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Massachusetts Institute of Technology

Materials Design 2022 UGM Webinar Series

Materials Innovations for Separations

Jeffrey C. Grossman

Massachusetts Institute of Technology

October 04, 2022

Materials Design UGM

UGM 2022

The Materials Design annual user event will be online for 2022.

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Prof. Georg Kresse
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Prof. Jörg Behler
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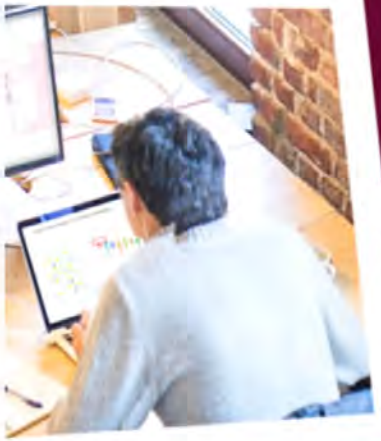

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Materials Innovations for Separations

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October 04, 2022

Materials Design UGM Presenter

Professor Jeffrey C. Grossman

Head of Department of Materials Science and Engineering

Massachusetts Institute of Technology, USA

Webinar Speakers

Katherine Hollingsworth

khollingsworth@materialsdesign.com

Dr. Clive Freeman

cfreeman@materialsdesign.com

Materials Design UGM Webinar Series

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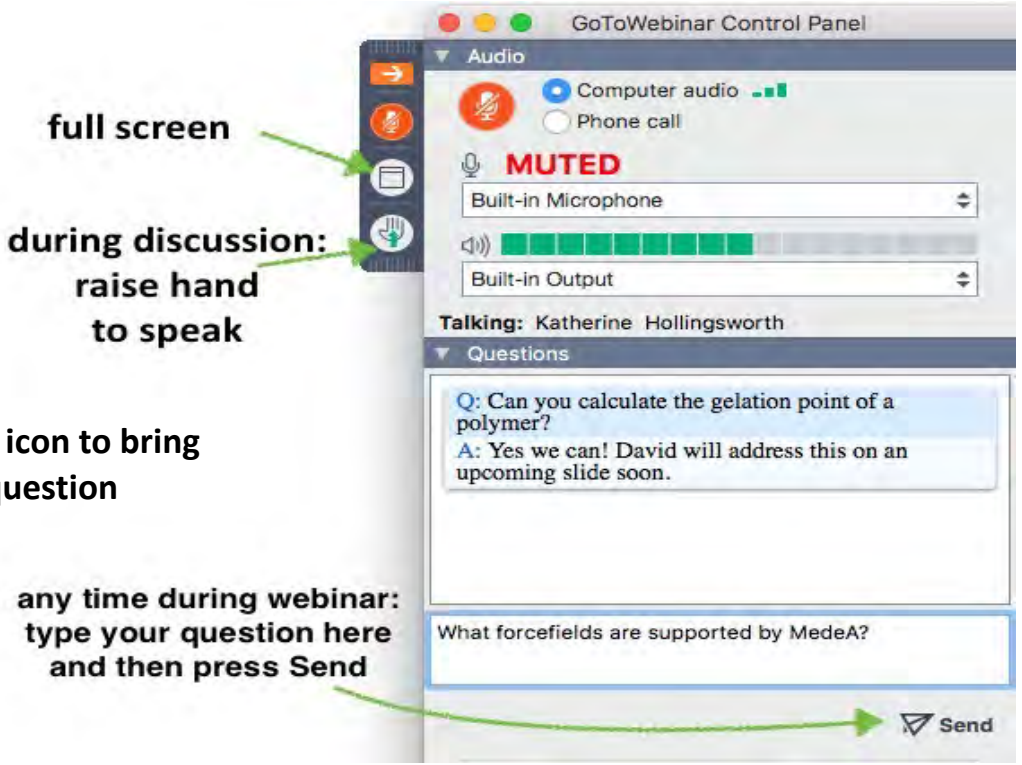
Please Ask Questions!



Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

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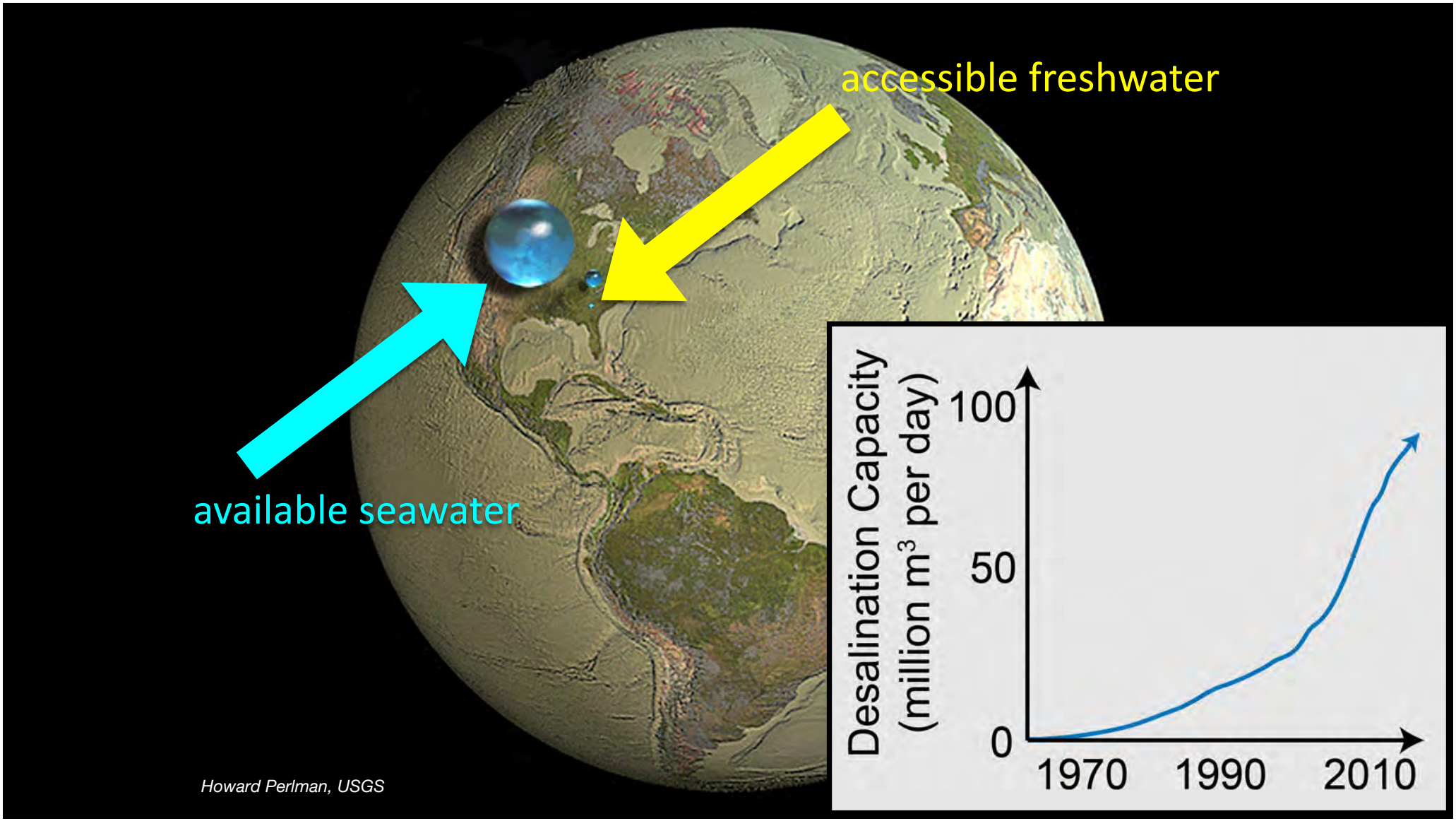
Materials Innovations for Chemical Separations

Jeffrey C. Grossman

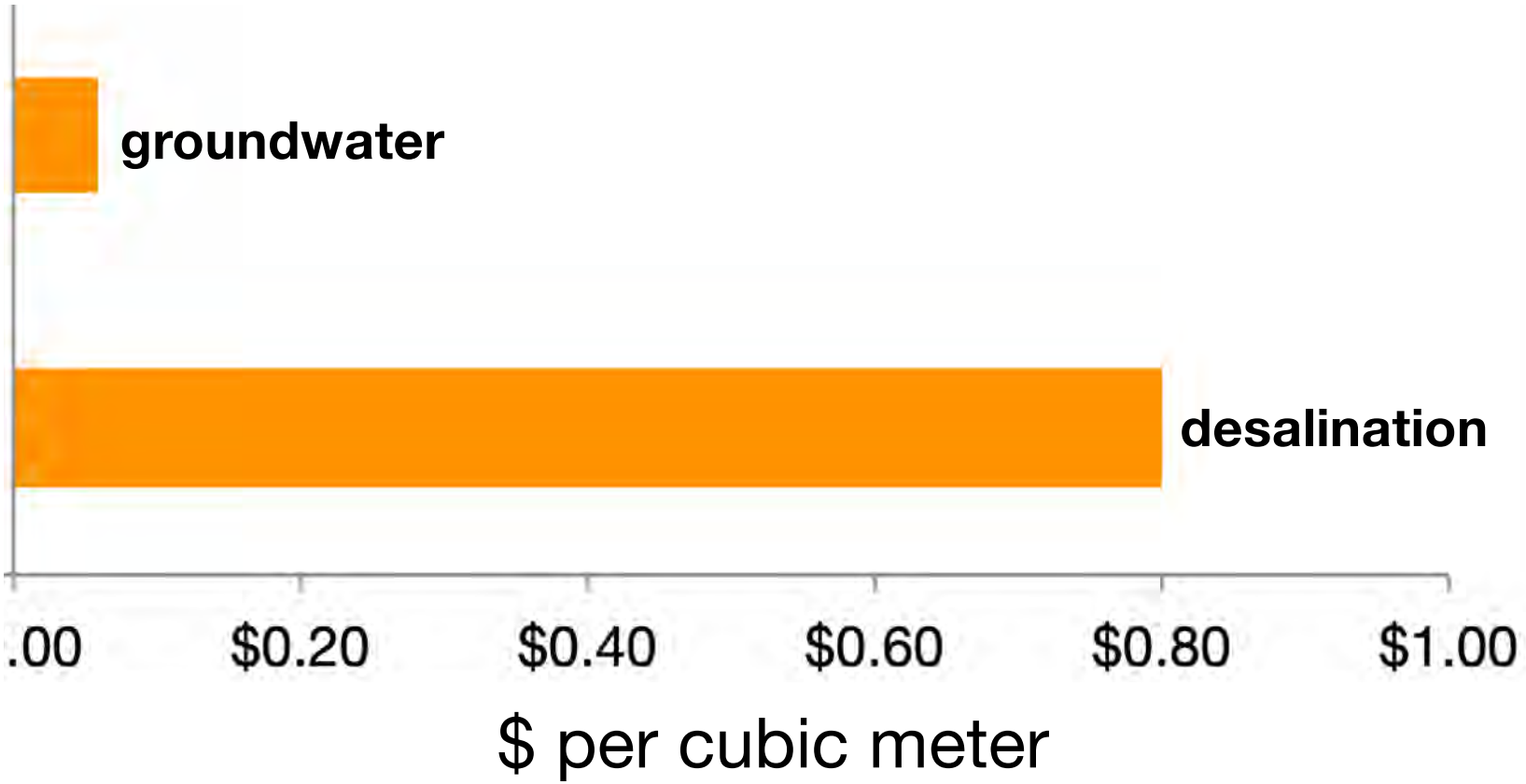
Department of Materials Science and Engineering
Massachusetts Institute of Technology

jcg@mit.edu

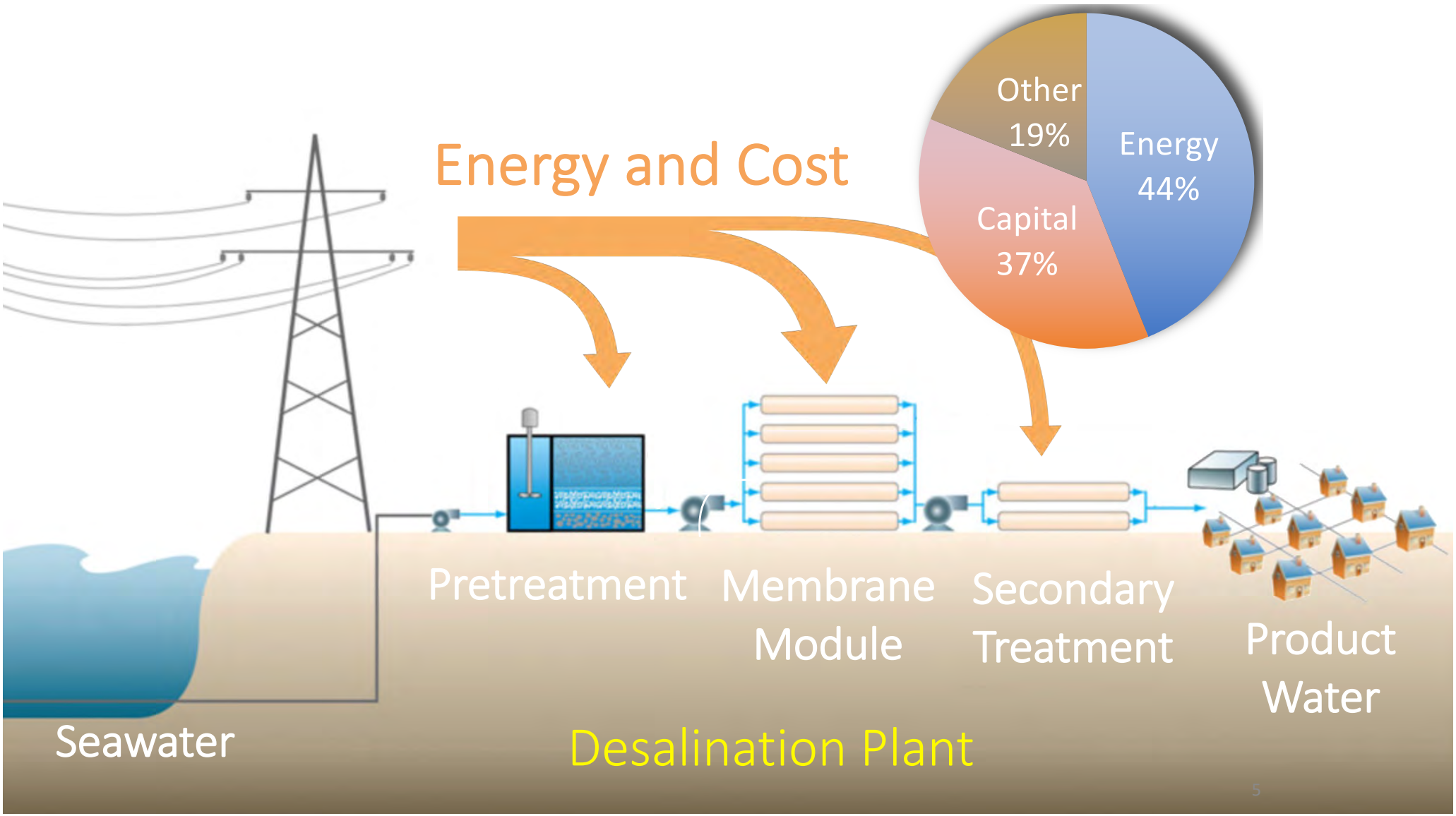
Materials Design User Group Meeting | 10.04.2022

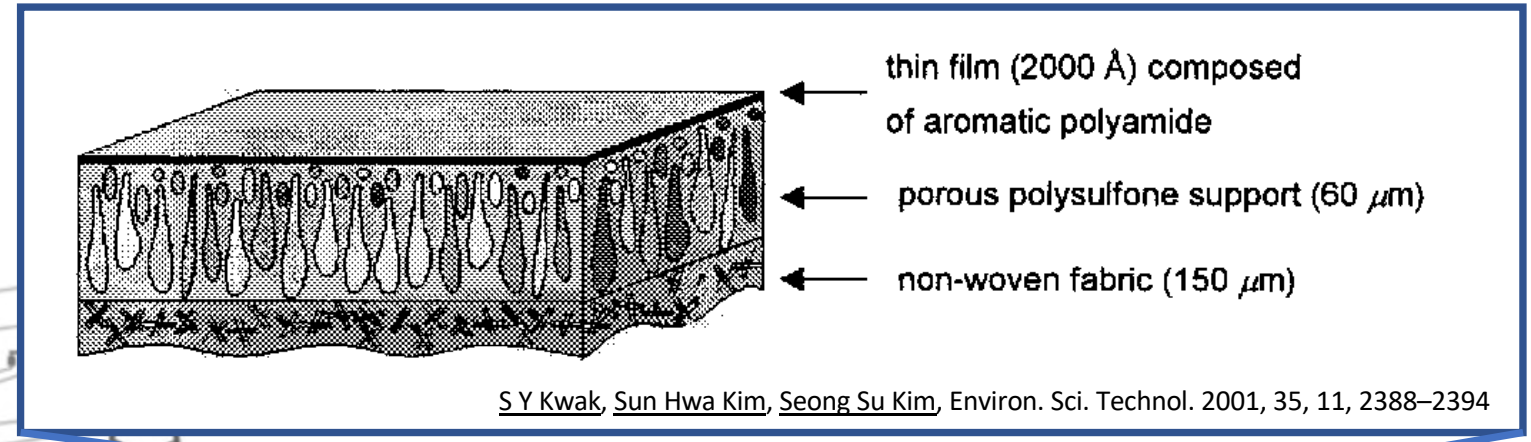

accessible freshwater
available seawater
Howard Perlman, USGS
Desalination Capacity
(million m3 per day)
100
50
0
1970
1990
2010

Desalination remains expensive



2030 Water Resources Group


Energy and Cost
Other
19%
Energy
44%
Capital
37%
Pretreatment
Membrane
Module
Secondary
Treatment
Product
Water
Seawater
Desalination Plant



S Y Kwak, Sun Hwa Kim, Seong Su Kim, Environ. Sci. Technol. 2001, 35, 11, 2388–2394

Pretreatment

Membrane Module

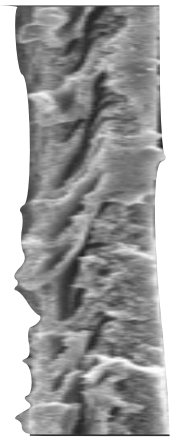
Secondary Treatment

Product Water

Seawater

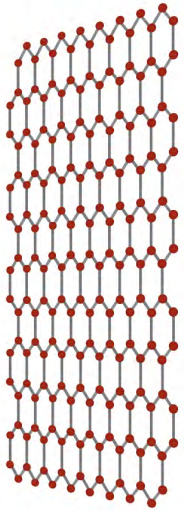
Desalination Plant

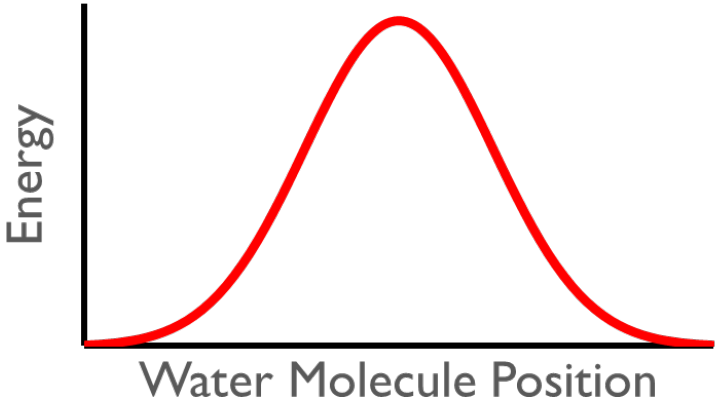
A smaller energy hill for water

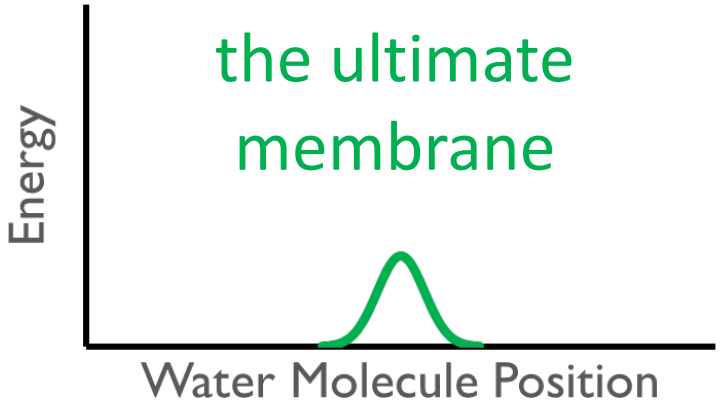


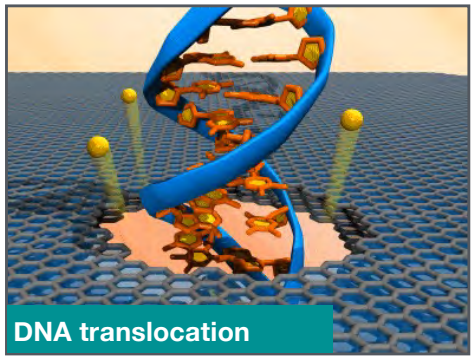
Polyamide

Graphene

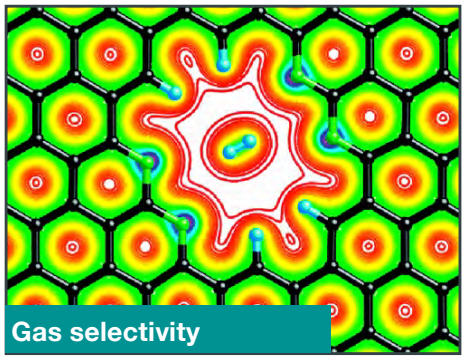




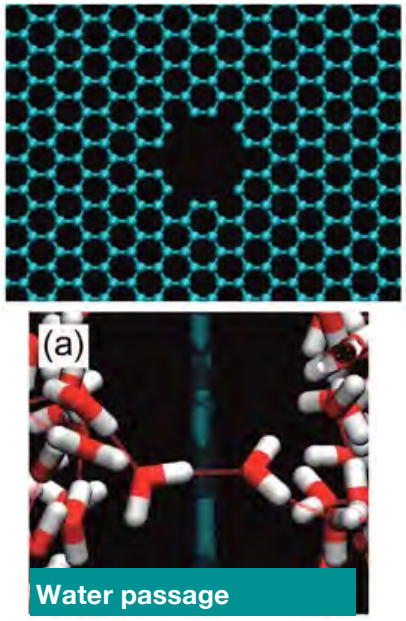




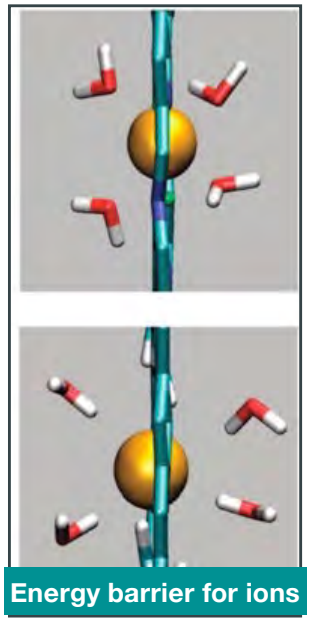
Merchant et al., Nano Letters, 2010



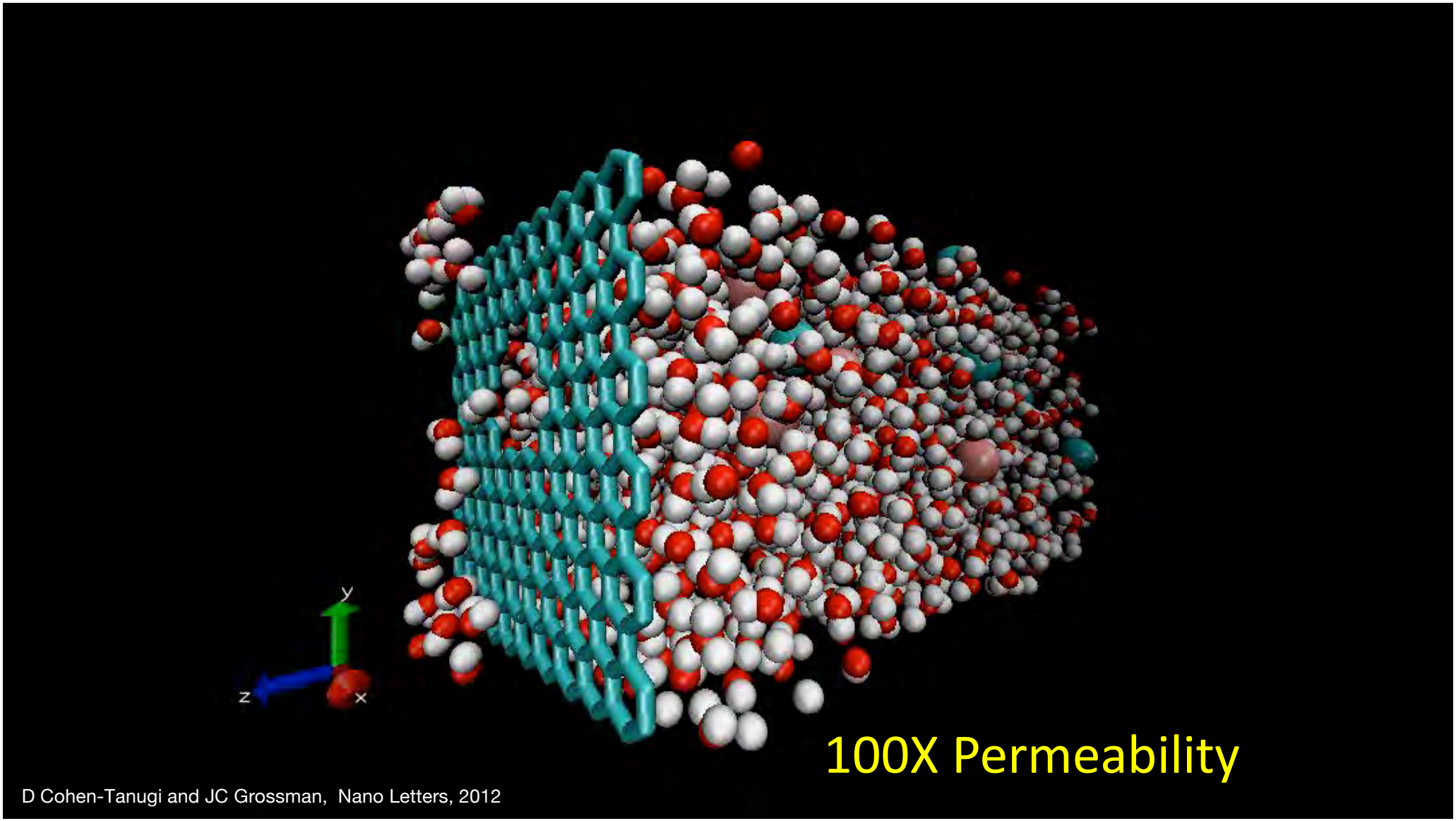
Jiang et al., Nano Letters, 2009



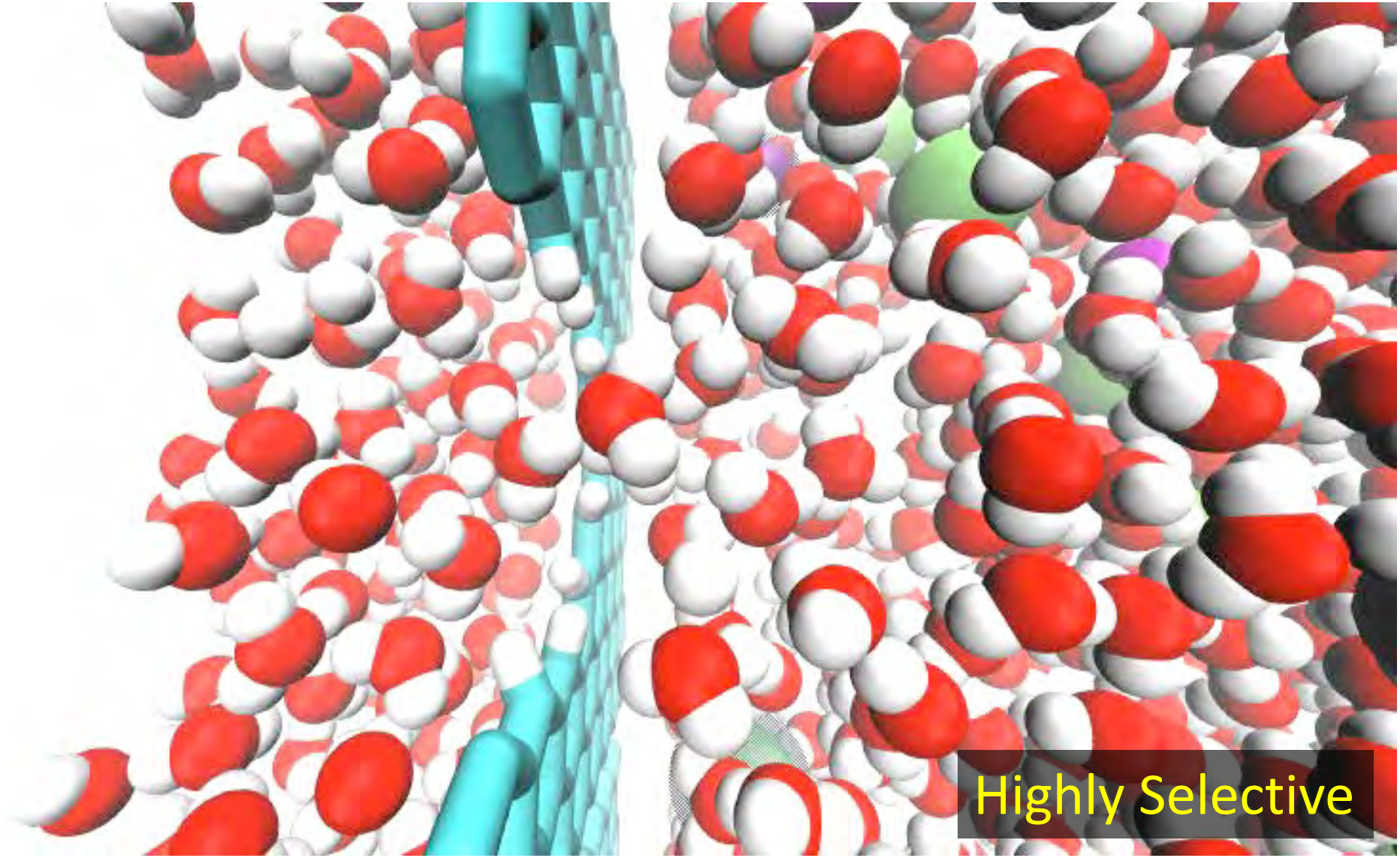
Suk et al., J. Phys. Chem. Lett., 2010

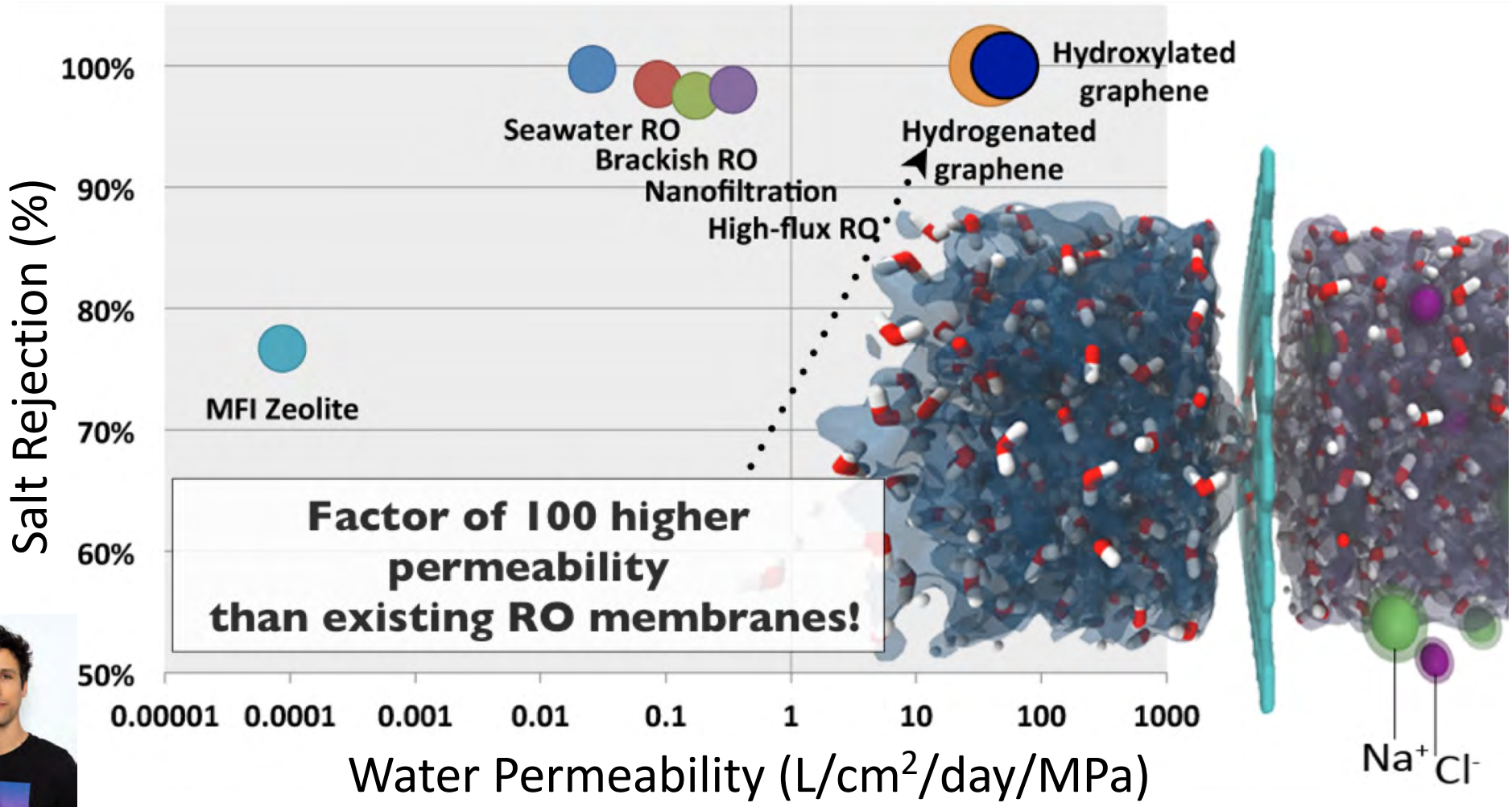


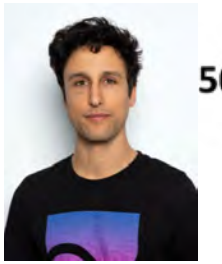
Sint et al., JACS, 2008



D Cohen-Tanugi and JC Grossman, Nano Letters, 2012

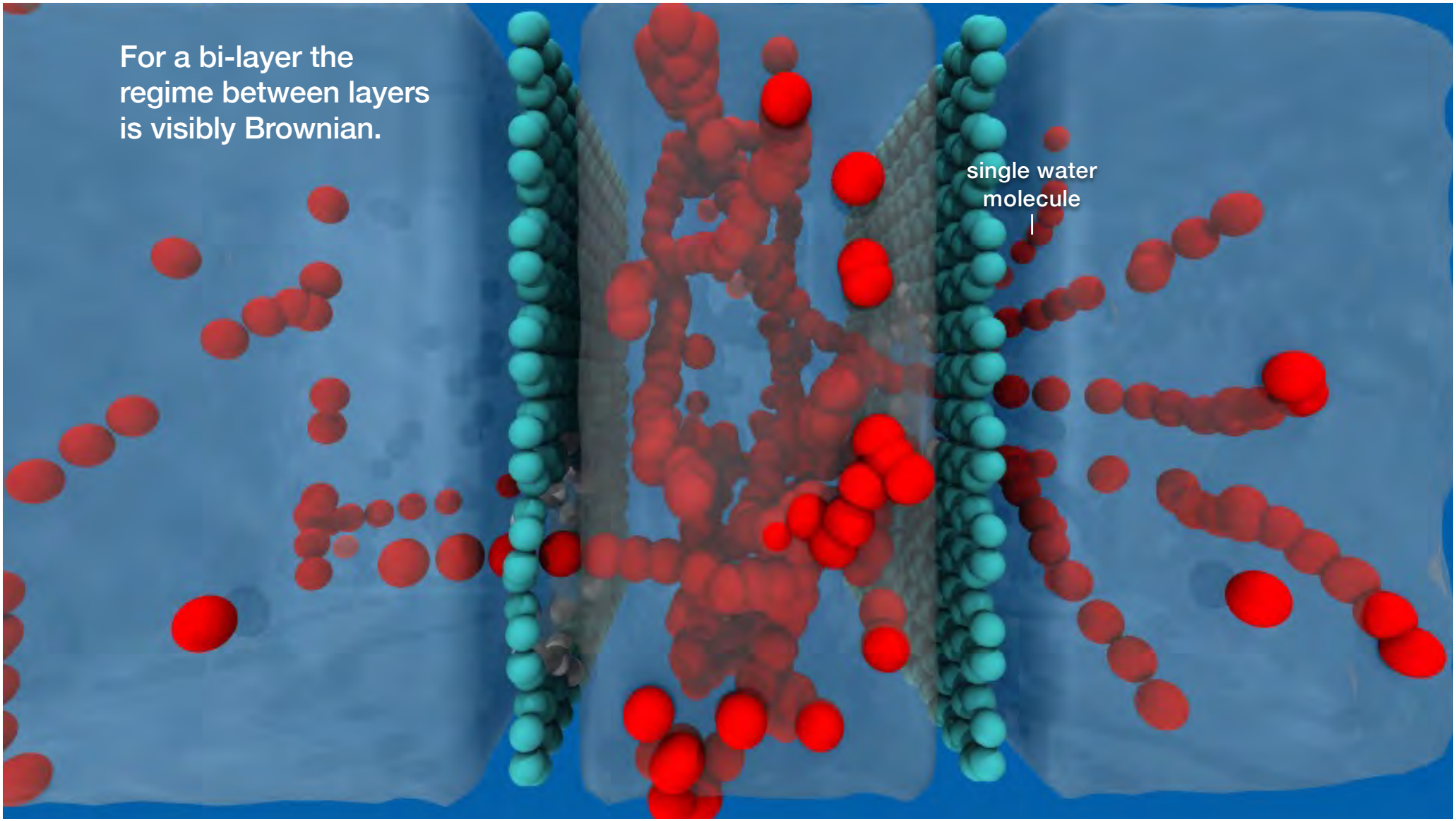

Highly Selective

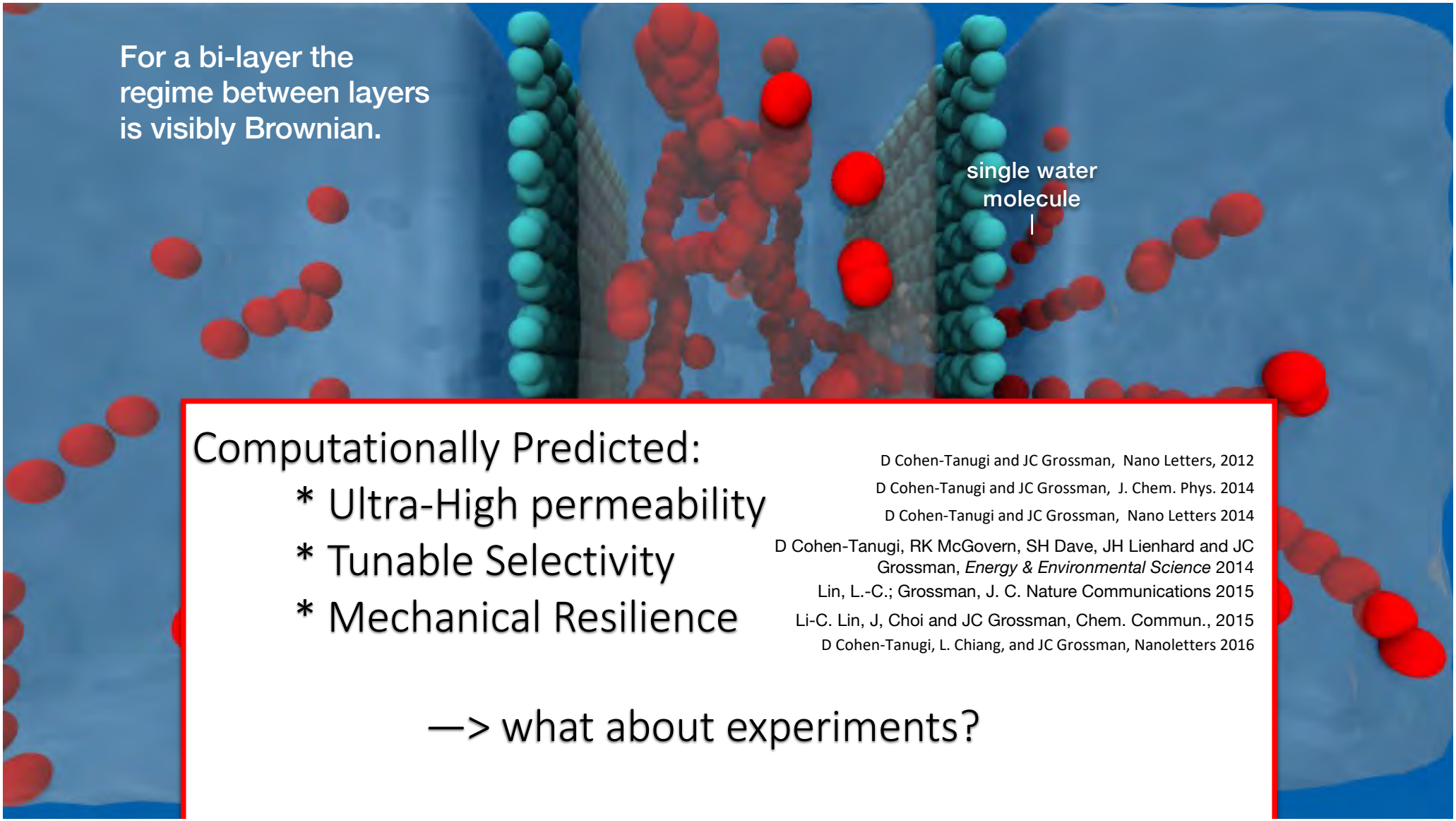




David Cohen-Tanugi

D. Cohen-Tanugi, J.C. Grossman, *Nano Lett.* 2012, **12**, 7, 3602–3608


For a bi-layer the
regime between layers
is visibly Brownian.
single water
molecule



Computationally Predicted:

* Ultra-High permeability
* Tunable Selectivity
* Mechanical Resilience

D Cohen-Tanugi and JC Grossman, Nano Letters, 2012

D Cohen-Tanugi and JC Grossman, J. Chem. Phys. 2014

D Cohen-Tanugi and JC Grossman, Nano Letters 2014

D Cohen-Tanugi, RK McGovern, SH Dave, JH Lienhard and JC Grossman, *Energy & Environmental Science* 2014

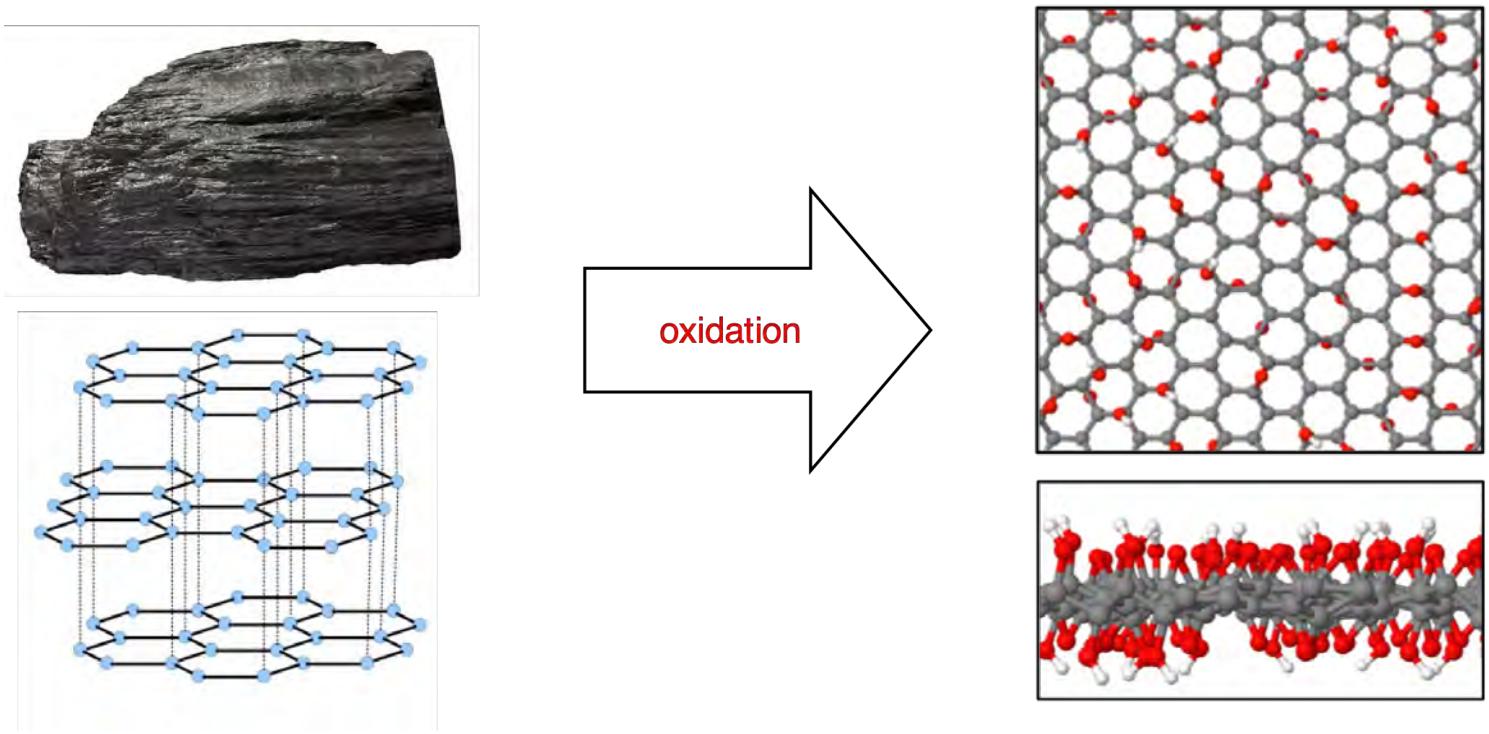
Lin, L.-C.; Grossman, J. C. Nature Communications 2015

Li-C. Lin, J, Choi and JC Grossman, Chem. Commun., 2015

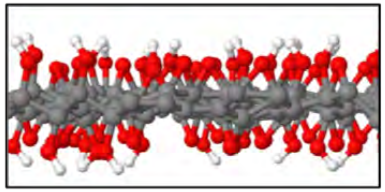
D Cohen-Tanugi, L. Chiang, and JC Grossman, Nanoletters 2016

—> what about experiments?

Experiments motivated by simulations:
Graphene oxide (GO) is a scalable feedstock.



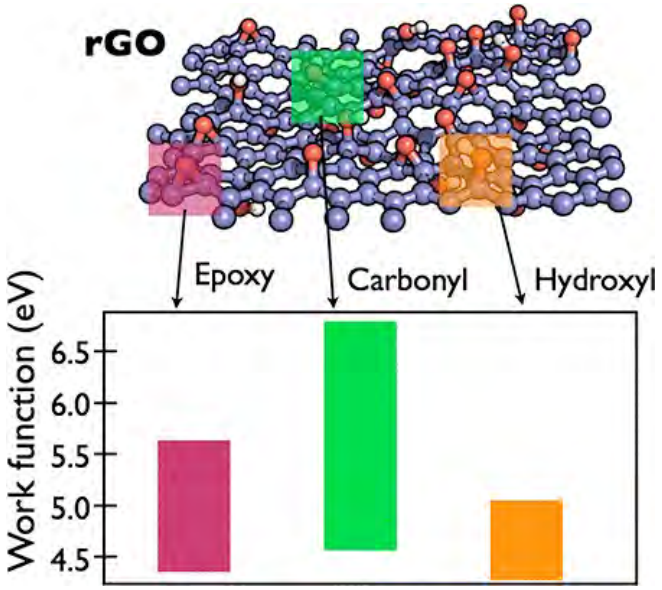
Material choice for experiments: graphene-oxide (from oxidation of graphite)



	CVD Graphene	Graphene Oxide
Solution processable	✗	✓
Energy inputs	✗ 1000 C Vacuum	✓ 150 C ✓ atmosphere
Consumables	✗ Copper substrate	✗ Strong oxidizers ("greener chemicals") ✓
Sheet size	✓ inches	✗ 0.5-50 microns
Yield (laboratory)	✗ 10^{-6} grams/hour	✓ 200 grams/hour
Cost (current retial)	✗ \$80 x 10^5 / gram	✓ \$100/gram

Controlling O in GO & rGO

Reduced Graphene Oxide

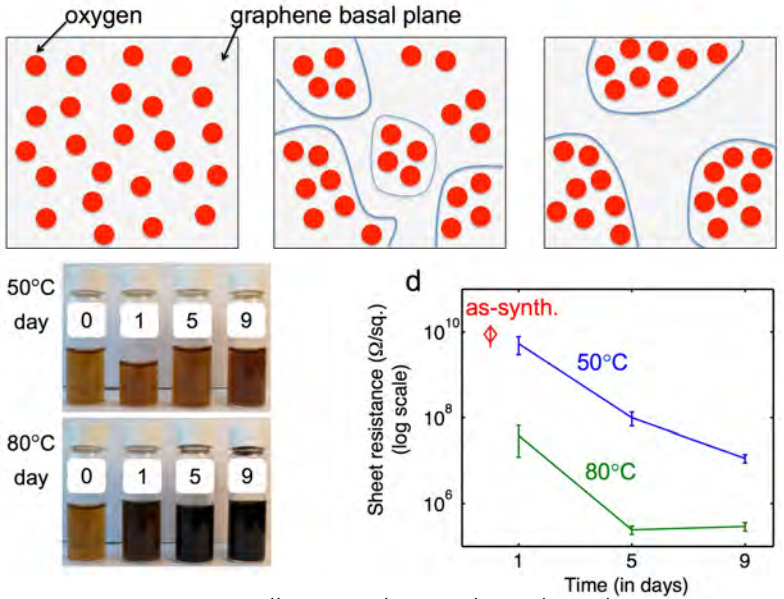


P. Kumar, M. Bernardi & J.C. Grossman, ACS Nano **2013**, 7, 1638.

Control through epoxy:hydroxyl ratio in rGO

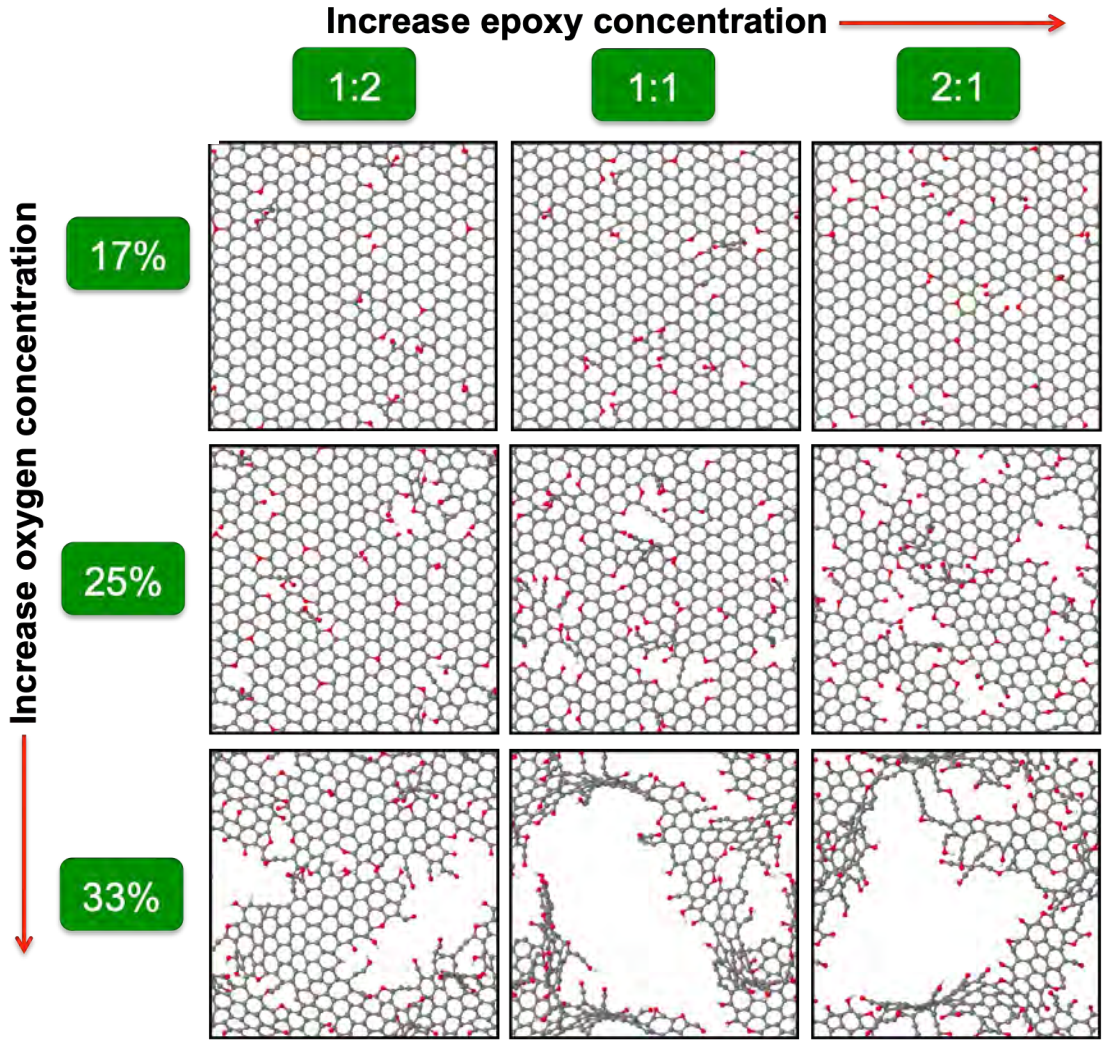
Control through oxygen clustering in GO

Graphene Oxide



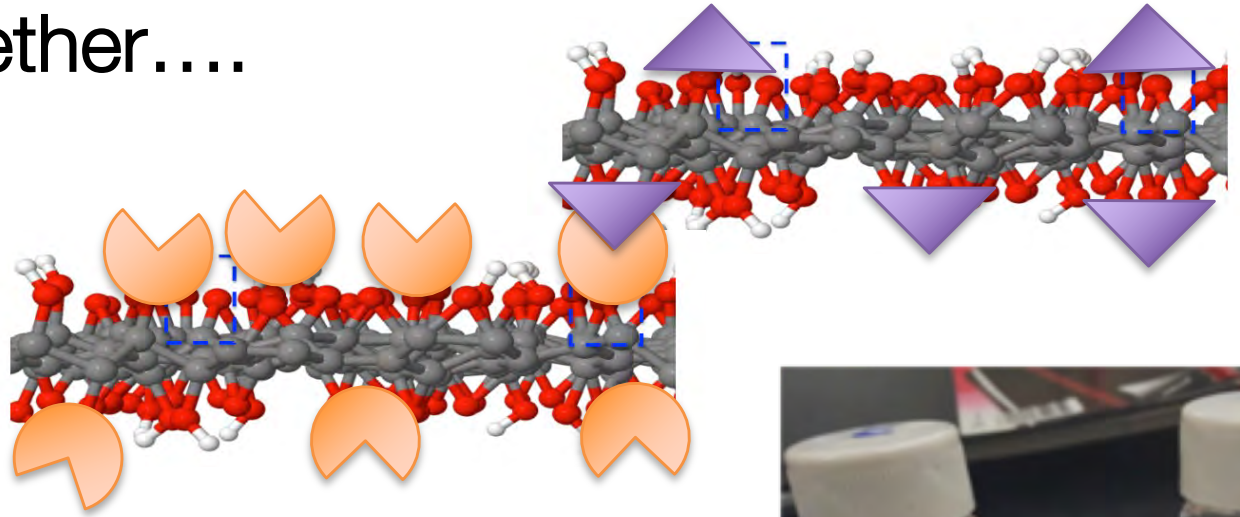
P. Kumar, N. Bardhan, et. al, Nat. Chem. (2014).
P. Kumar et al, Carbon 100 90-98 (2016)

Control carbon removal during reduction

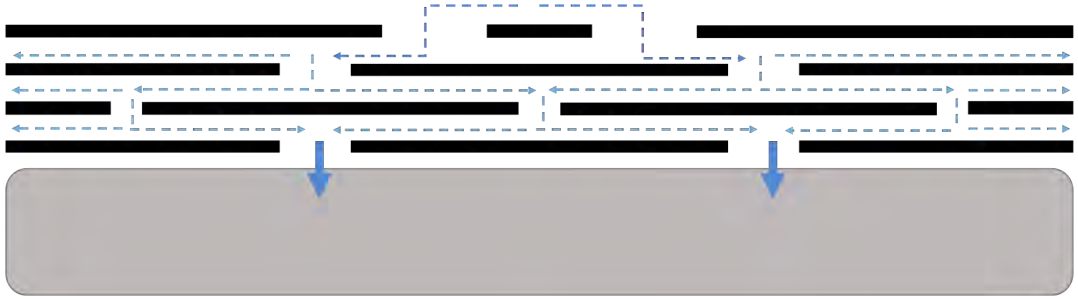


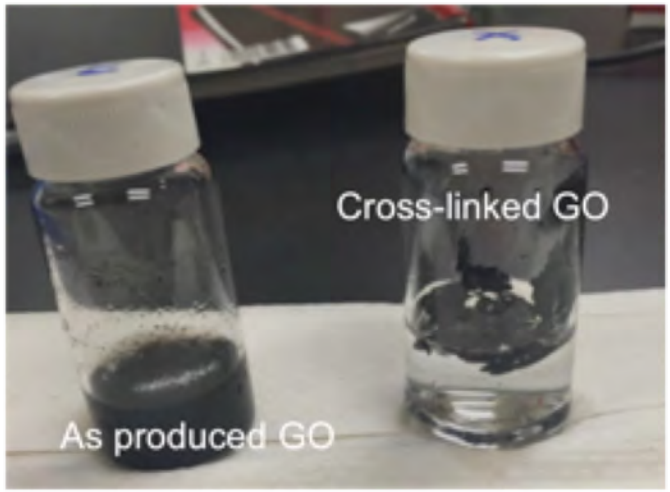
Lin, L.-C.; Grossman, J. C. Nature Communications 2015

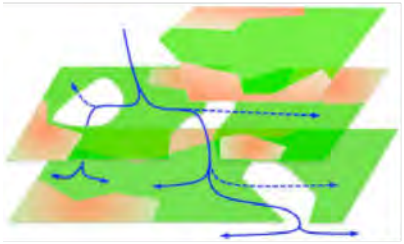
The key to unlocking Graphene-Oxide as a membrane is in locking it together….

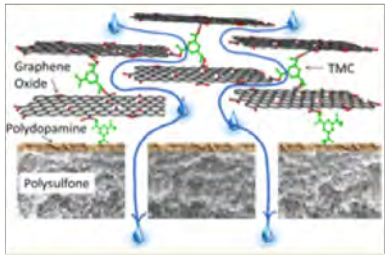


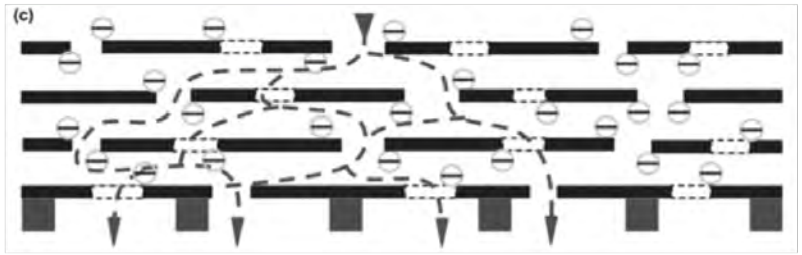
Robust membrane fabrication



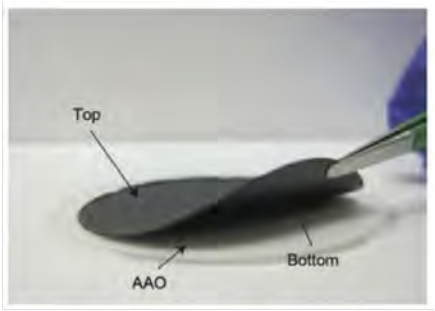


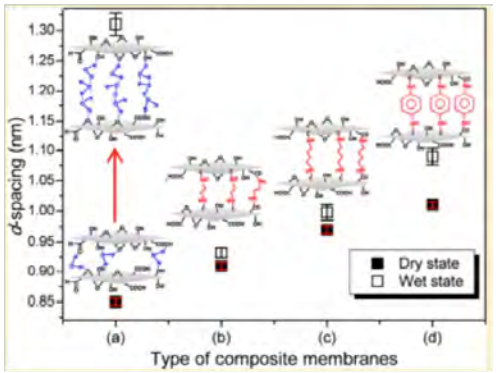




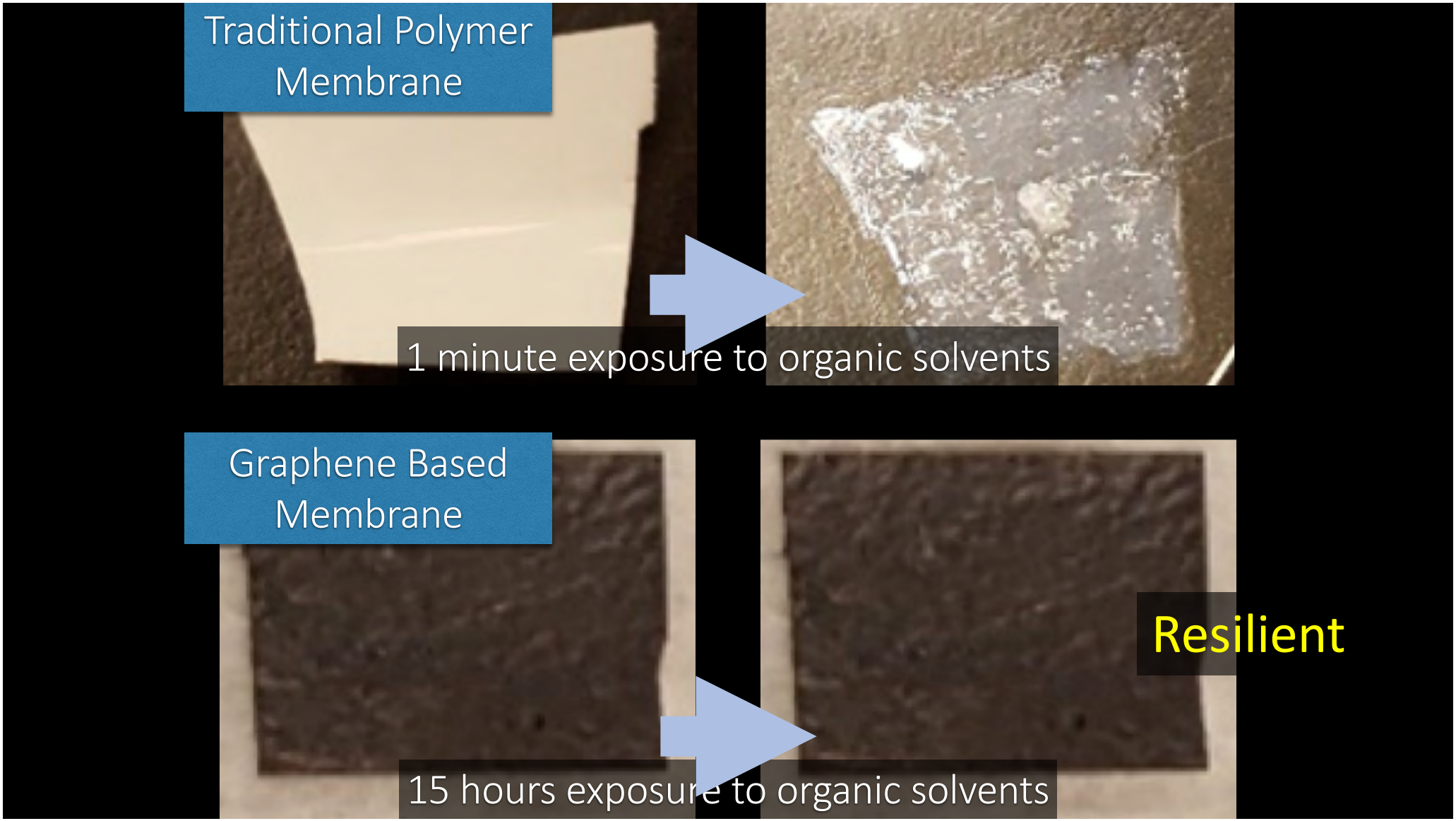


- Boukhvalov, D. W. et al. Origin of Anomalous Water Permeation Through Graphene Oxide Membrane. Nano Lett. 2013, 130719121245003.
- Hu, M.; Mi, B. Enabling Graphene Oxide Nanosheets as Water Separation Membranes. Environ. Sci. Technol. 2013, 47, 3715–3723.
- Han, Y. et al. Ultrathin Graphene Nanofiltration Membrane for Water Purification. Adv. Funct. Mater. 2013, 23, 3693–3700.

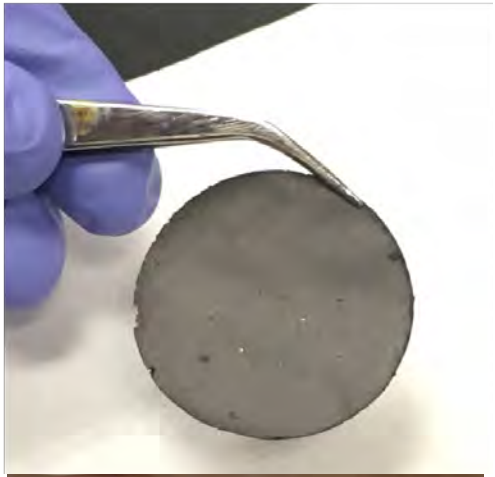


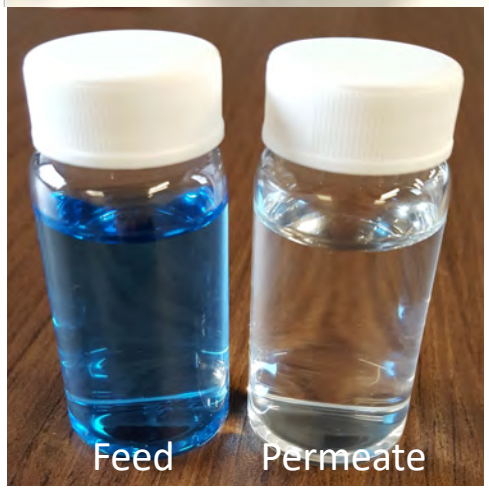


- Yeh, C.-N. et al. On the Origin of the Stability of Graphene Oxide Membranes in Water. Nature Publishing Group 2015, 1–5.
- Hung, W.-S. et al. Cross-Linking with Diamine Monomers to Prepare Composite Graphene Oxide-Framework Membranes with Varying D-Spacing. Chemistry of Materials 2014, 26, 2983–2990.


Traditional Polymer Membrane
1 minute exposure to organic solvents
Graphene Based Membrane
15 hours exposure to organic solvents
Resilient

Our GO membrane performance

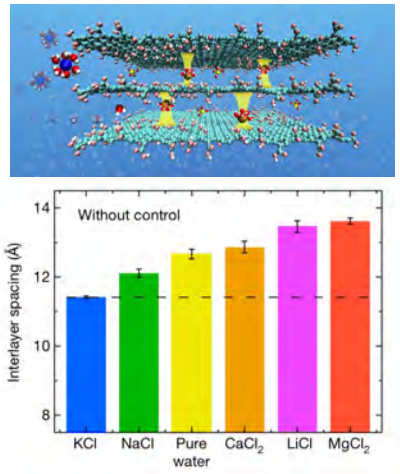




- 1.5 nm/250 Da rejection
- No loss of performance due to chlorine
- Broad pH stability
- High temperature resilience
- Stable in solvents including water, acetone, ethanol, DMF, DCM

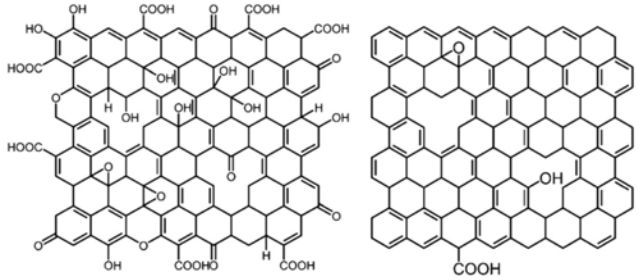
Many Advances

Tuning interlayer spacing



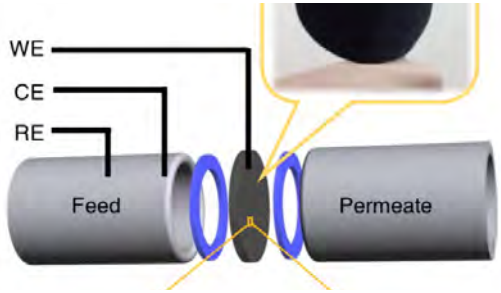
Chen et al., *Nature*, **2017**, 550, 380-383

Reduction of GO sheets



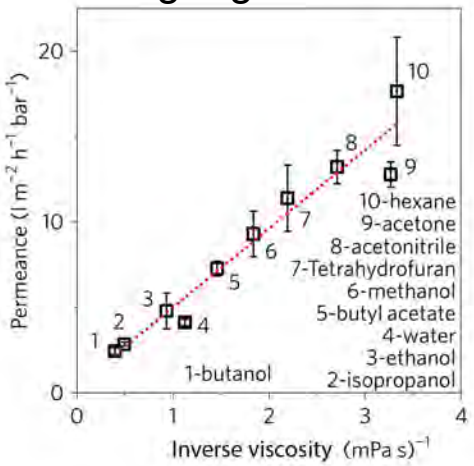
Huang et al, *Advanced Materials*, **2016**, 28, 8669-8674

Electrostatic Modulation



Chi Cheng et al, Nature Nanotechnology, **2018**, 685-690

Filtering organic solvents



Yang et al., *Nature Materials*, **2017**, 16, 1198-1202

20 Reviews on Graphene Oxide Membranes in 4 Year Period!

What's *missing?*

- Application to **high-value** realistic streams
- Viable **scale-up** of membrane production

MATERIALS SCIENCE

Graphene Oxide Membranes for Ionic and Molecular Sieving

Baoxia Mi

ELSEVIER

A review of graphene-based characteristics, preparation

Na Song[a,b], Xueli Gao[a,b,*], Zhun Ma

[a] Key Laboratory of Marine Chemistry Theory and Technolog
[b] College of Chemistry and Chemical Engineering, Ocean Uni
[c] College of Chemical and Environmental Engineering, Shando

GRAPHICAL ABSTRACT

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Perspective

pubs.acs.org/JPCL

Membranes mad
bonding stacked
enable precise, superfast sieving of ions and
molecules.

Graphene-Based Membranes for Molecular Separation

Cite this: *Chem. Soc. Rev.*, 2015, 44, 5016

Gongping Liu, Wanqin Jin* and Nanping Xu

Graphene is a well-known two-dimensional material that exhibits preeminent electrical, mechanical and thermal properties owing to its unique one-atom-thick structure. Graphene and its derivatives (*e.g.*, graphene oxide) have become emerging nano-building blocks for separation membranes featuring distinct laminar structures and tunable physicochemical properties. Extraordinary molecular separation properties for purifying water and gases have been demonstrated by graphene-based membranes, which have attracted a huge surge of interest during the past few years. This tutorial review aims to present the latest groundbreaking advances in both the theoretical and experimental chemical science and engineering of graphene-based membranes, including their design, fabrication and application. Special attention will be given to the progresses in processing graphene and its derivatives into separation membranes with three

Journal of Membrane Science 484 (2015) 95–106

Contents lists available at ScienceDirect

CrossMark

...embranes for

...eh [a,*]

[b] Mechanical Engineering Program, Texas A&M University at Qatar, Doha, Qatar

HIGHLIGHTS

- Graphenes are exceptional materials for the next generation water separation membranes.
- Graphenes prove ultrafast permeance, excellent mechanical strength and precise ionic sieving.
- Modified NPG and GO membranes showed exceptional antifouling properties.
- Need full understanding of the transport mechanism of NPG and GO membranes
- Mechanical performance of fully wetted NPG and GO membranes must be addressed.

ARTICLE INFO

Article history:

ABSTRACT

Membrane desalination and water purification technologies have become important energy

Angewandte Highlights

Membranes

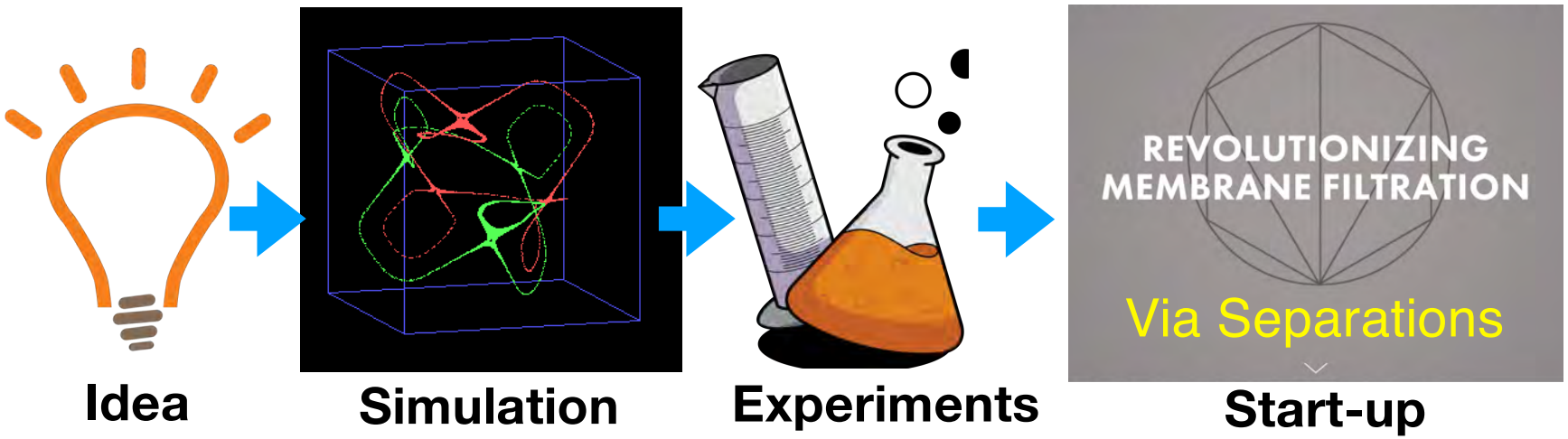
DOI: 10.1002/anie.201404407

Graphene Oxide: A New Platform for High-Performance Gas- and Liquid-Separation Membranes**

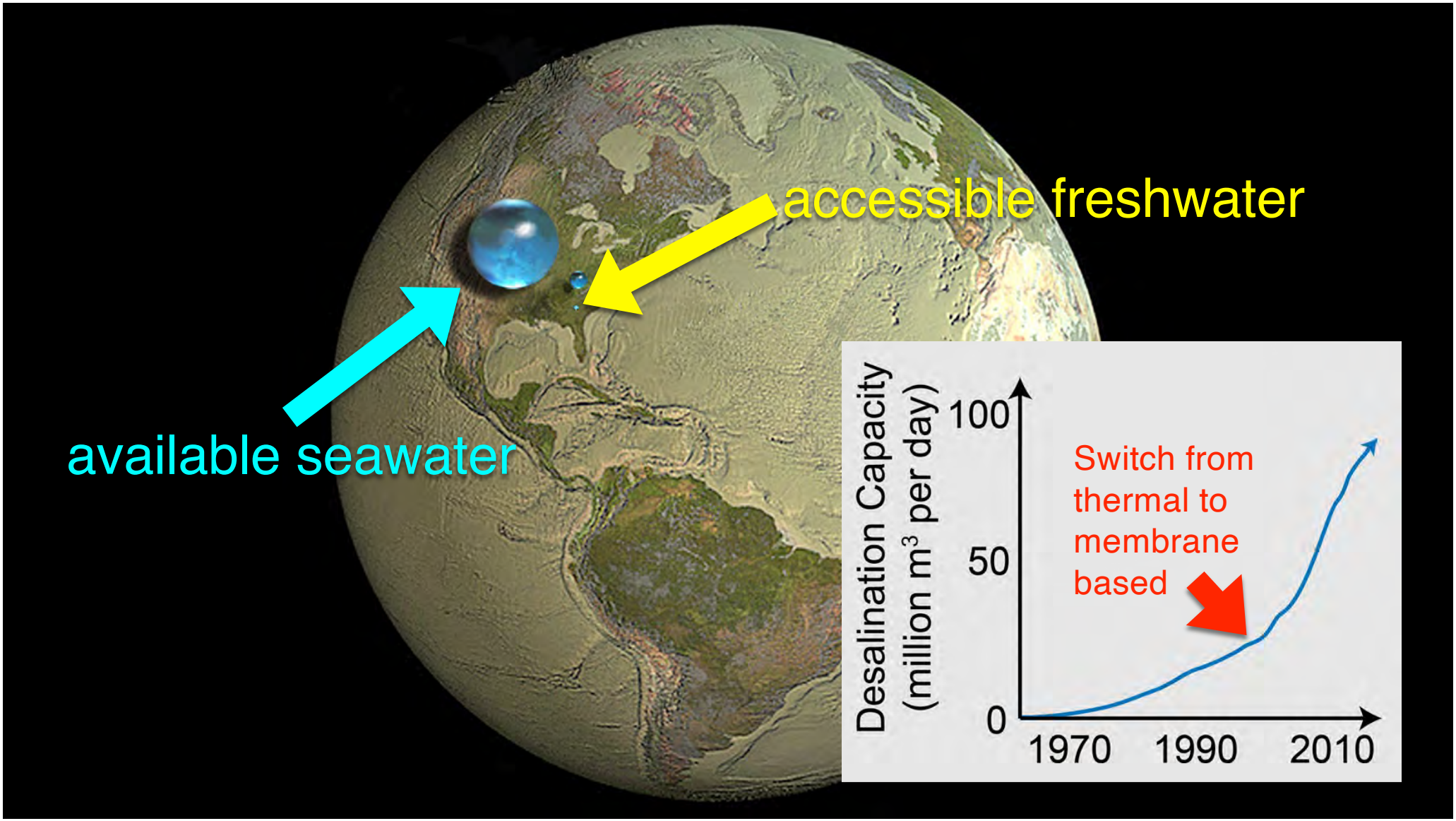
*Zachary P. Smith and Benny D. Freeman**

gas separation · graphene oxide · layered compounds · membranes · water purification

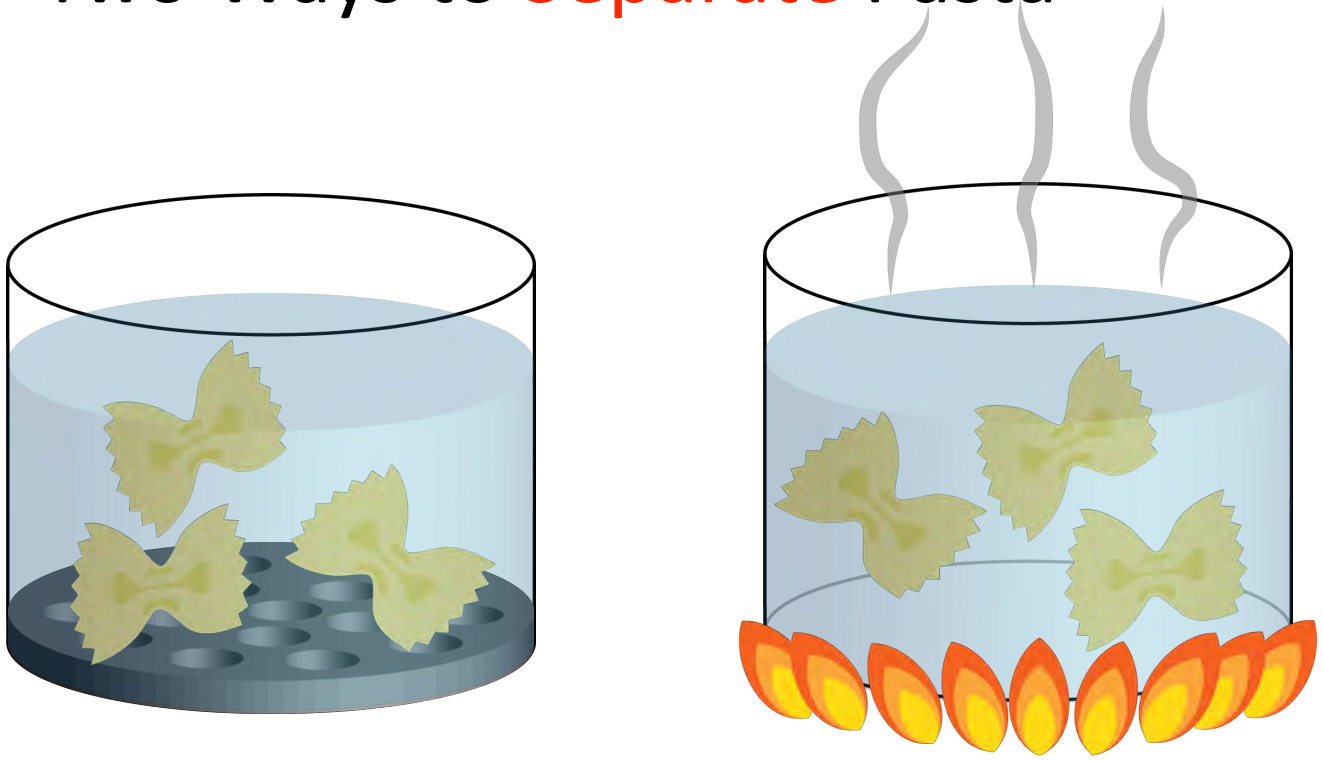
Commercialization in 5 Years



- Tight coupling between computation/experiment
- Early willingness to assess markets + technoeconomics
- Investment for “tough tech” (The Engine)


accessible freshwater
available seawater
Desalination Capacity
(million m³ per day)
100
50
0
1970
1990
2010
Switch from
thermal to
membrane
based

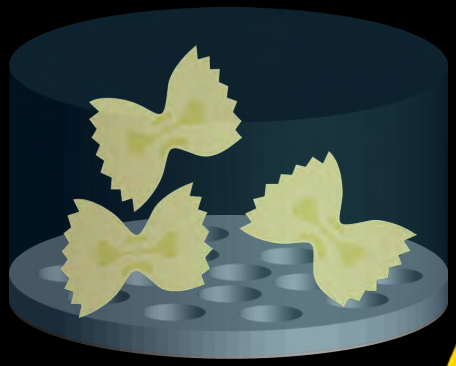
Two Ways to Separate Pasta



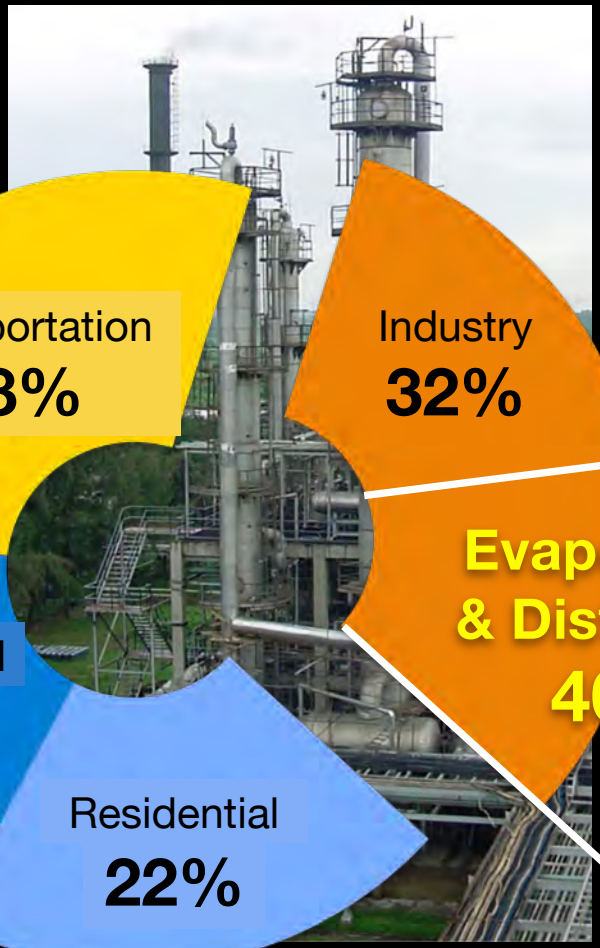
Membrane ← Thermal

>80% Energy savings

Two Ways to Separate 1-10 nm Particles



★Desalination



US Energy Consumption (2015)

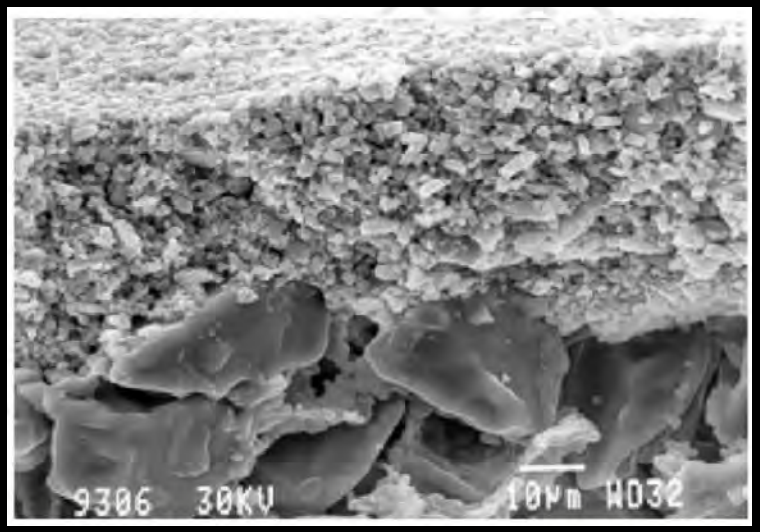
★Sugars
★Small proteins
★Amino acids
★Molecular chemicals
★Antibiotics
★Dissolved salts
★Acids
★Bases
★Dissolved oils
★Dyes

see Sholl, Lively, Nat. vol. 532 (2016)

Robust Membrane Materials

No robust option

Ceramic materials

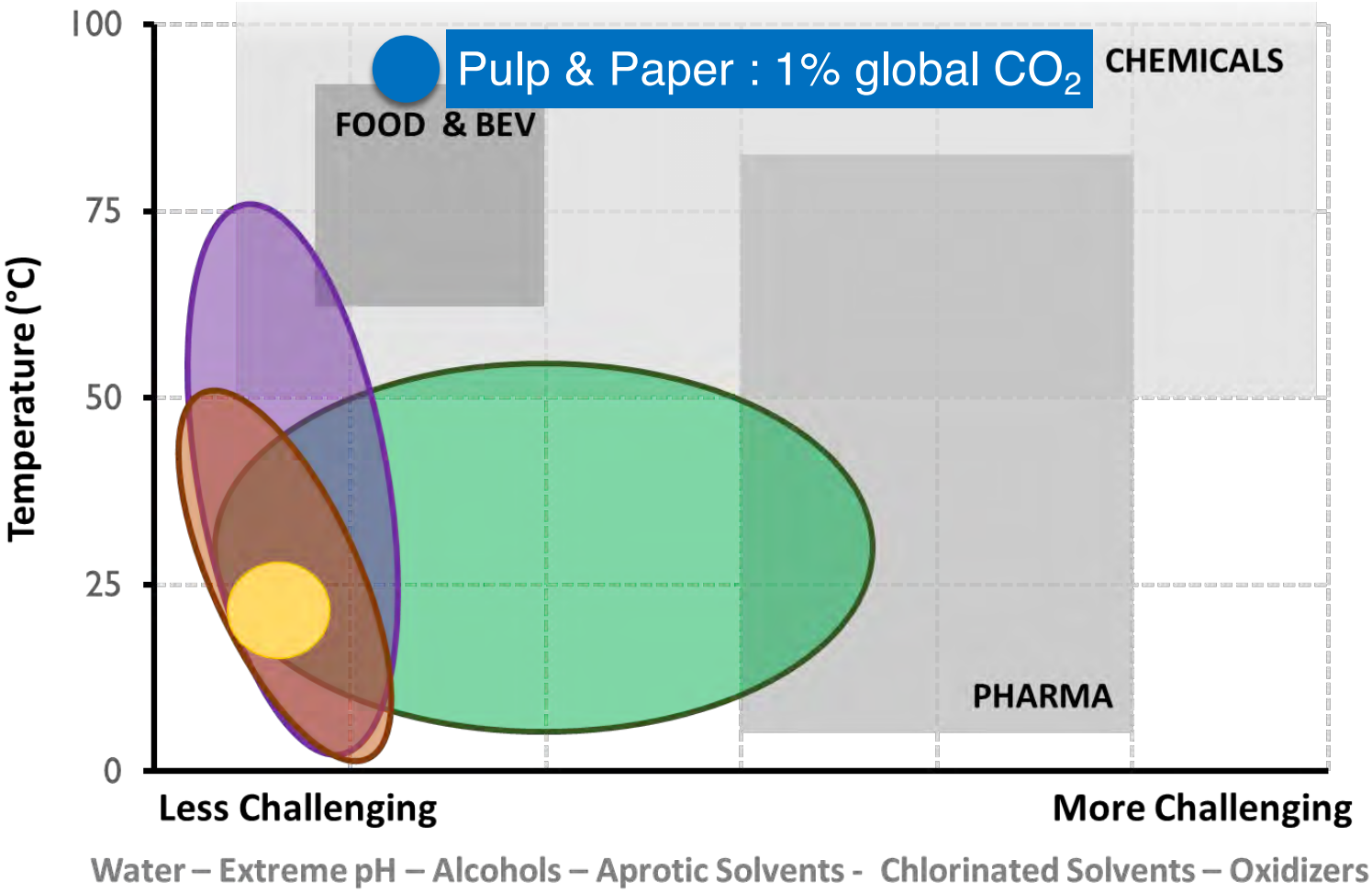


Macrofiltration

Nanometers Microns Millimeters

Shreya Dave

Brent Keller



S. Dave, B. Keller, K. Golmer, and JCG, Joule 2017

Focus of research

Commercial polymer membranes

High T polymer membranes

Emerging solvent resistant membranes

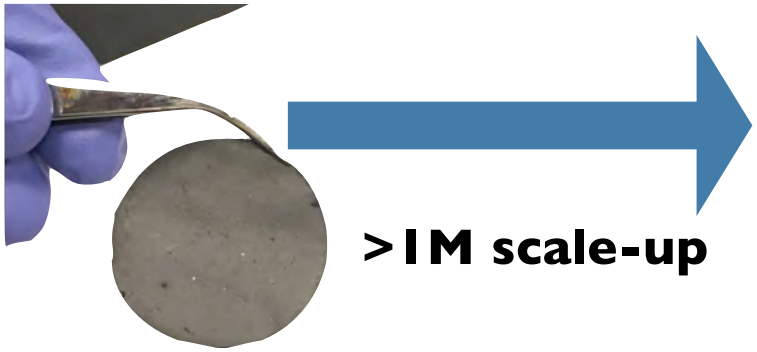
Shreya Dave

Brent Keller

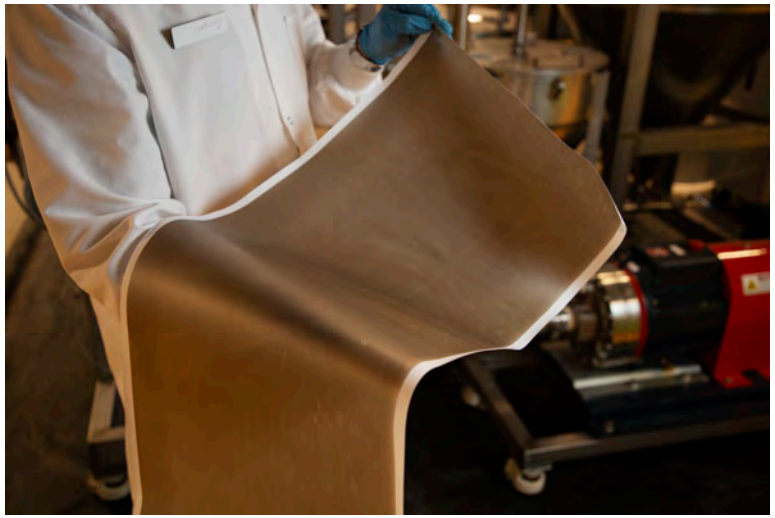
REVOLUTIONIZING MEMBRANE FILTRATION

ViaSeparations

Cost-Effective, Robust, Graphene-based filtrations for Industrial Applications



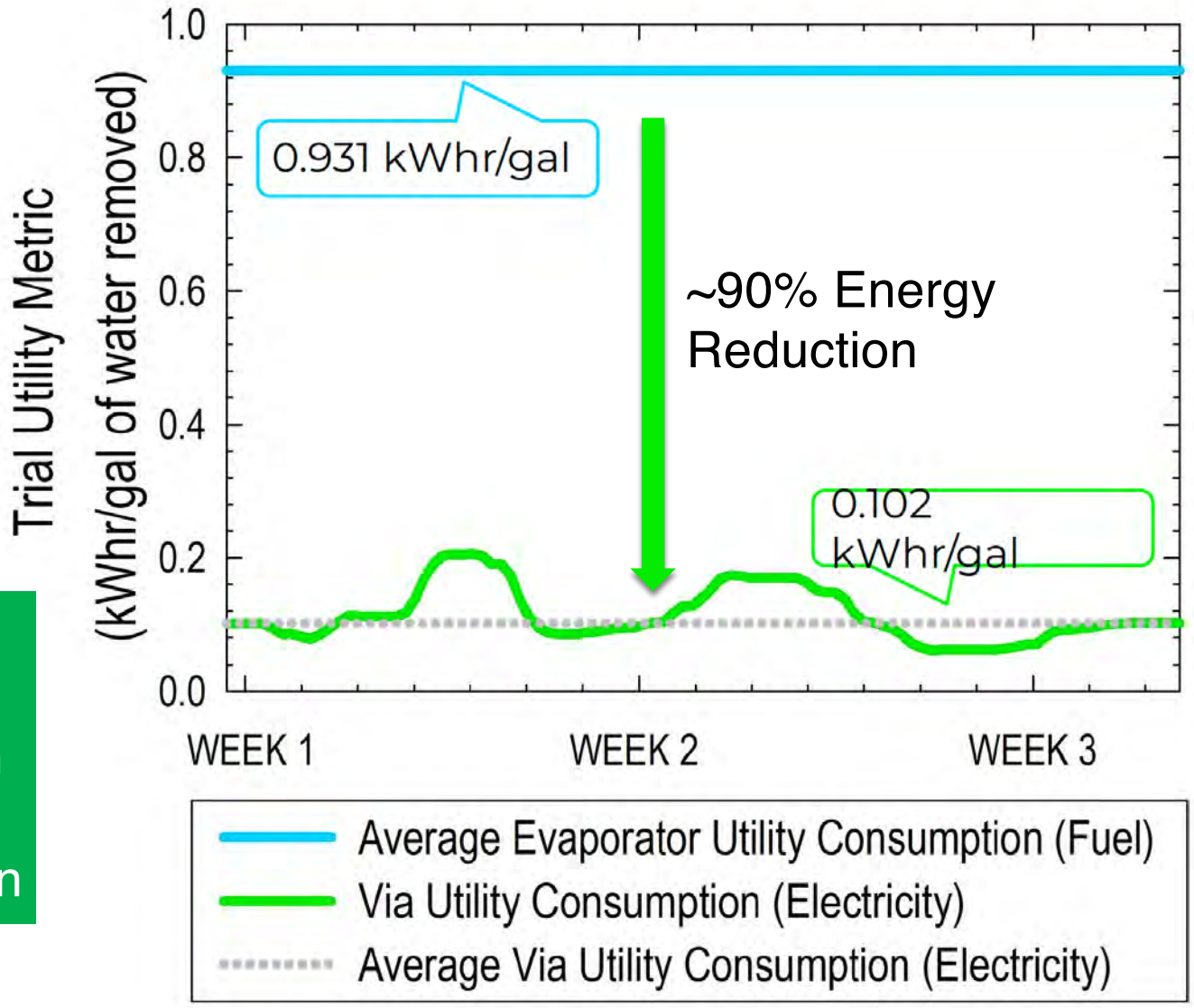
>1M scale-up



Better Plants®
U.S. DEPARTMENT OF ENERGY

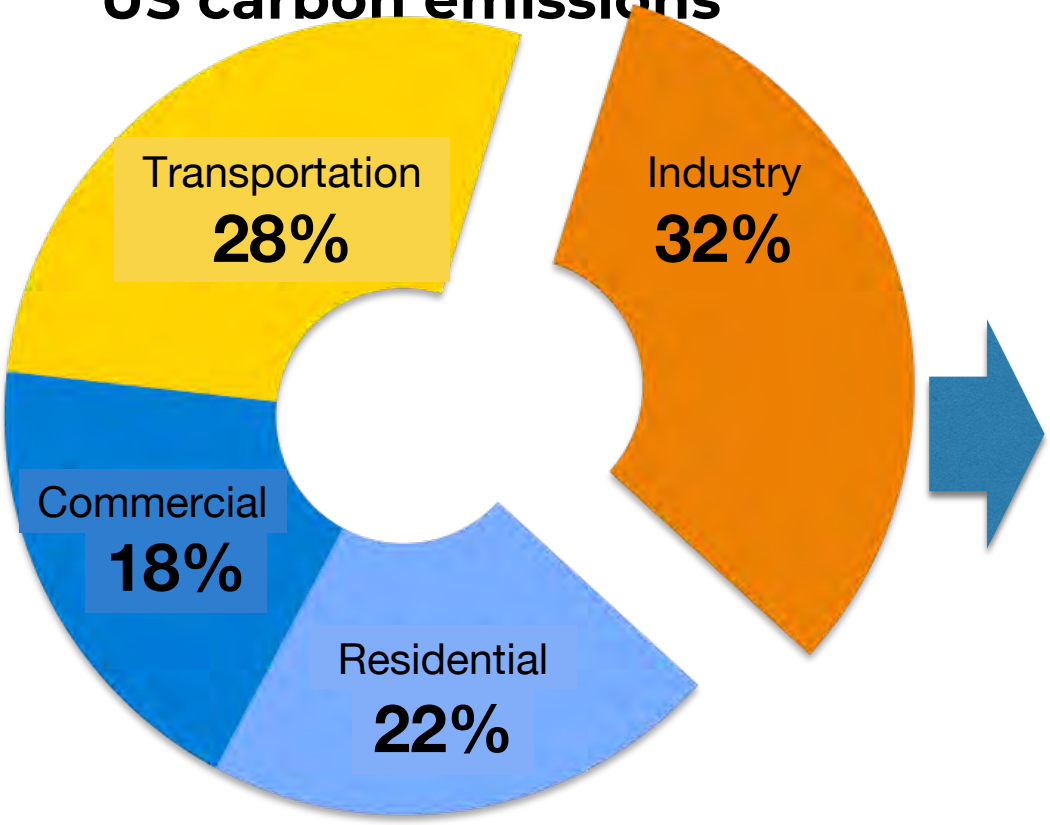
AHLSTROM MUNKSJÖ

Industry Technology validation programs confirm ~90% reduction in energy compared to existing thermal separation

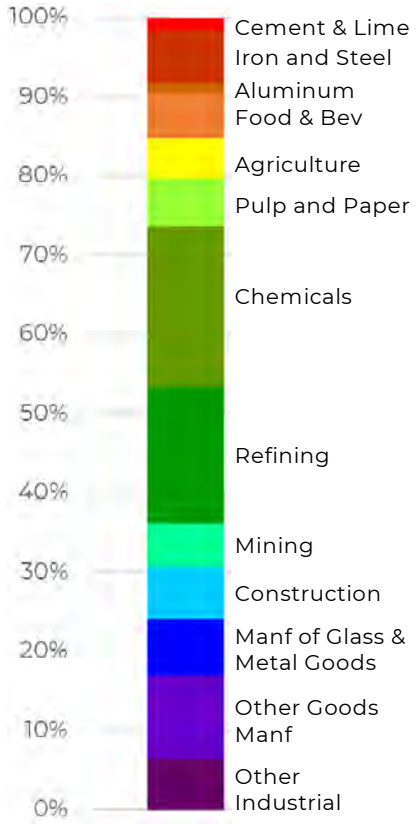


Separations exceed cement, lime, iron and steel emissions

US carbon emissions



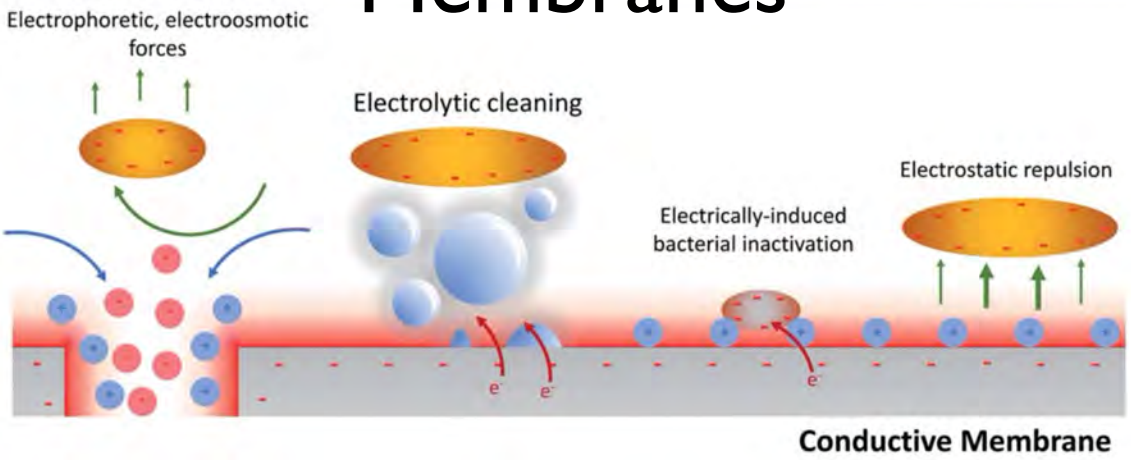
Breakdown by industry



Separations cuts across "tough-to-decarbonize" industries

Sources: US EIA, LBNL, ORNL, EERE, EPA, USDA, & Royal Society

Beyond Resilience: Electrified Membranes

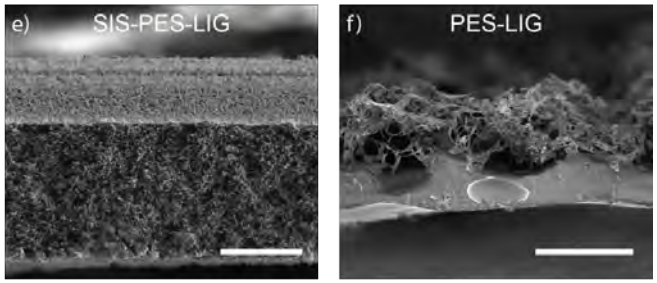


Jatin Patil

Asmita Jana

"**Conductive carbonaceous membranes: recent progress and future opportunities**," J.J. Patil, A. Jana, B.A. Getachew, D.S. Bergsman, Z. Gariepy, B..D. Smith, Z. Lu, and JCG, J. Mater. Chem. A, 9 (2021).

Lased polymers

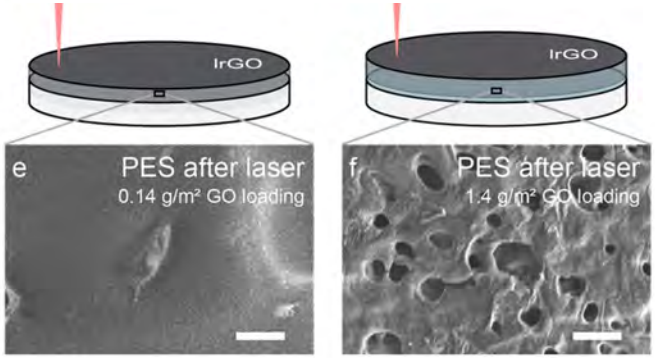


D.S. Bergsman, B.A. Getachew, C.B. Cooper, and JCG, Nat. Comm. 11, 3636 (2020)

David Bergsman

Beza Getachew

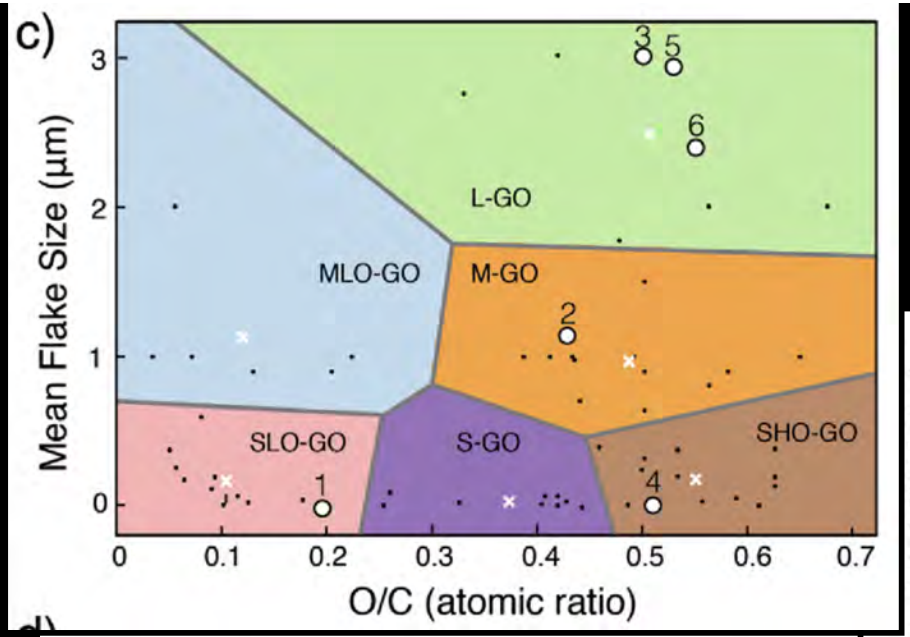
Lased GO/polymer hybrids



Tony Straub

A.P. Straub, D.S. Bergsman, B. A. Getachew, L. M. Leahy, J. J. Patil, N. Ferralis, and JCG (Nanoletters, 2021)

Experimental Consistency an issue with GO



Graphene oxide standard[illegible]on and classifi[illegible]
support the leap from lab[illegible]ustr[illegible]

Carlo A. Amadei [a], Paula Arribas [a, b], C[illegible]

[a] John A. Paulson School of Engineering and Applied Sciences, Harvard University[illegible]idge, MA
[b] Department of Applied Physics I, Faculty of Physics, Complutense University of [illegible]rid, Madrid

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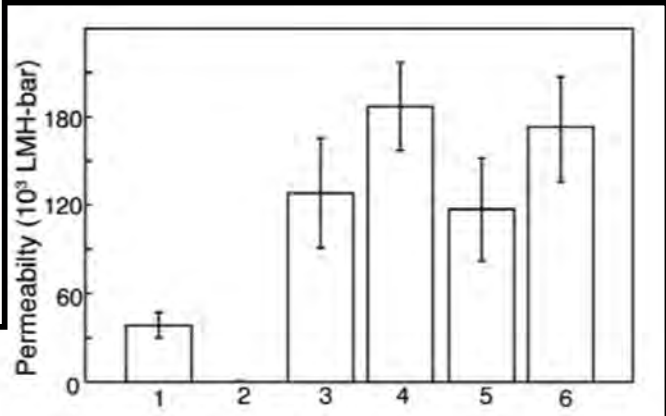
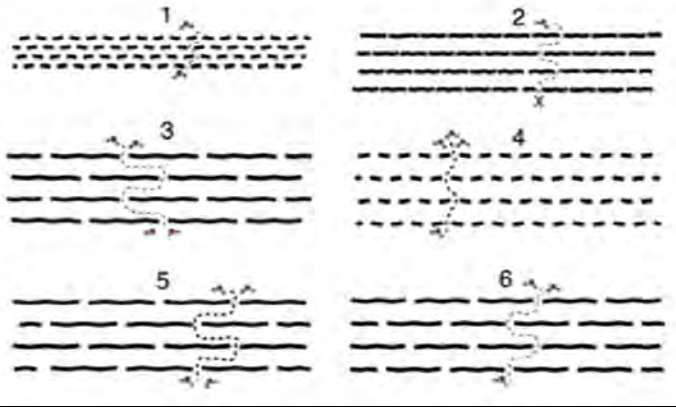
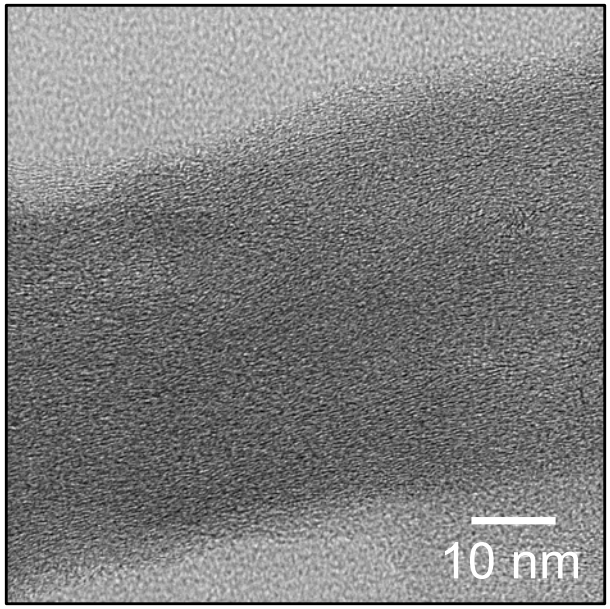
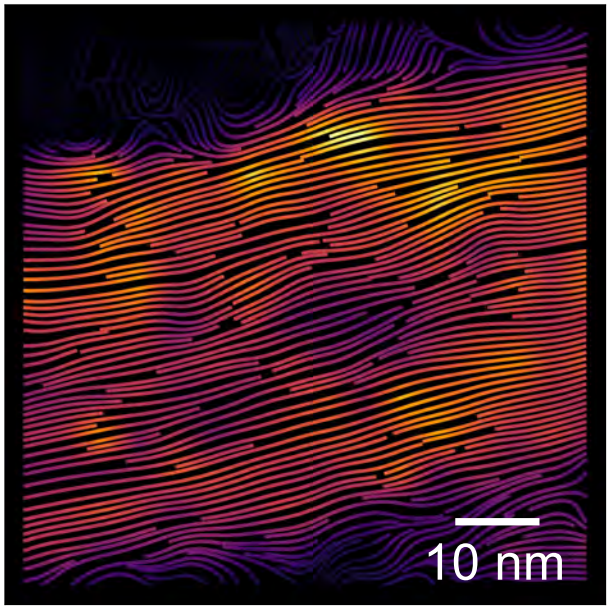
ABSTRACT

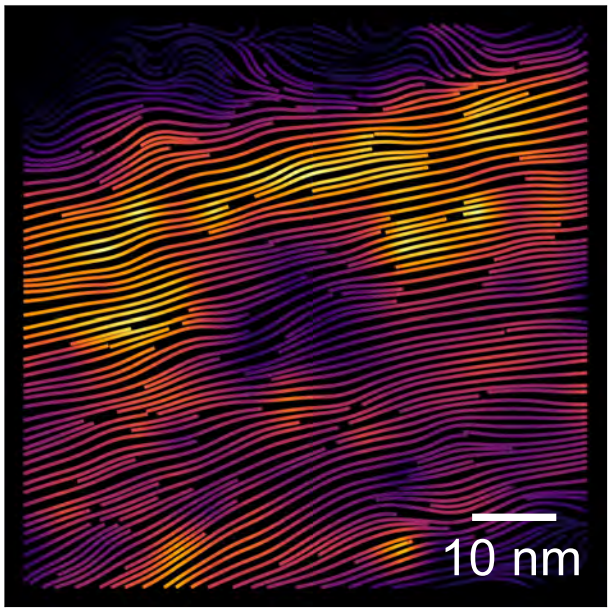
Although graphene oxide (GO) has
implementation remains controver





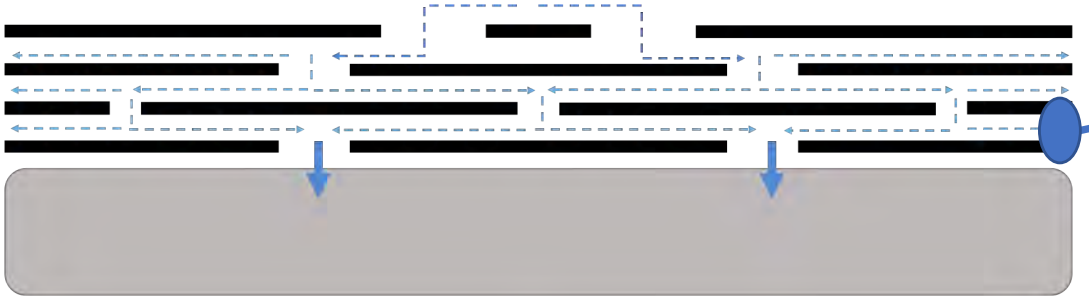


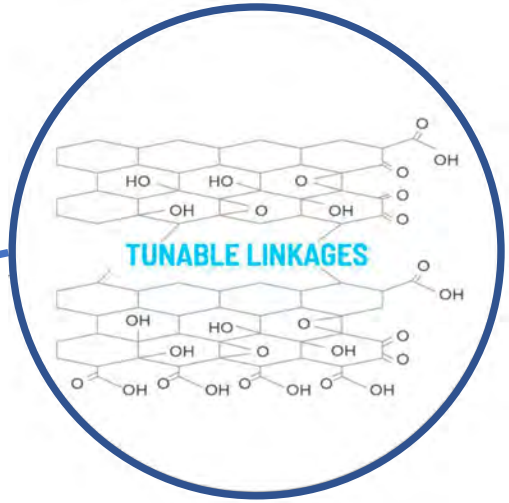


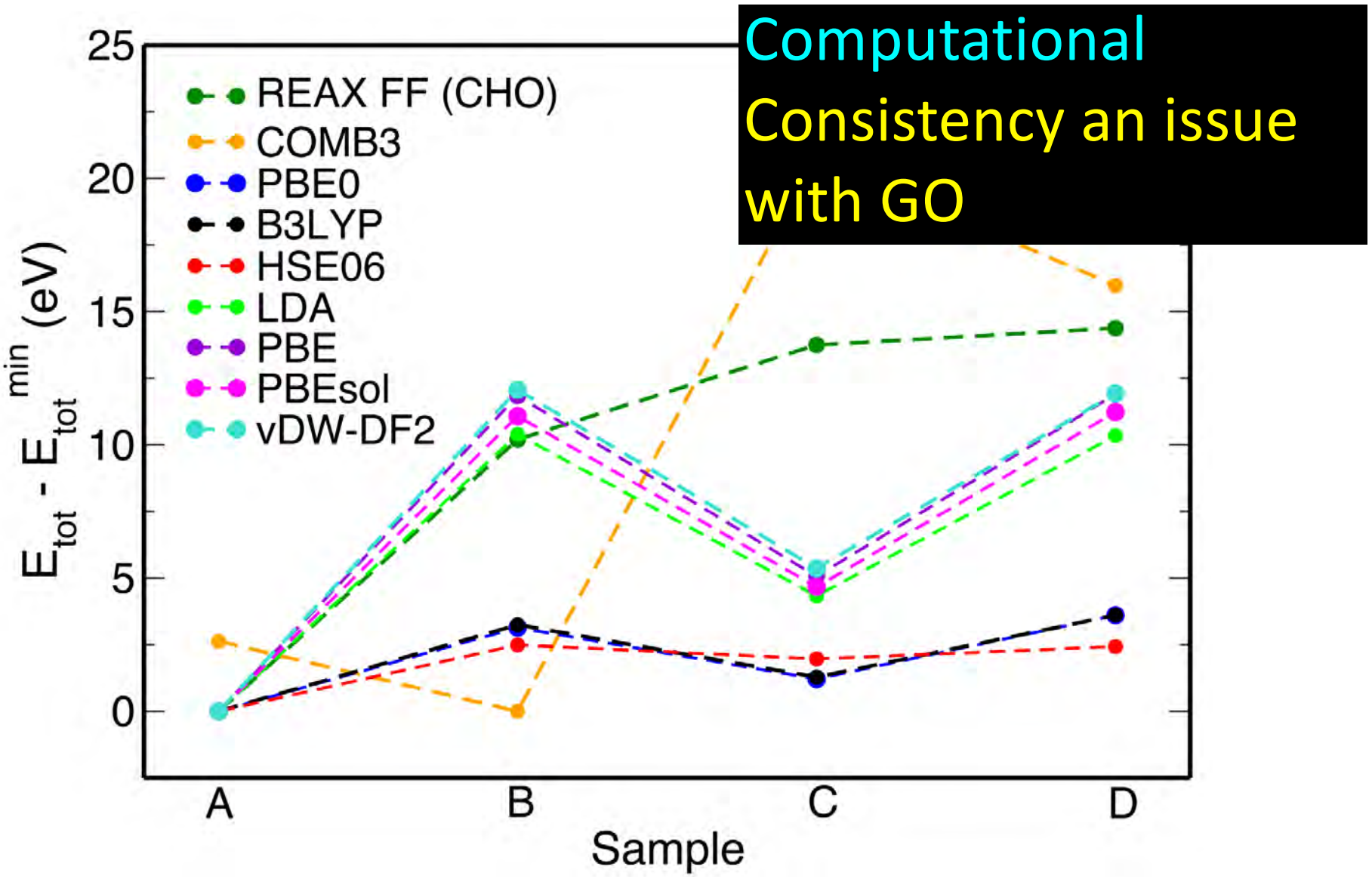


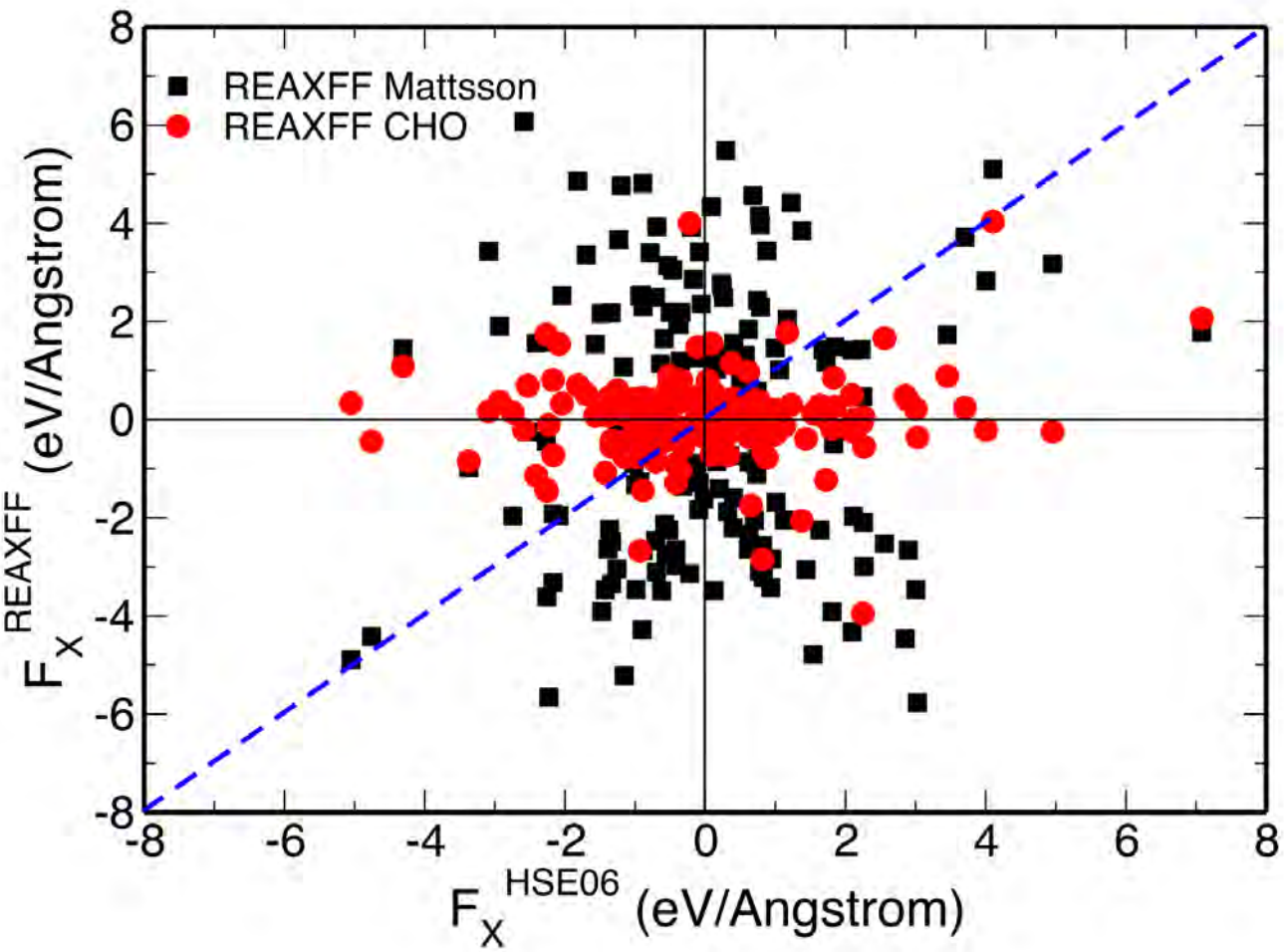
In collaboration with National Energy Technology Laboratory and Oak Ridge National Laboratory

Understanding the Tunability






Computational Consistency an issue with GO
REAX FF (CHO)
COMB3
PBE0
B3LYP
HSE06
LDA
PBE
PBEsol
vDW-DF2
$E_{tot} - E_{tot}^{min}$ (eV)
25
20
15
10
5
0
A
B
C
D
Sample



- Discrepancies >> with >> oxidation, esp. epoxy groups
- Errors due to incorrect description of dihedrals when O is present rather than inaccurate treatment of C hybridization

Bronze

Industry

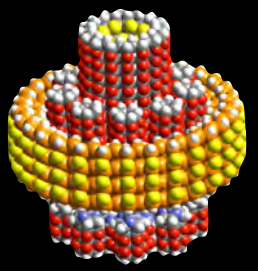
Silicon

The Age We Live

Stones

Iron

Plastics



Atom
Scale
Materials
Design

Group and Support

SAMSUNG

TeraGrid equinor

NSF

U.S. DEPARTMENT OF ENERGY

arpa·e Advanced Research Projects Agency • ENERGY

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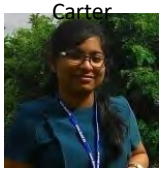
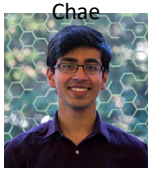
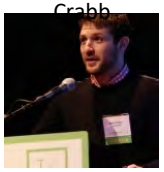


Asmita Jana

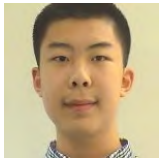


Jatin Patil



Adam Trebach

Tian Xie



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Zhengmao Lu

Thomas Sannicolo

Brendan Smith

Taishan Zhu

Yanming Wang

Xining Zhang

Question and Answer Session

Dr. Clive Freeman

Materials Design

Professor Jeffrey Grossman

Massachusetts Institute of Technology

Announcements

ugm.materialsdesign.com

MedeA Training

Thursday, October 6th

Dr. René Windiks

Materials Design

Next Week's Plenary Session

****Wednesday, October 12th***

Professor Jörg Behler

University of Göttingen

Question and Answer Session

Dr. Clive Freeman

Materials Design

Professor Jeffrey Grossman

Massachusetts Institute of Technology

Questions about Materials Design UGM

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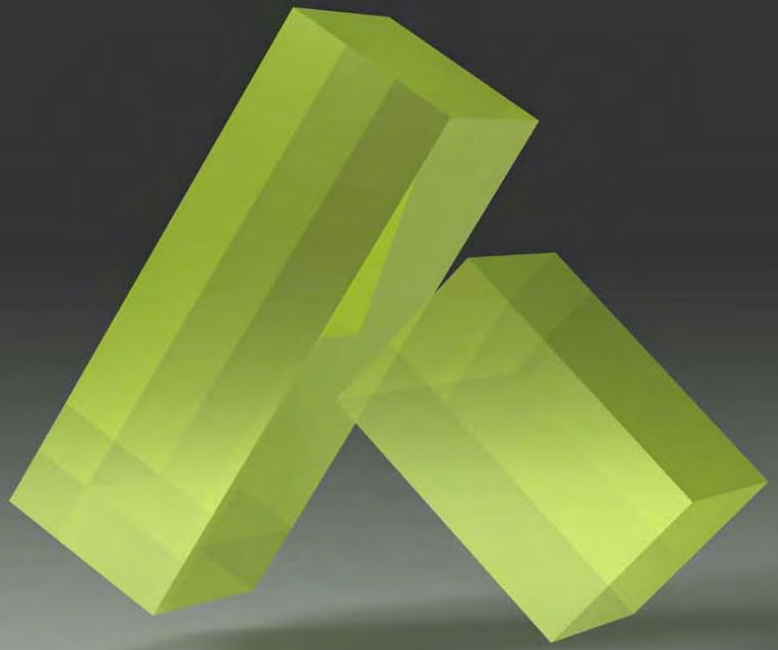

MedeA

Innovation by Simulation