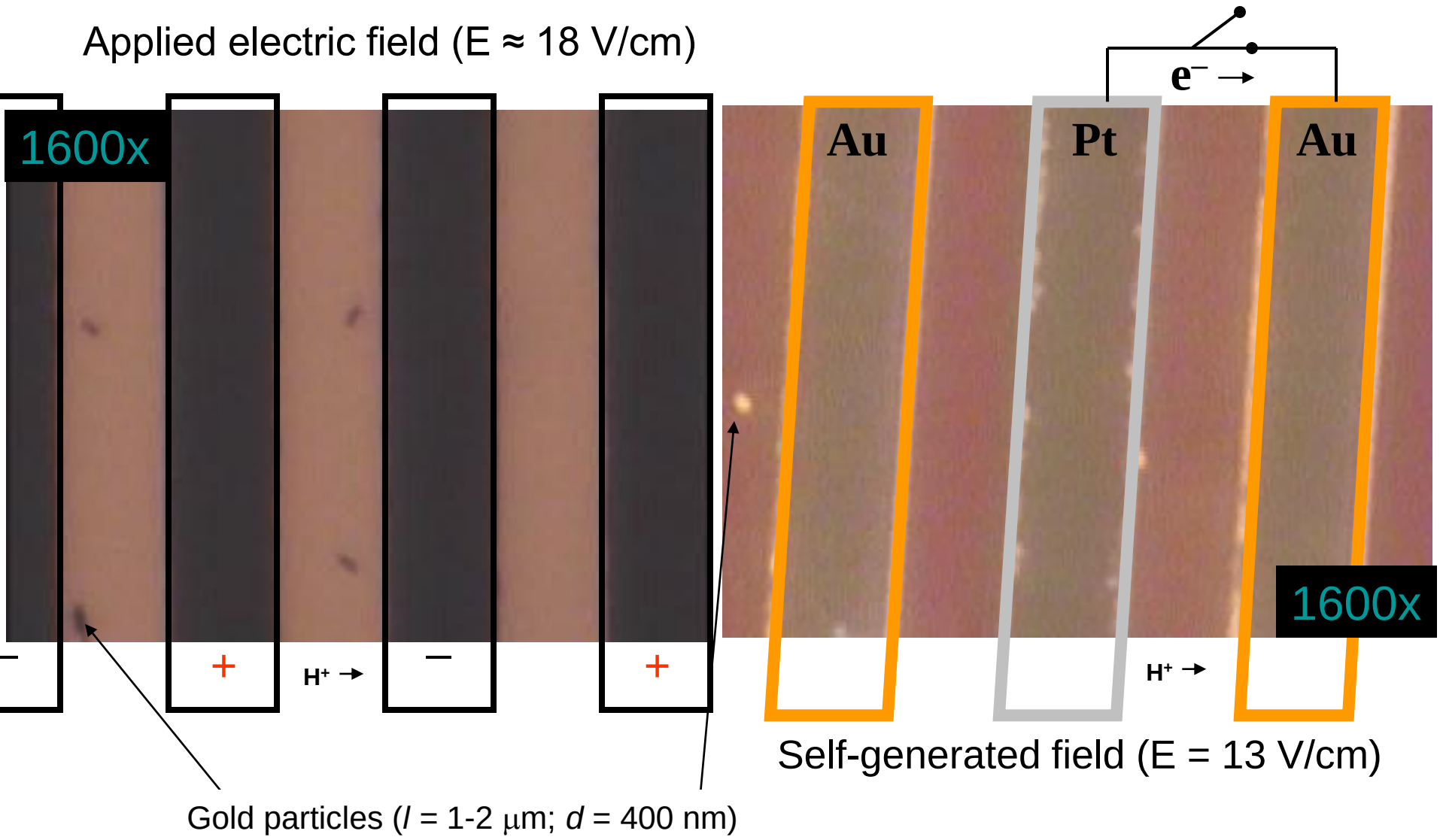
$$\left|\zeta_w\right| > \left|\zeta_p\right|$$

borosilicate glass — Au tracers

| –60 mV | > | –40 mV |

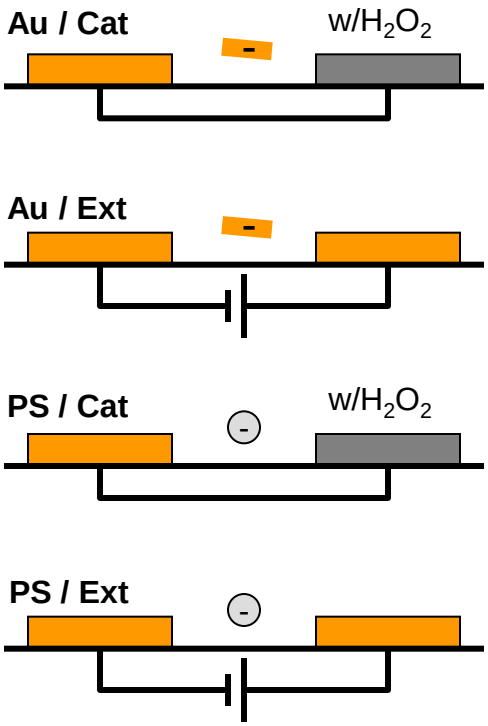
W. F. Paxton, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

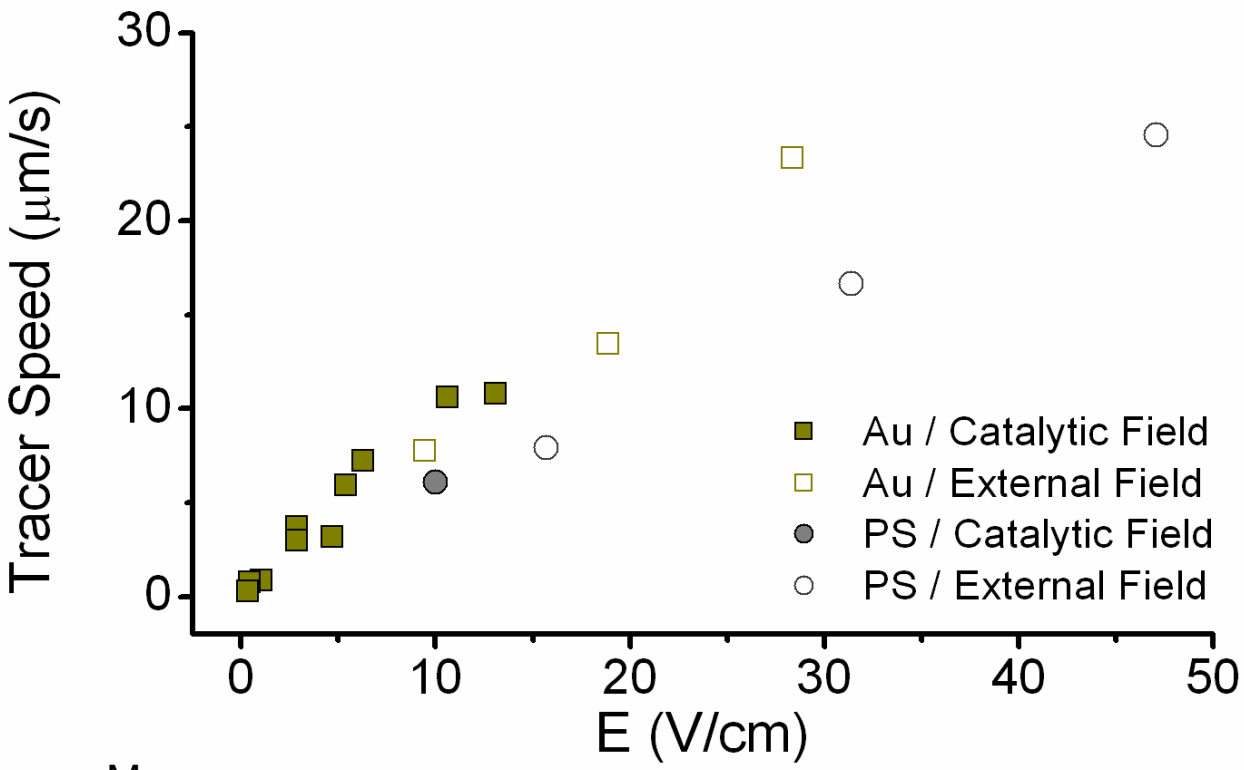
Electric Field and Motility Comparison



W. F. Paxton, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

Tracer Speed vs. E-Field



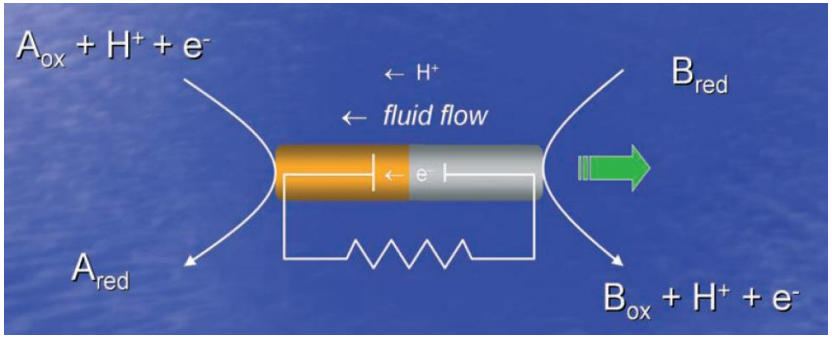


Tracer	ζ_p (mV)	Measure Slope ($\times 10^9$ m^2/(V·s)
Au/Cat	-40(8)	7.8(8)
Au/Ext	-40(8)	8(1)
PS/Ext	-46(4)	7.2(2)

$$v_{obs} = \frac{\varepsilon\left(\zeta_p - \zeta_w\right)}{\mu}\frac{J}{\sigma}$$

W. F. Paxton, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

And Then What Happened?



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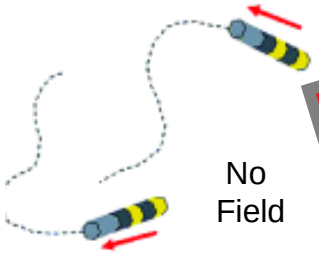
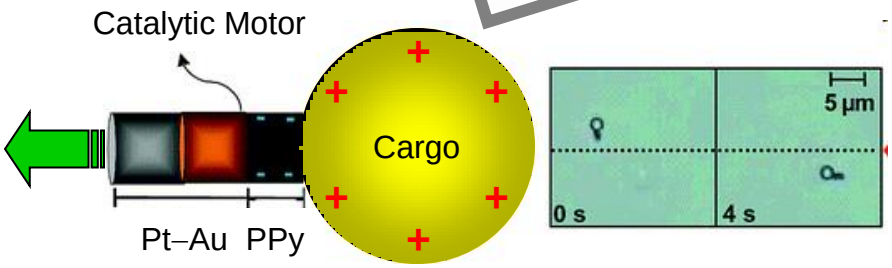
Y. Wa… *angmuir* **2006,** *22,* 10451–10456.



T. R. Kline, **W. F. Paxton,**
Angew. Chem. Int. Ed. **200**

Y. Hong et al. *Phys. Rev. Lett.,* **2007,** *99,* 178103.



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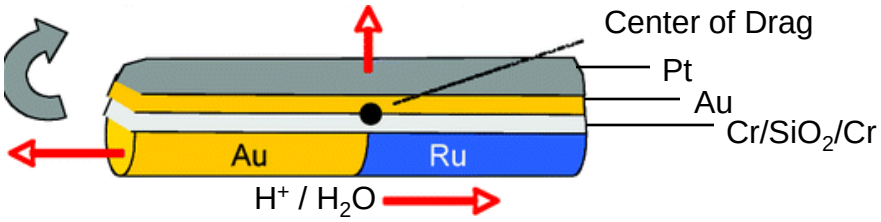
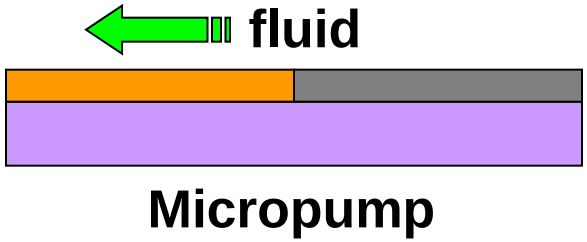


Y. Wang et al. *J. Am. Chem. Soc.* **2009,** *131,* 9926–9927.

Catalytically Induced Electrokinetics

- **Motors** to power nanoscale machines
  - Pt/Au particles in H_2O_2 solutions: smallest autonomous non-biological *motor*
  - Motion due to catalytically-induced electrokinetics

- **Micropumps** to pump fluid on chip
  - No moving parts
  - Fluid/tracer velocity a function of electric field ($E=J/\sigma$)
  - Energy supplied locally and chemically



- Motion due to bimetallic redox chemistry:
  - Pt/Au rods in H_2O_2 act as miniature fuel cells
  - Rod speed a function of catalytic activity

Acknowledgements

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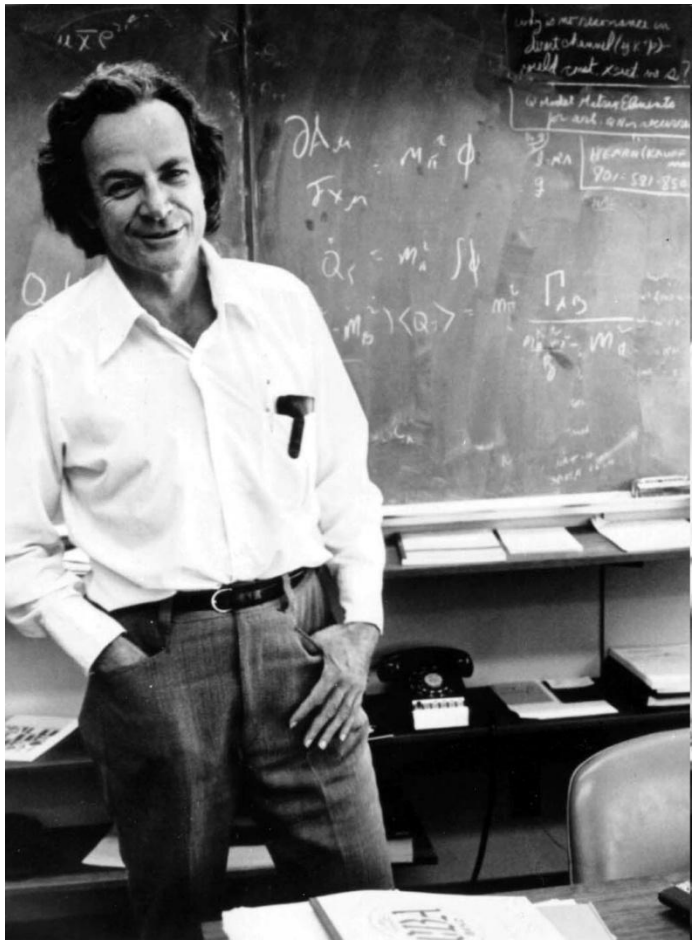
- Penn State Center for Nanoscale Science

CENTER FOR nanoscale science

Los Alamos NATIONAL LABORATORY

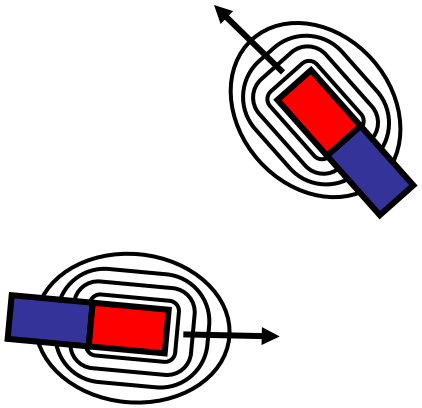
Sandia National Laboratories

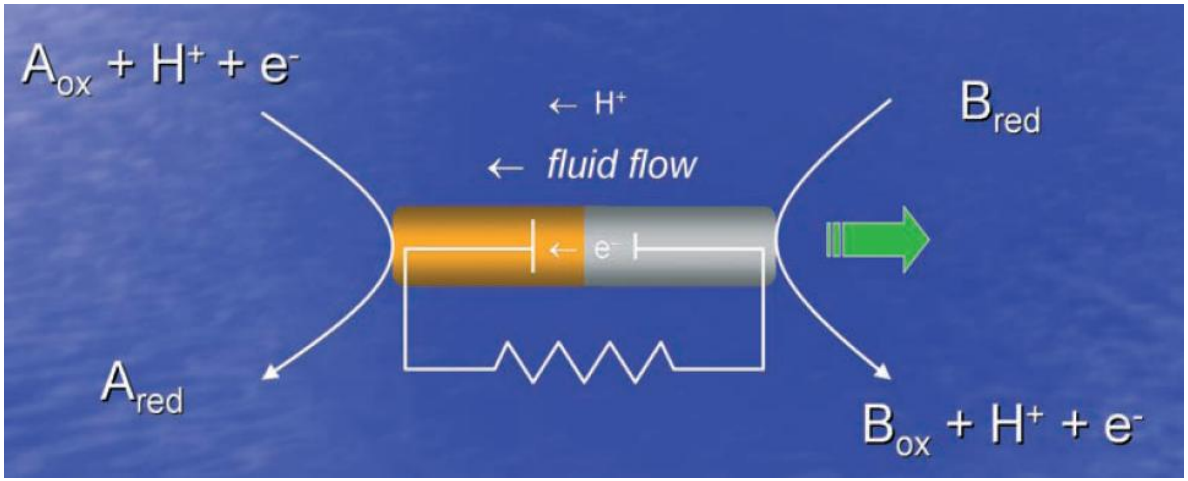
Now, you might say, “Who should do this and why should they do it?” Well, I pointed out a few of the economic applications, but I know that the reason that you would do it might be just for fun. But have some fun!



A Tale of Two Projects…

Autonomous Motion of Catalytic Nanorods





Surface Functionalization Using Click Chemistry