SAND2011-3722C

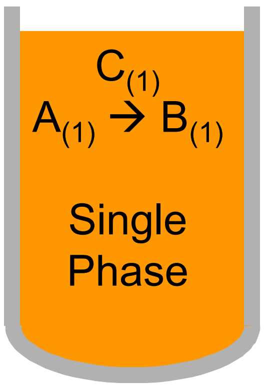
Catalytically Induced Electrokinetics for Motors and Micropumps

Wally Paxton

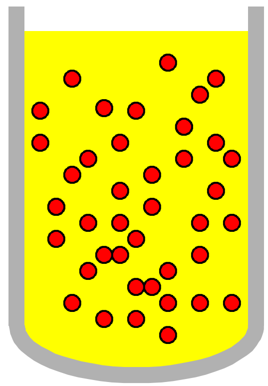
June 3, 2011

Catalysis in Nanotechnology

Homogeneous Catalysis



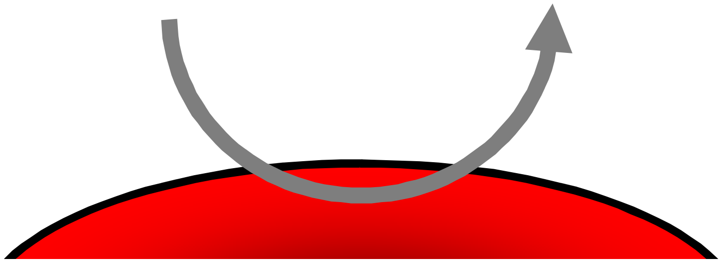
Heterogeneous Catalysis



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

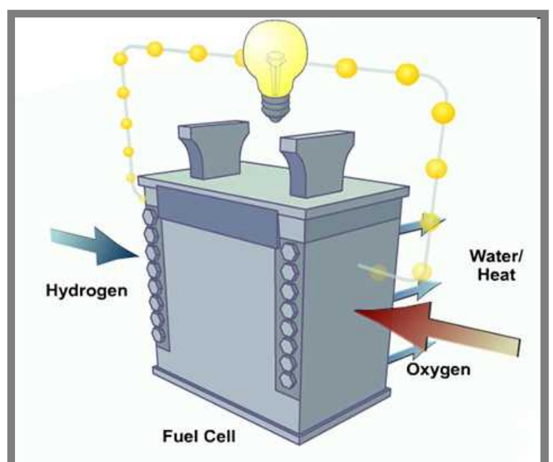
Multiple Phases

Reactants Products



Occurs at the Catalyst Surface
→ ***Spatial Control of Reactions***

Efficient / Controllable Chemical Transformations



Electrocatalysts for Fuel Cells

Catalyst Miniaturization

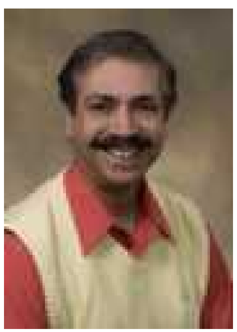
Nanostructures for catalytic applications

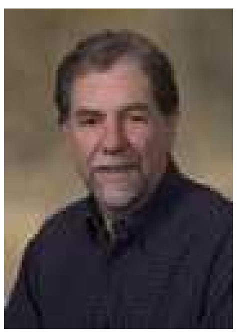
Understand size/shape effects on catalytic properties

Consequences of Spatially-Confined Reactions

Exploiting those Consequences

Scaling of Chemical Locomotion

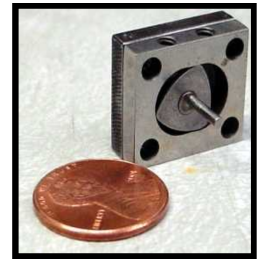




Ayusman Sen

Tom Mallouk

www.porsche.com



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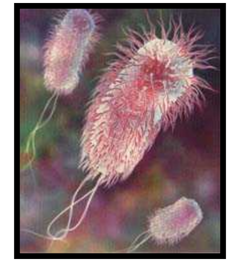
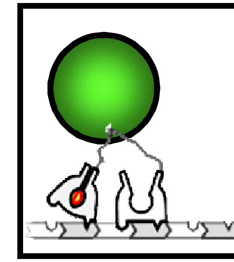


www.fuga.ru



mc11.mcri.ac.uk

m — mm — µm — nm

Macroscale

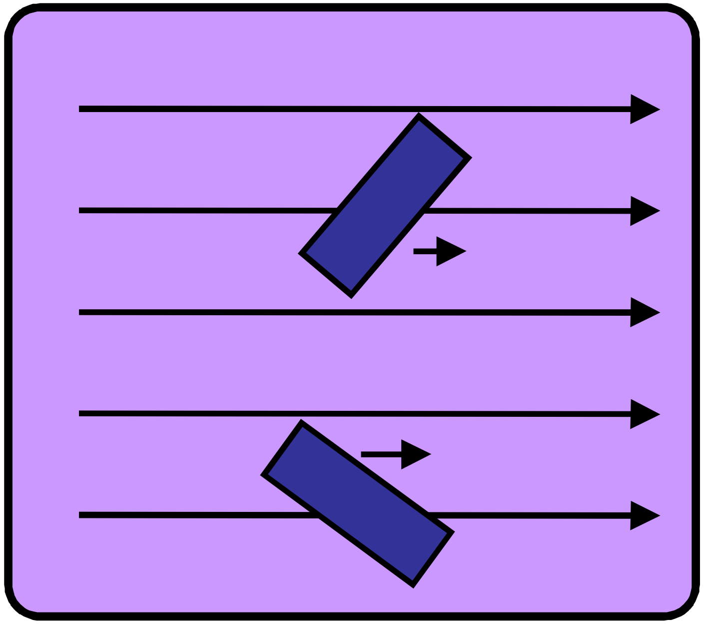
- Inertia important
- Body forces (gravity)

Micro/nanoscale

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

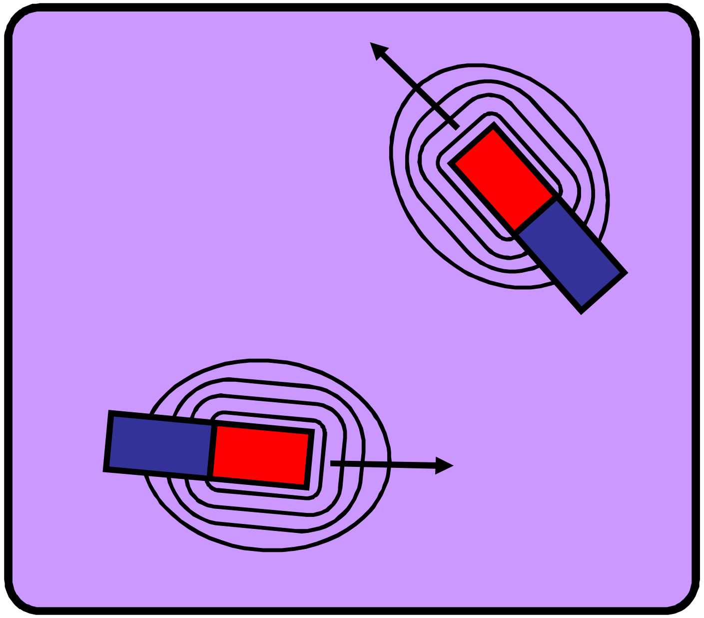
Gradient-Based Motion

External Fields[a]



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

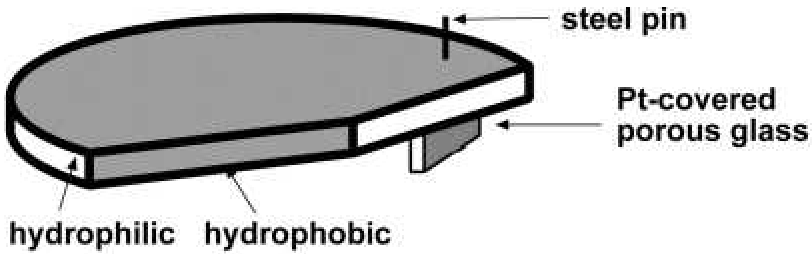
Self-generated Fields[b]



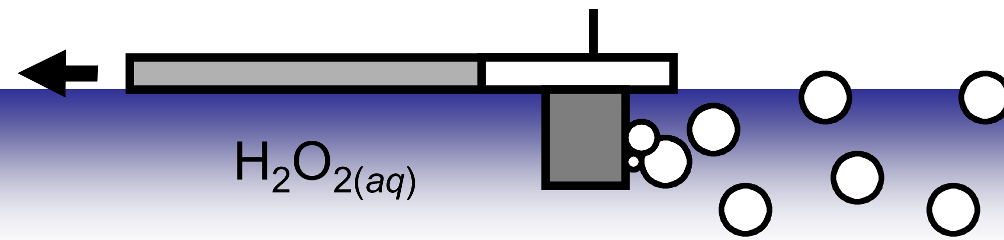
- Catalytically generated fields:
  (*chemical, thermal, electric*)
- Energy harvested locally
- Particles move independently
- Catalysis and asymmetry

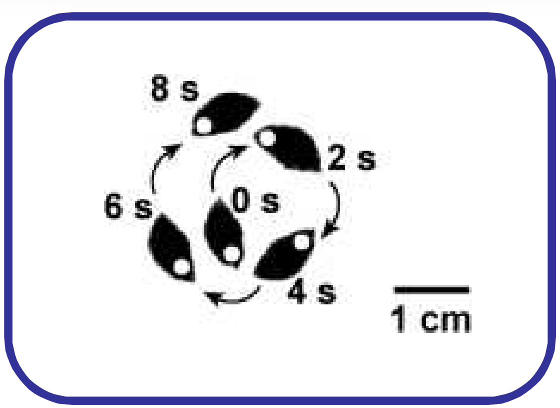
[a] J. L. Anderson, *Ann. Rev. Fluid. Mech.* **1989,** *21,* 61-99. [b] **W. F. Paxton**, T. E. Mallouk, A. Sen, *Chem.—Eur. J.* **2005,** *11*, 6462-6470.

A Catalytic Motor



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

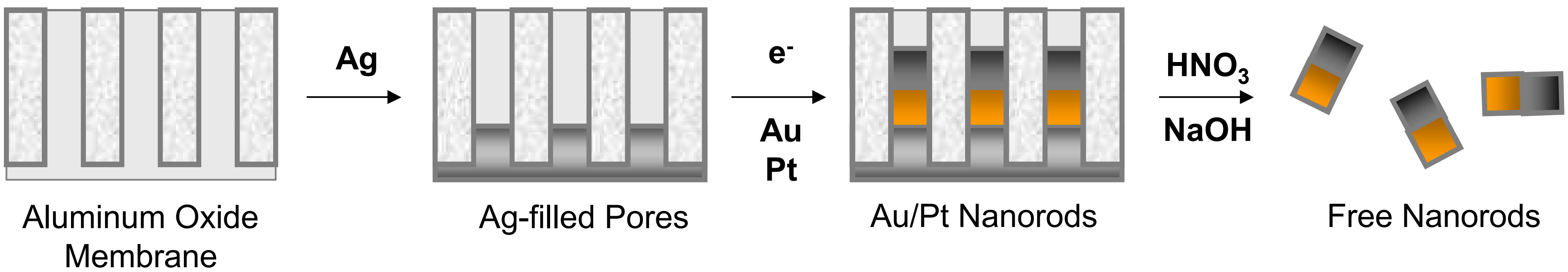


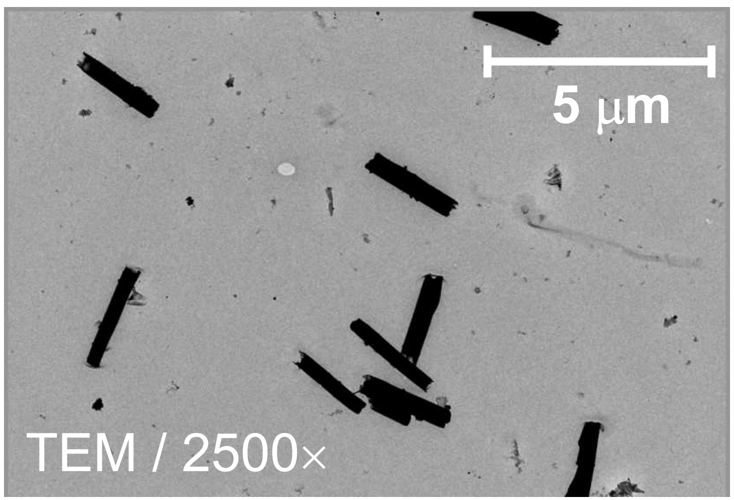


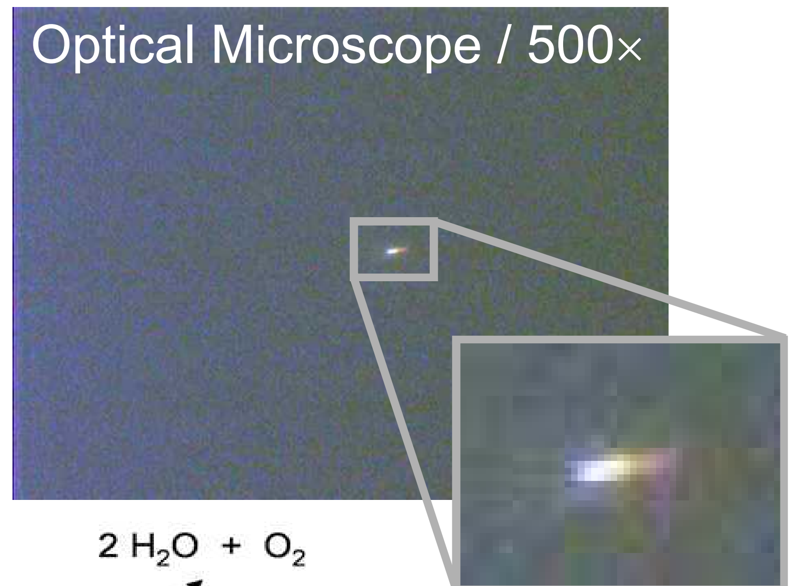
How small can we make these?

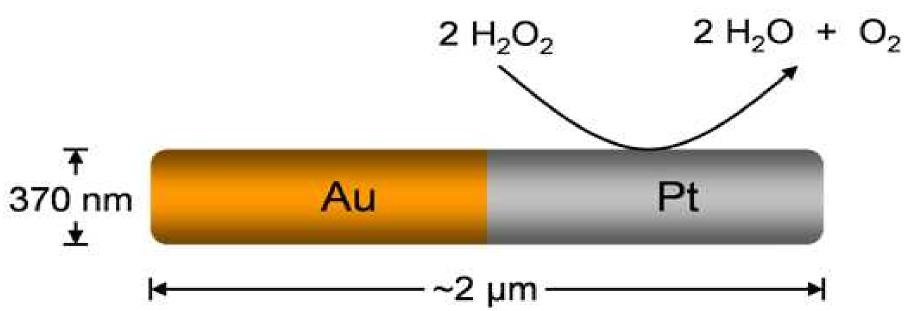
R. F. Ismagilov, A. Schwartz, N. Bowden, G. M. Whitesides, *Angew. Chem. Int. Ed.* **2002,** *114,* 674-676.

Miniaturizing Catalytic Motors



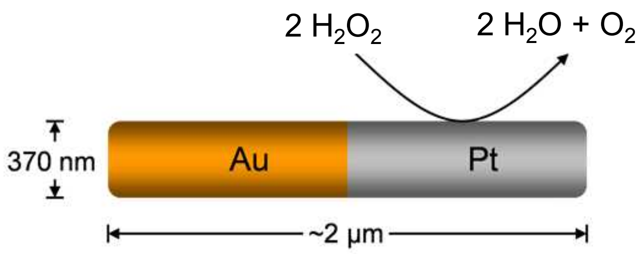


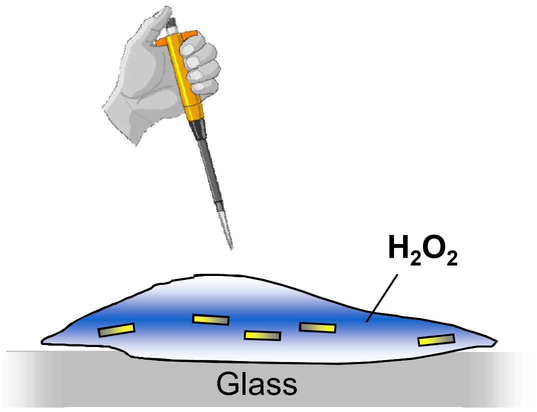




W. F. Paxton, et al. *J. Am. Chem. Soc.* **2004,** *126,* 13424–13431.

Diffusion vs. Catalytic Motors



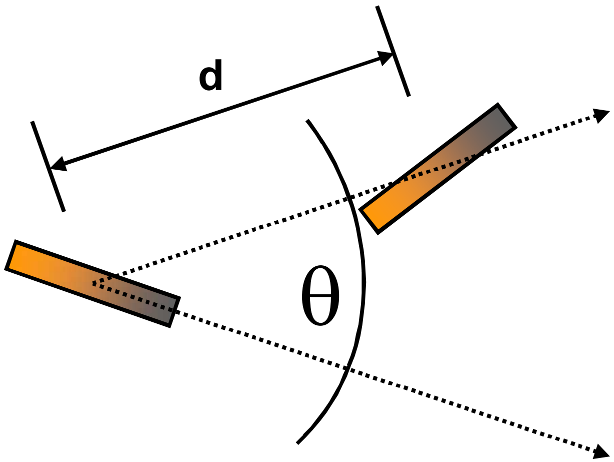


Pt/Au rods in *H_2O (DI)*

Pt/Au rods in *3% H_2O_2*

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

H_2O_2 Concentration Effect

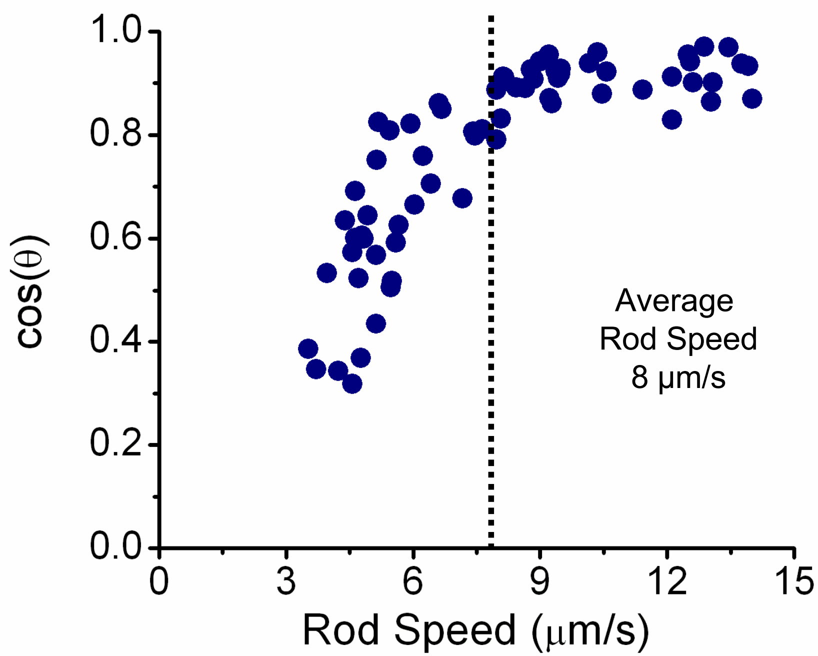


Displacement = d

Directionality = cos(θ)

Axial velocity = cos(θ) × d / t

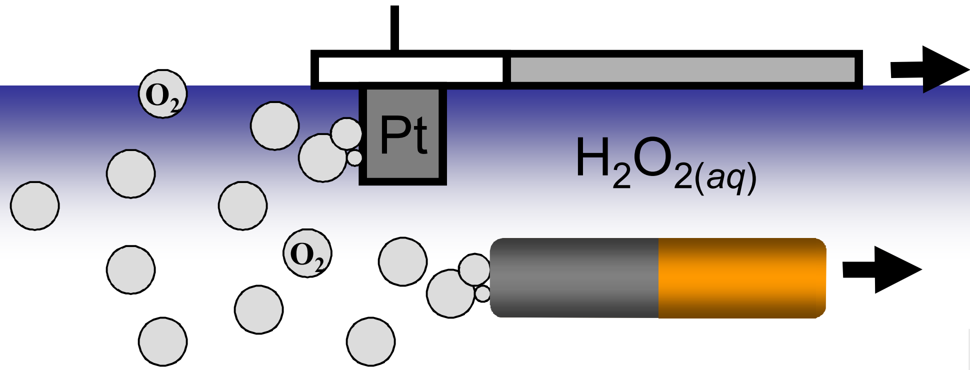
H_2O_2 (%)	Average Speed (μm/s)	cos(θ)	Axial Velocity (μm/s)
5	8	0.8	6.6
3	8	0.8	6.6
1.5	6	0.7	3.8
0.3	5	0.6	3.4
0.03	4	0.2	0.9
0	3	0.01	0.0

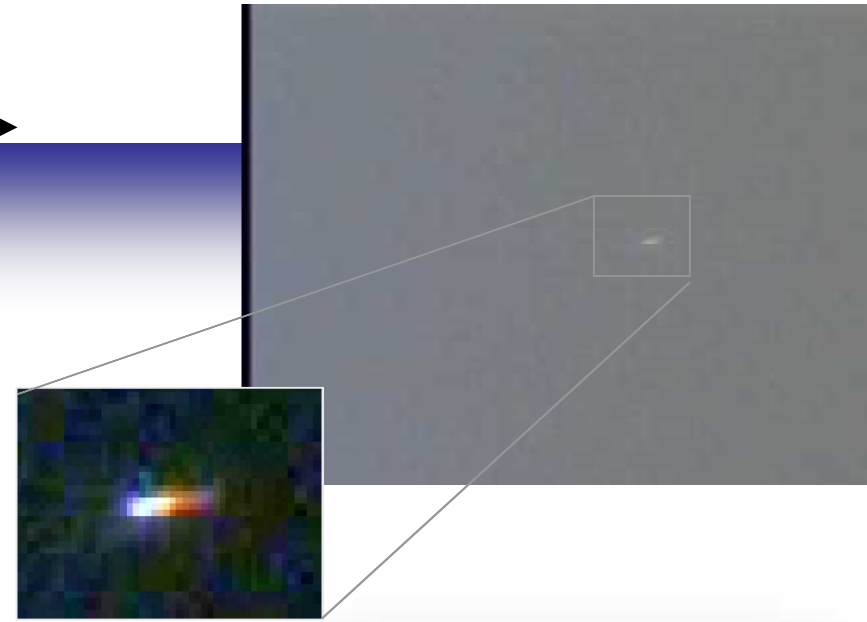


W. F. Paxton, et al. *J. Am. Chem. Soc.* **2004,** *126,* 13424–13431.

Why Do They Swim?

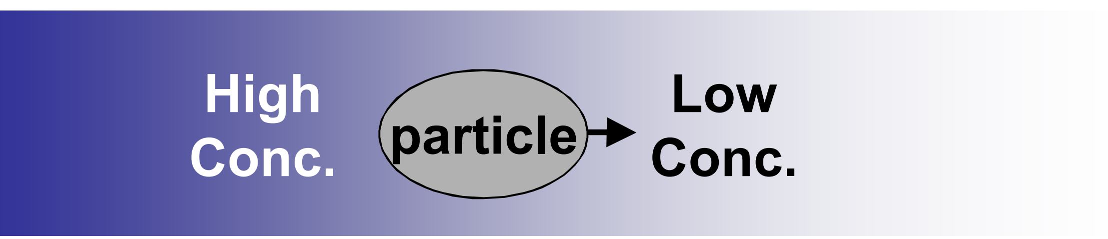
Bubble Propulsion?



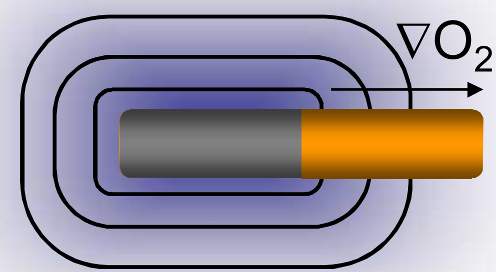


No bubbles near motors
Predicts motion in wrong direction

Diffusiophoresis?[a,b]



Pushes particle to
lower concentration region



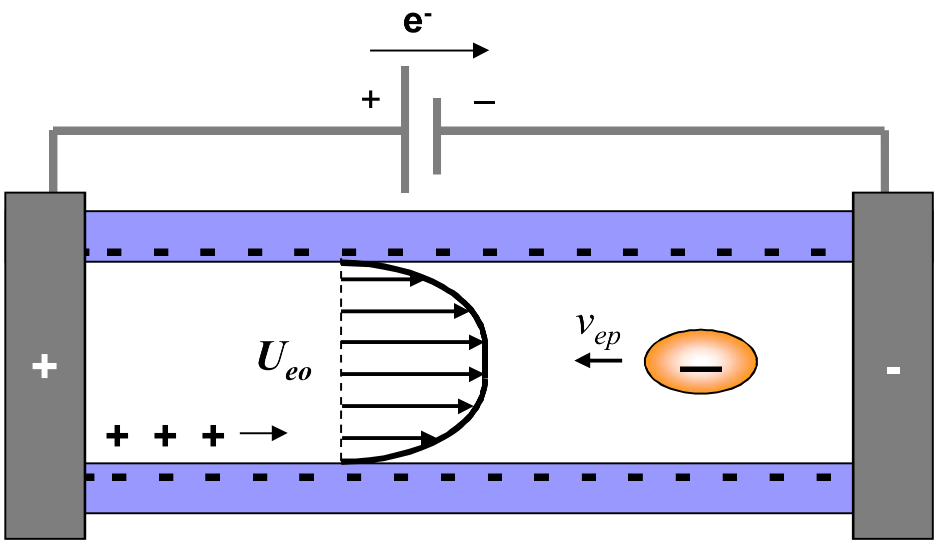
O_2 gradient acts on *gold* end

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

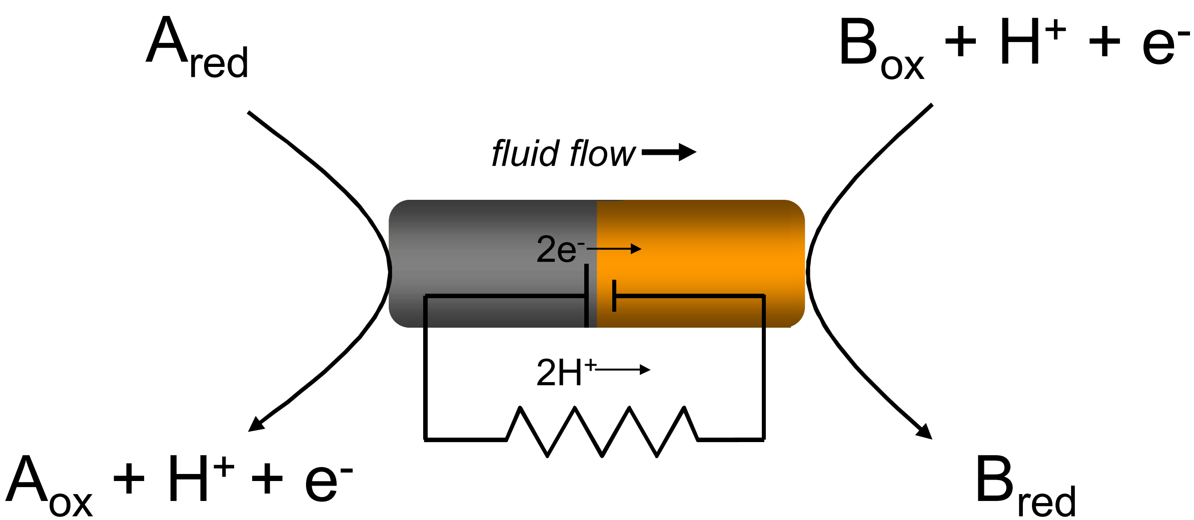
$$U_{eo} = \frac{\zeta_w \varepsilon E_x}{\mu}$$

Electrophoresis

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

Observed velocity

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



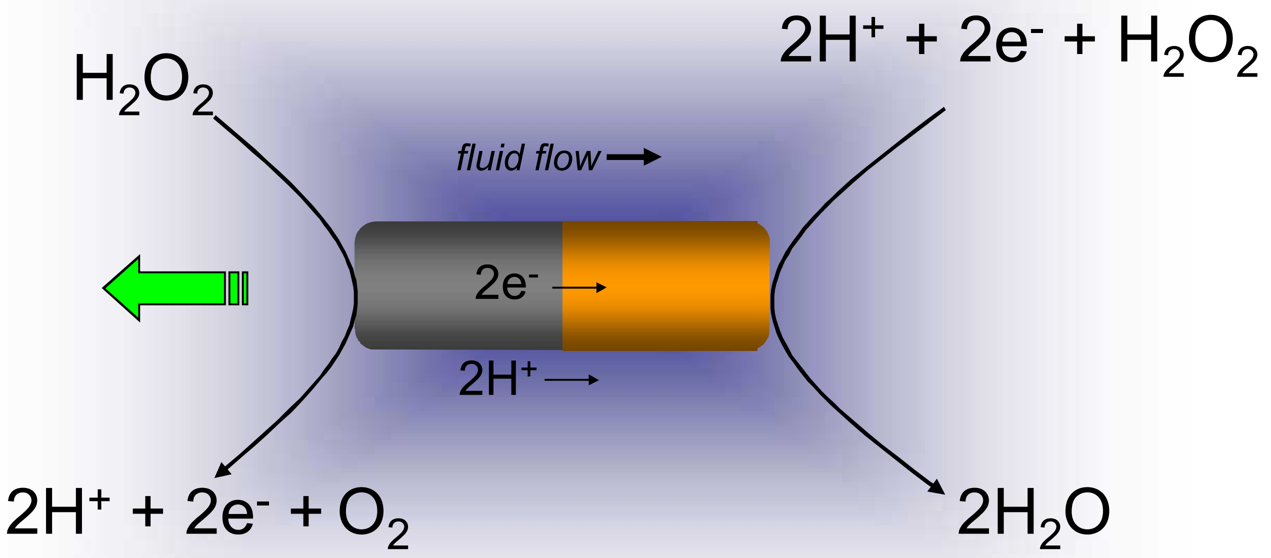
Electrochemical Reaction

↓

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.

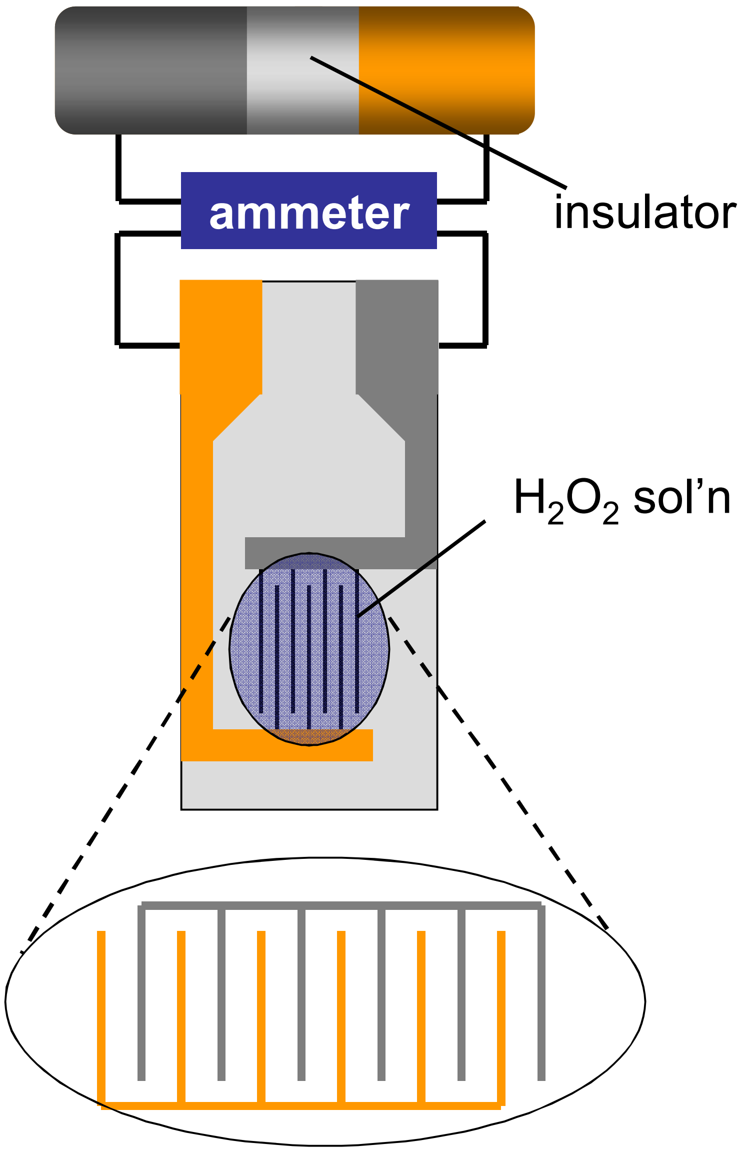
[b] **W. F. Paxton**, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

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
  - $\sigma = 4.1$ μS/cm
  - **E = 13.1 V/cm**



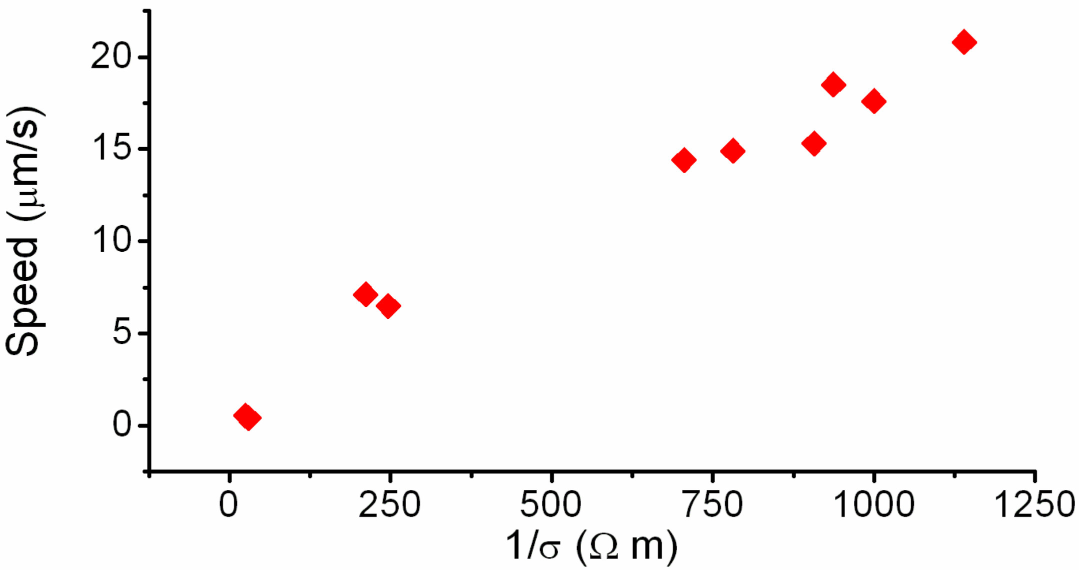
W. F. Paxton, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

Rod Speed vs. Conductivity

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

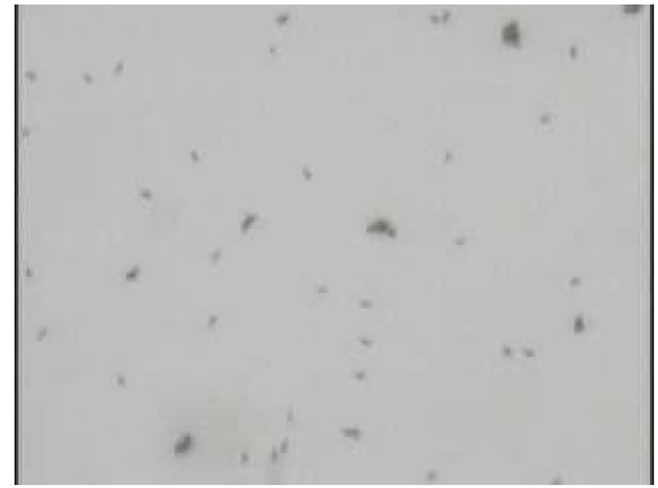
$$v = \frac{\zeta \varepsilon}{\mu} \frac{J}{\sigma} f$$

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

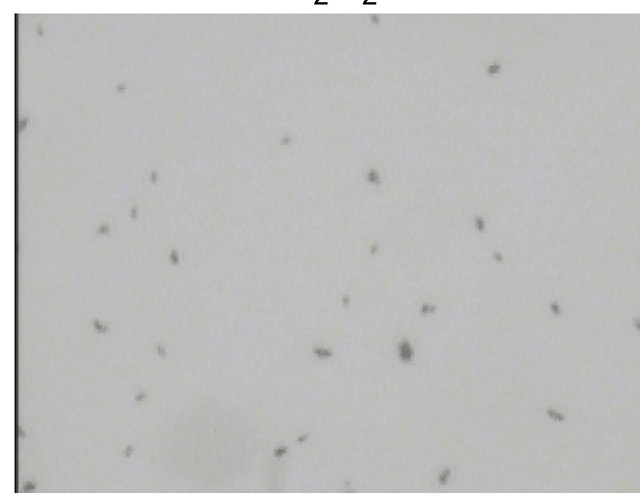


slowing due to increased conductivity

PtAu rods / 3% H_2O_2



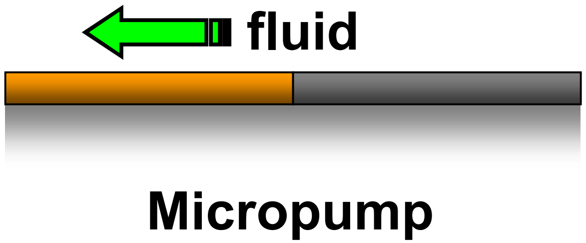
PtAu rods / 3% H_2O_2 / 3 mM $NaNO_3$



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

From Motors to Micropumps

- Suspended motor moves itself.

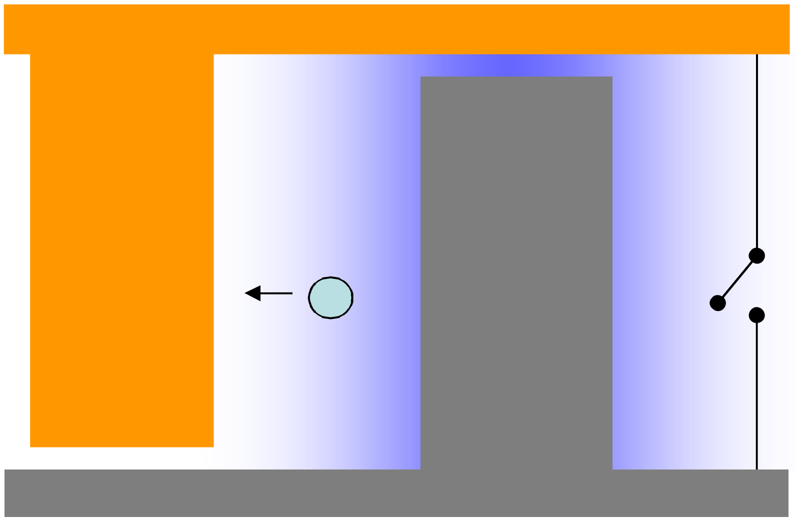


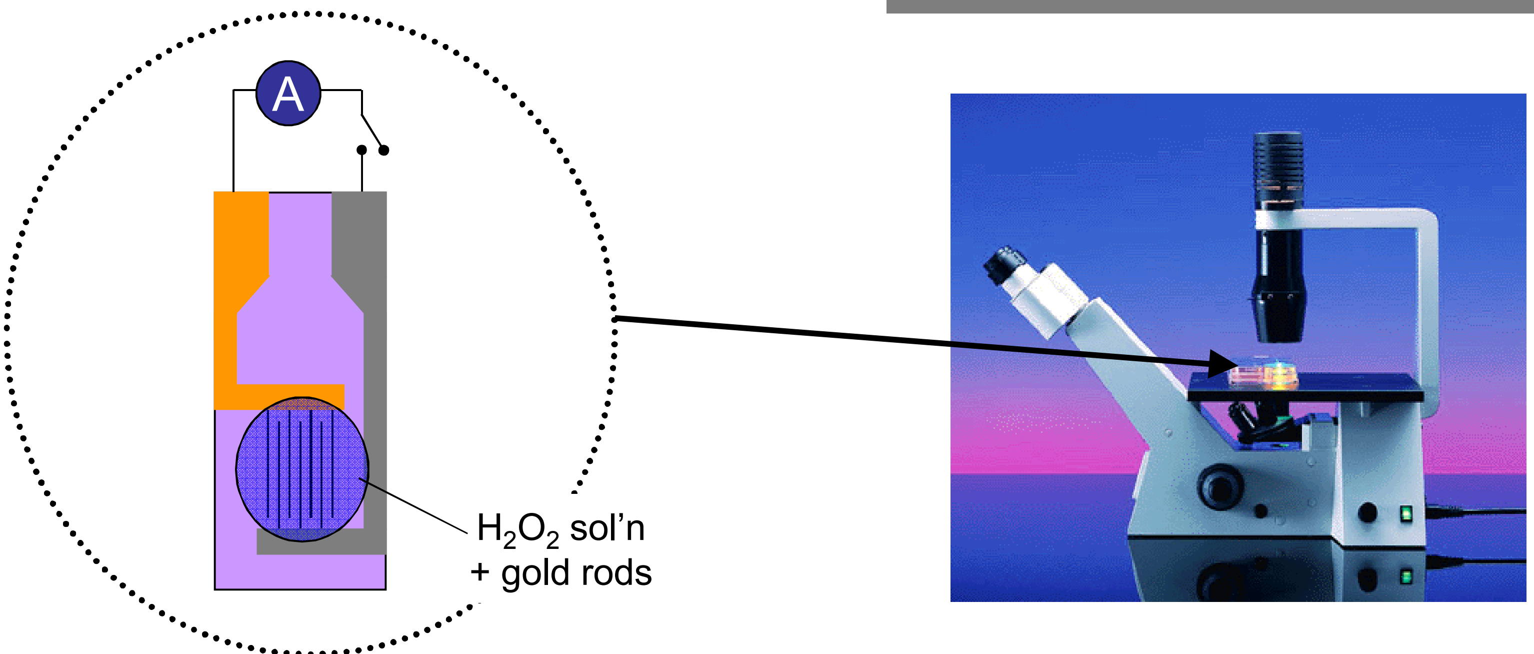
- Immobilized motor moves surrounding fluid.

Microelectrode Experiments

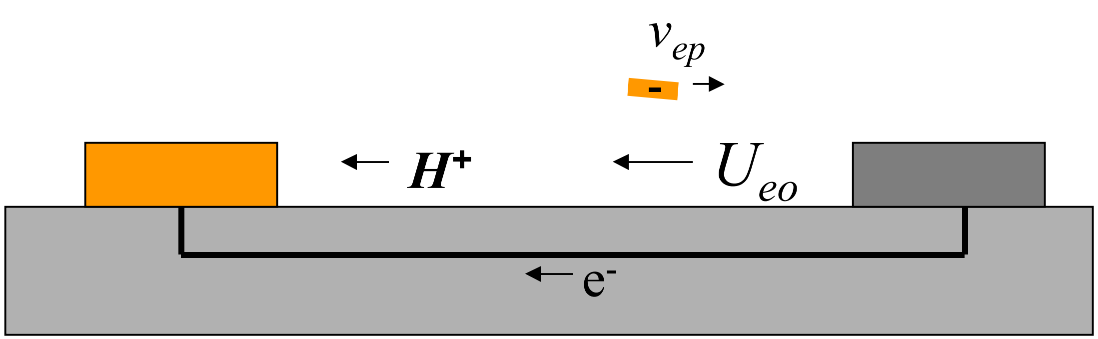
- O_2 gradient:
  motion independent of switch.

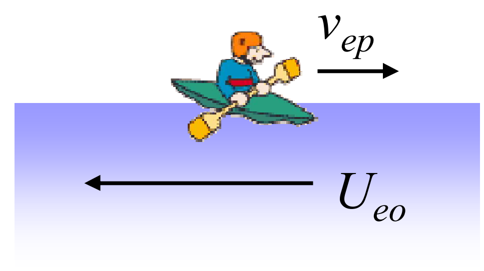
- Electrokinetics:
  "off" = diffusion only
  "on" = linear motion





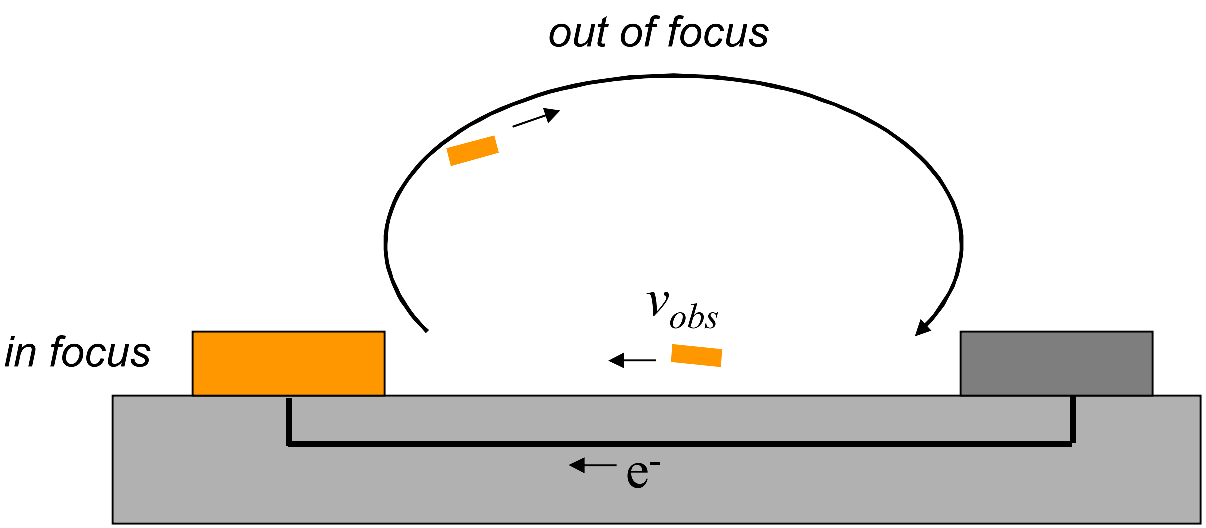
Catalytically Induced Electrokinetics





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

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



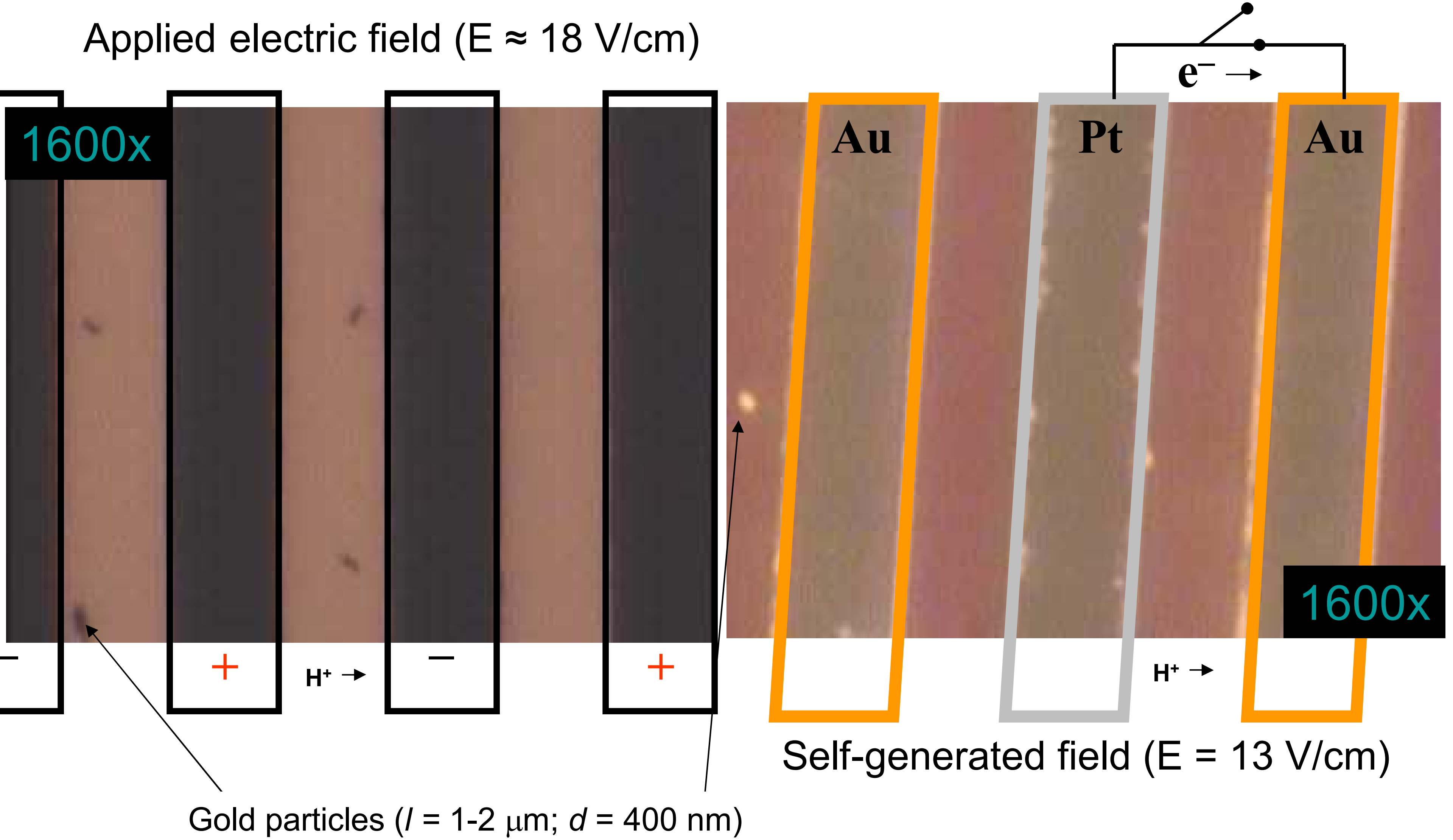
Electroosmosis dominates when

$$|\zeta_w| > |\zeta_p|$$

borosilicate glass		Au tracers
| –60 mV |	>	| –40 mV |

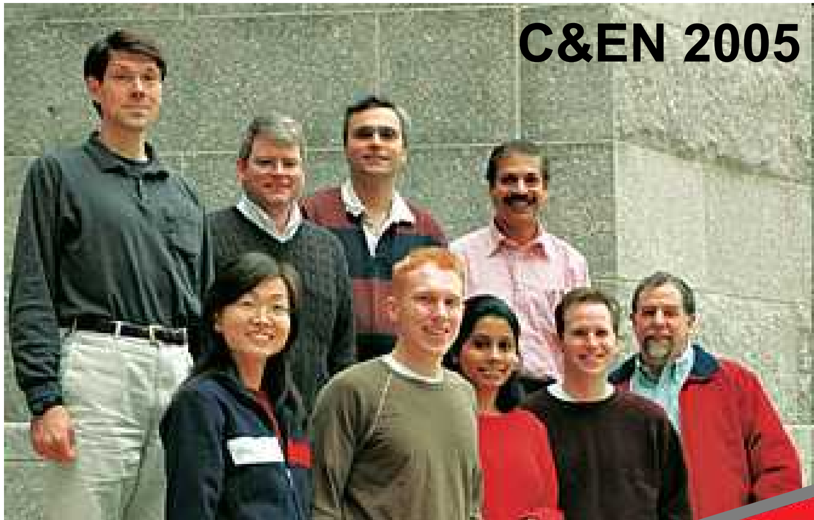
W. F. Paxton, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

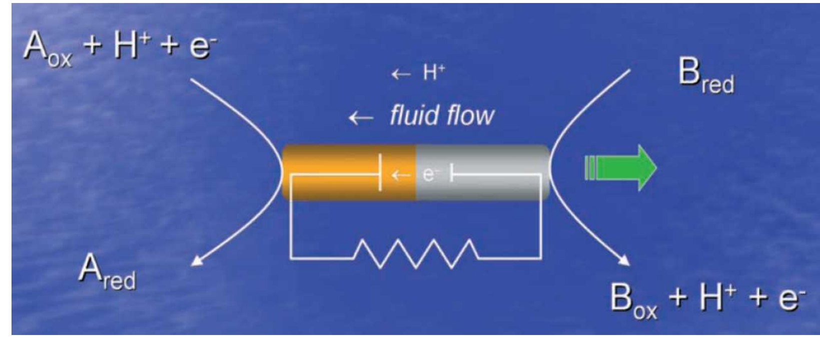
Electric Field and Motility Comparison



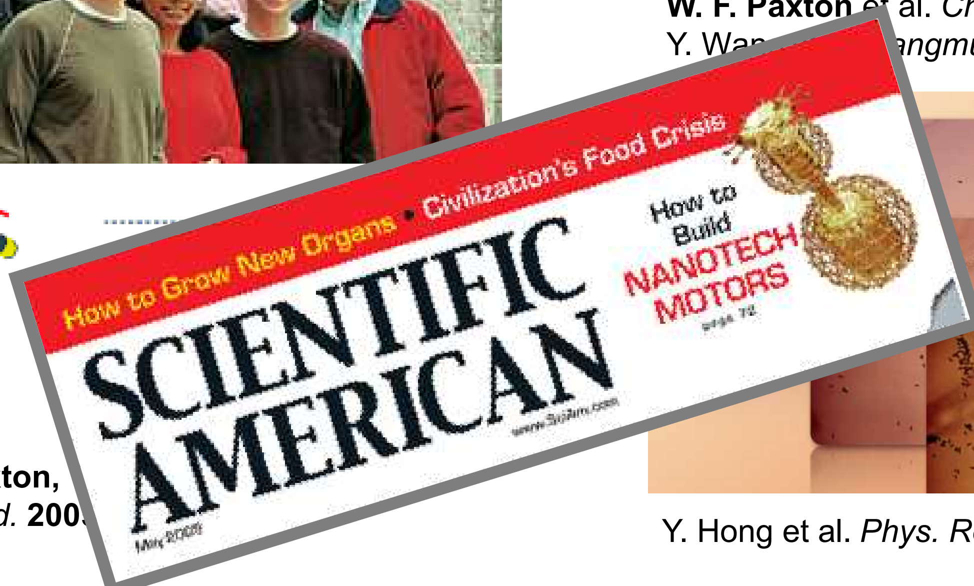
W. F. Paxton, et al. *J. Am. Chem. Soc.* **2006,** *128,* 14881-14888.

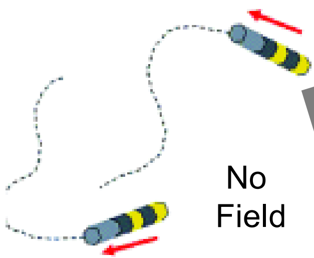
And Then What Happened?





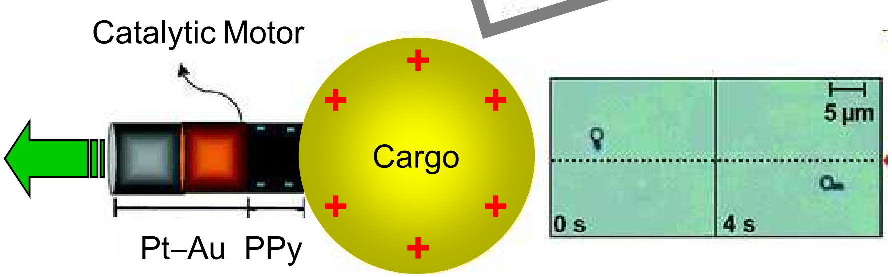
W. F. Paxton et al. *Chem. Eur. J.* **2005,** *11,* 6462–6470.
Y. Wa... *angmuir* **2006,** *22,* 10451–10456.



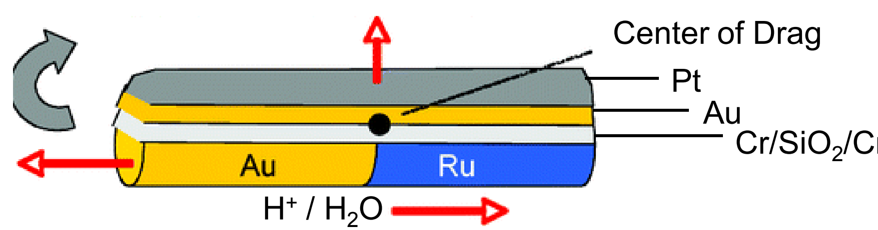


T. R. Kline, **W. F. Paxton,**
Angew. Chem. Int. Ed. **200**

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



S. Sundararajan et al. *Nano Lett.* **2008**, *8*, 1271–1276.

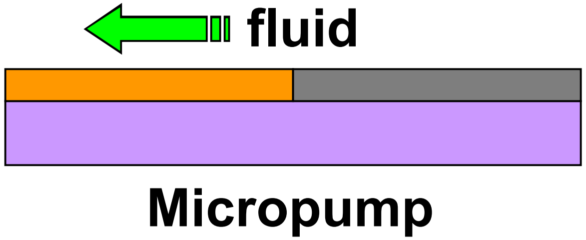


Y. Wang et al. *J. Am. Chem. Soc.* **2009,** *131,* 9926–9927.

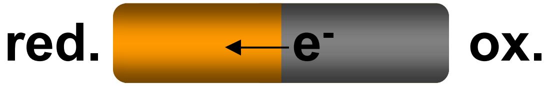
Catalytically Induced Electrokinetics

- **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

PENN STATE

- Professor Ayusman Sen
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- Dr Tim Kline – U Chicago / Arryx Inc
- Dr Shakuntala Sundararajan – Intel
- Dr Yang Wang
- Penn State MRSEC – NSF
- Penn State Center for Nanoscale Science

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Sandia National Laboratories