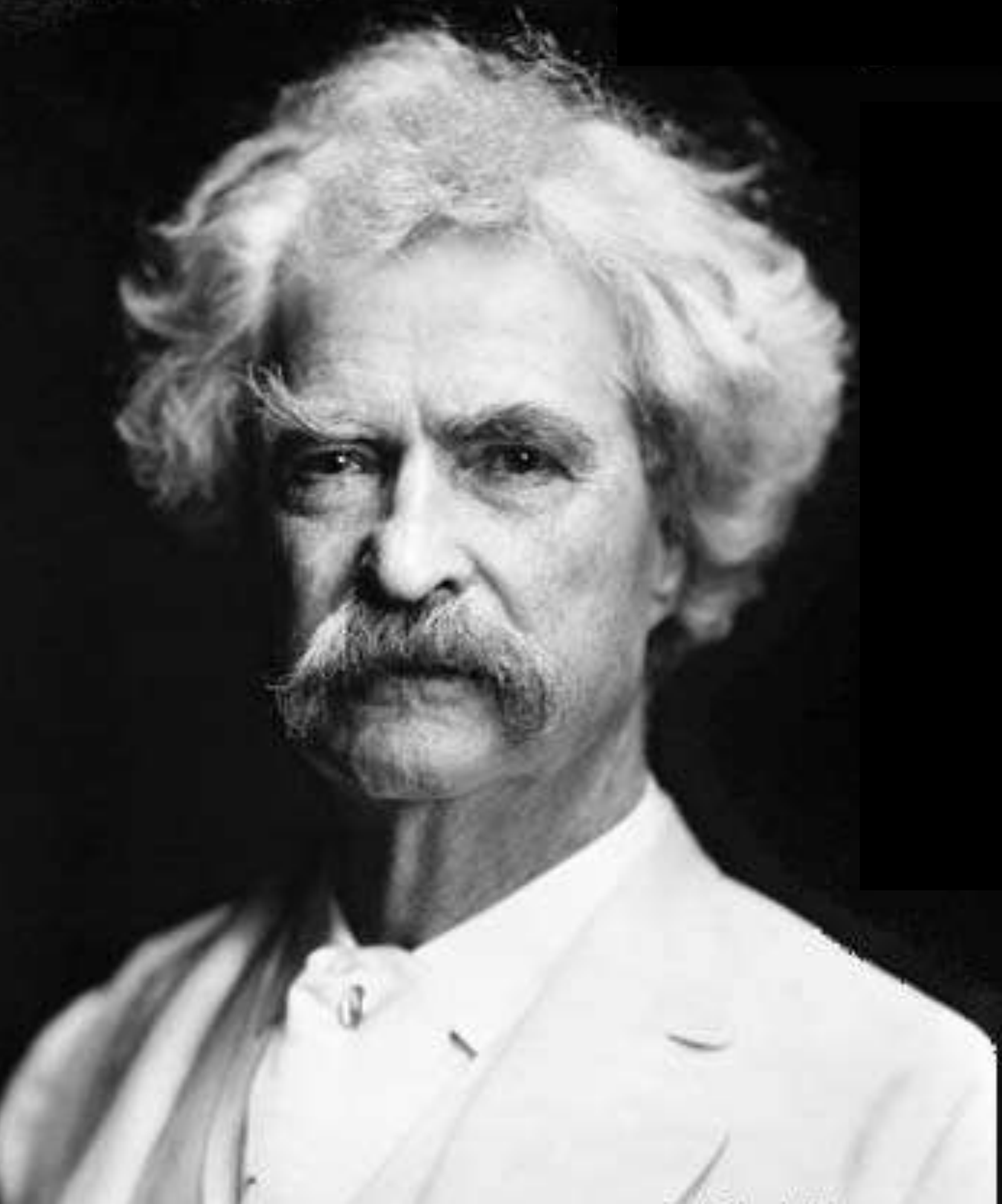
Nanotechnology-Enabled Water Treatment

A Vision to Enable Decentralized Water Treatment & Reuse and Address Challenges of the Water-Energy Nexus

Pedro J.J. Alvarez

2016 Clarke Prize Conference

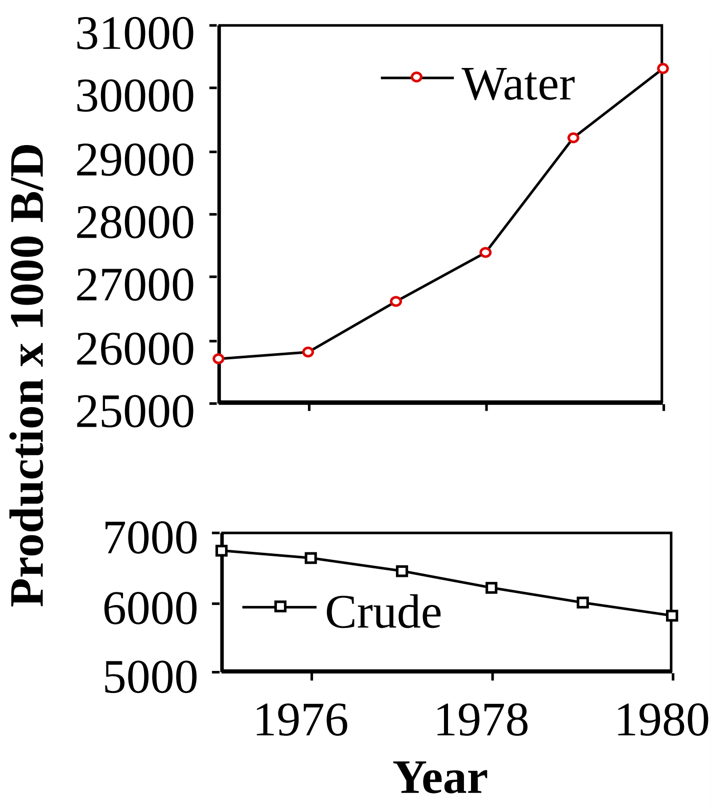


"Whiskey is for Drinking;

Water is for Fighting Over"

~Mark Twain

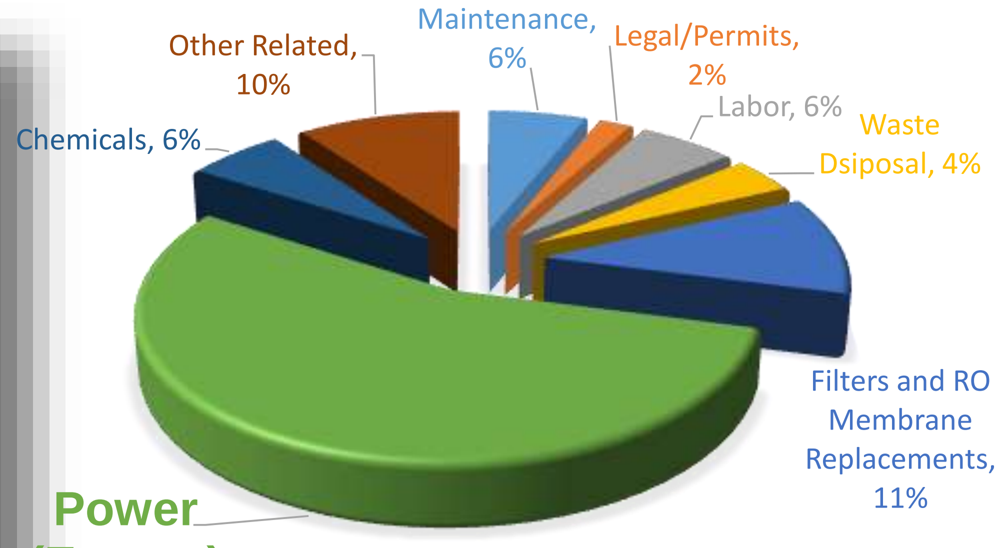
Importance of Water for Energy Production



Water is by far the largest byproduct of the fossil fuel industry
Water/Oil Ratio = 10 (US), 14 (Can.) **$1 trillion/yr challenge***

*http://www.twdb.state.tx.us/Desalination/TheFutureofDesalinationinTexas-Volume2/documents/B3.pdf

Energy for Water Treatment & Distribution

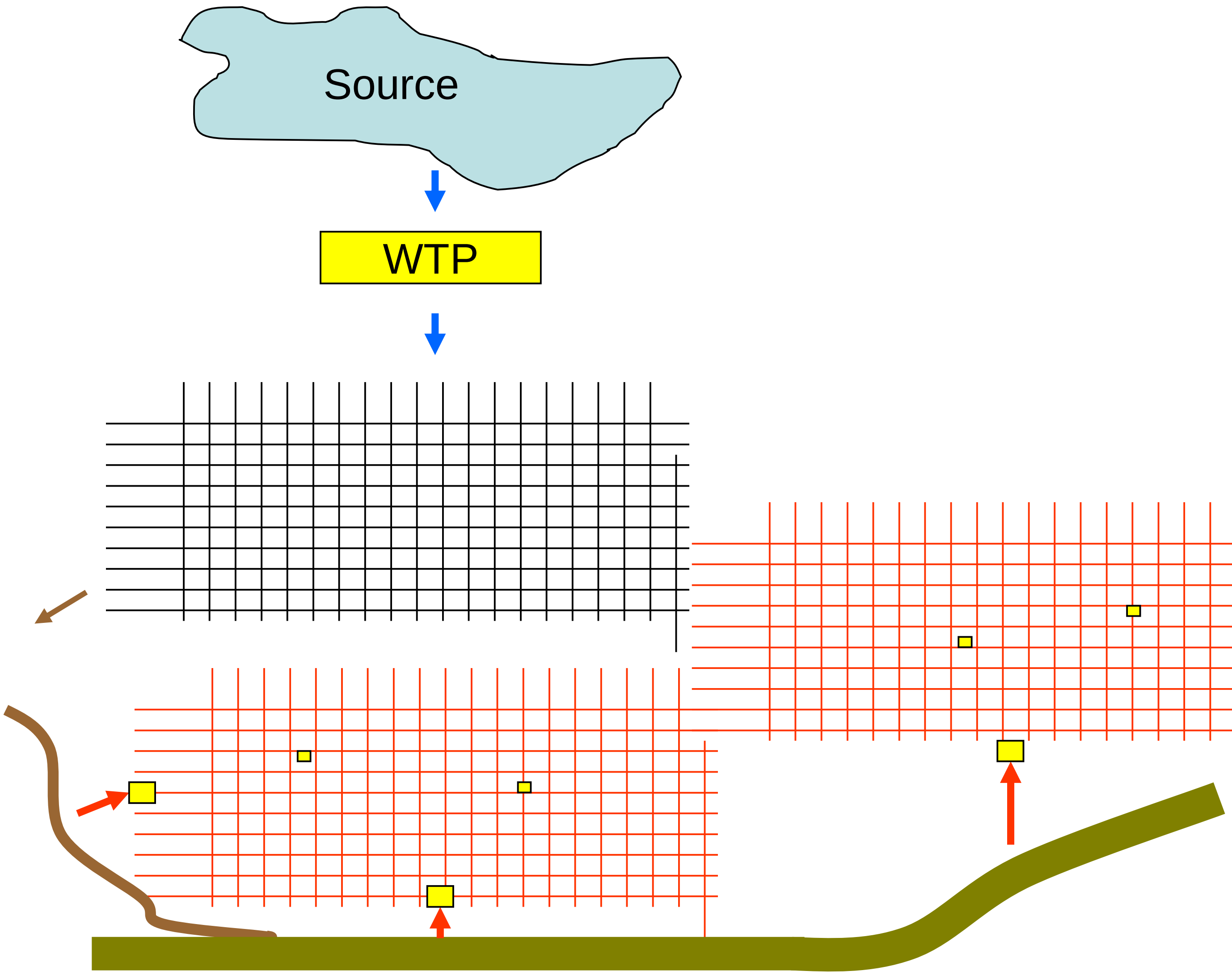


Desalination Operation and Maintenance Cost

20% of electrical energy use in cities is for moving water[1]

Desalination and wastewater reuse is very energy-intensive[2]

1. Electric Power Research Institute, Inc. Water & Sustainability (Volume 4): U.S. Electricity Consumption for Water Supply & Treatment –The Next Half Century. **2002**.
2. Water Reuse Association, Seawater desalination cost, January 2012



Integrate potable water, storm water, and wastewater systems to minimize freshwater withdrawal and energy consumption for transporting water?

Drivers for Decentralized (Distributed) Treatment

- Lack of adequate infrastructure (distribution systems, electricity)
- Match water supply with consumer location (avoid contamination during transport & storage)
- Reduce water losses and headloss in large and complex distribution systems (saves energy!)
- Use networks of ***both*** centralized & decentralized treatment to supplement supply with reclaimed water
- Differential treatment to match treated water quality for intended use, lowering treatment cost

VISION

Enable access to treated water almost anywhere in the world, by developing transformative and off-grid modular treatment systems empowered by nanotechnology that protect human lives and support sustainable development.

Focus on Two Applications

- Off-grid humanitarian, emergency-response and rural **drinking water** treatment systems

https://www.globalgiving.co.uk/projects/clean-water-for-peru/updates/

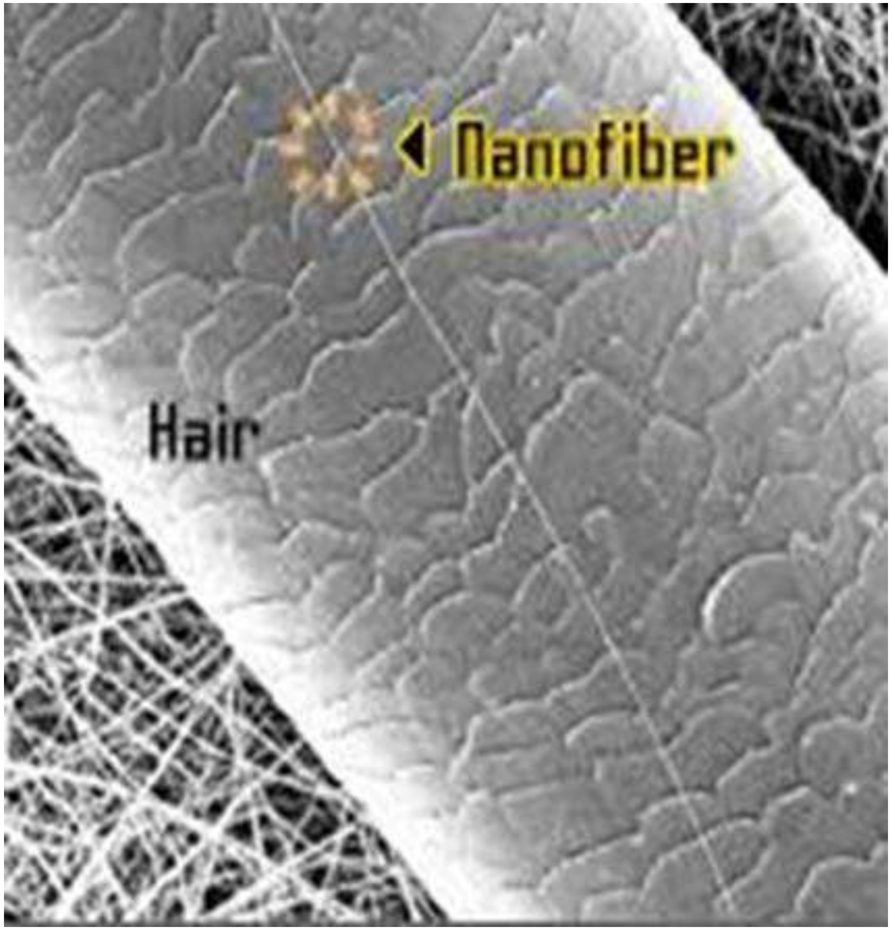
- Industrial **wastewater reuse** in remote sites (e.g., oil and gas fields, offshore platforms)

http://switchboard.nrdc.org/blogs/rhammer/fracking-2.jpg

Nano = Dwarf (Greek) = 10^{-9}

"Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications."

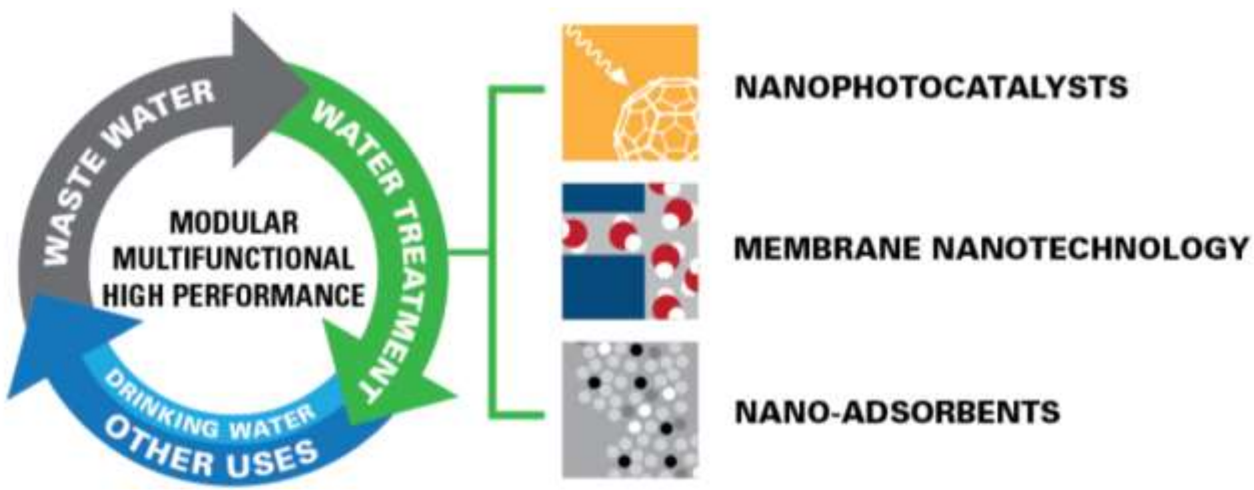
-National Nanotechnology Initiative



Why Nano?

Leap-frogging opportunities to:

- Develop high-performance multifunctional materials and systems that are easy to deploy, can tap unconventional water sources, and reduce the cost of remote water treatment
- Transform predominantly chemical treatment processes into modular and more efficient catalytic and physical processes that exploit the solar spectrum and generate less waste

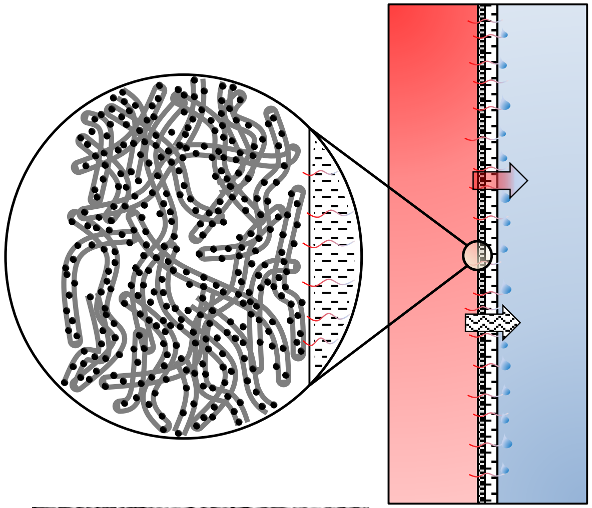


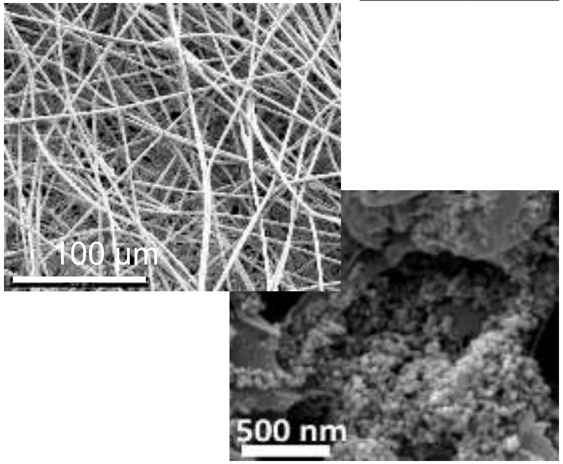
High- Level Research Questions

- How should we use novel nano-scale properties for water purification in a safe and efficient manner?
  (Use benign ENMs & immobilize them)

- How can nanomaterials be attached to surfaces or embedded into scaffolding without losing their functionality?

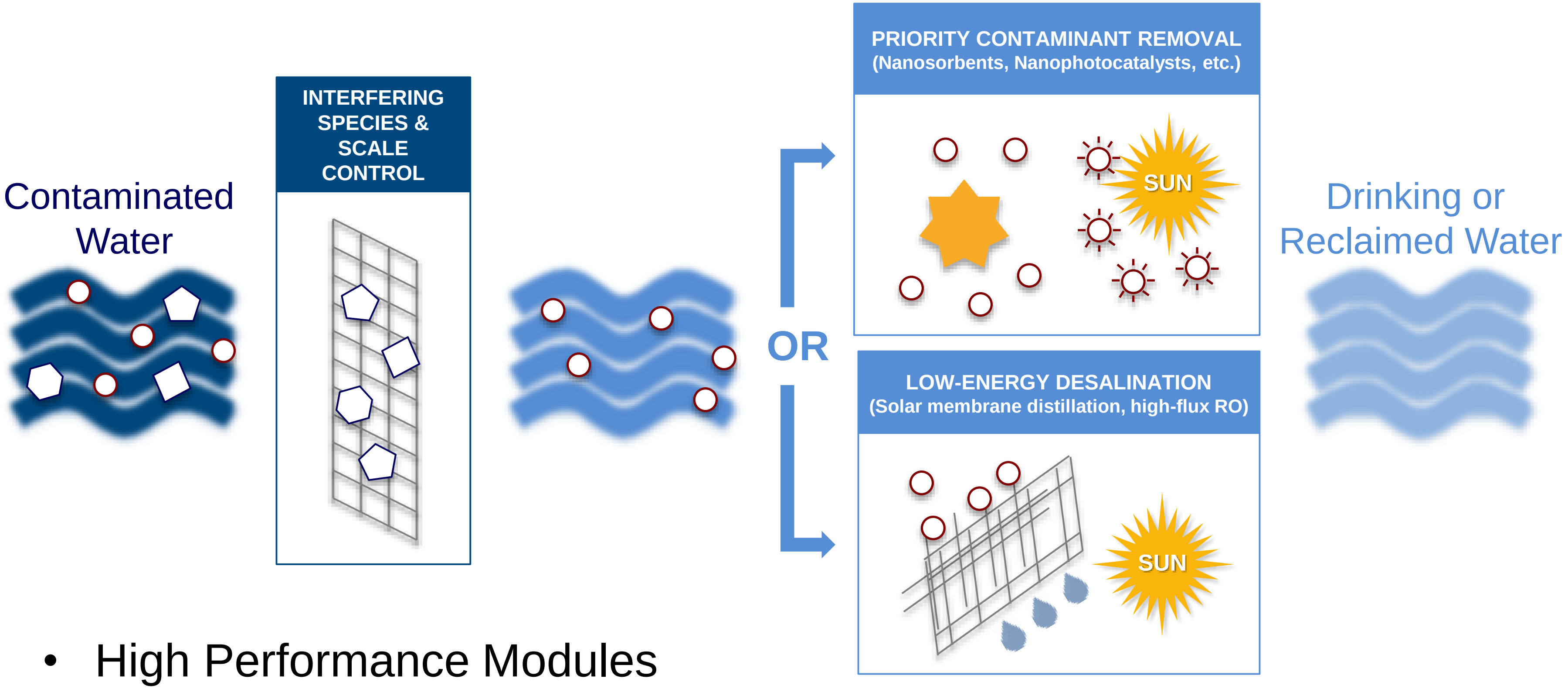
- How can we harness solar energy directly to reduce costs of water purification?





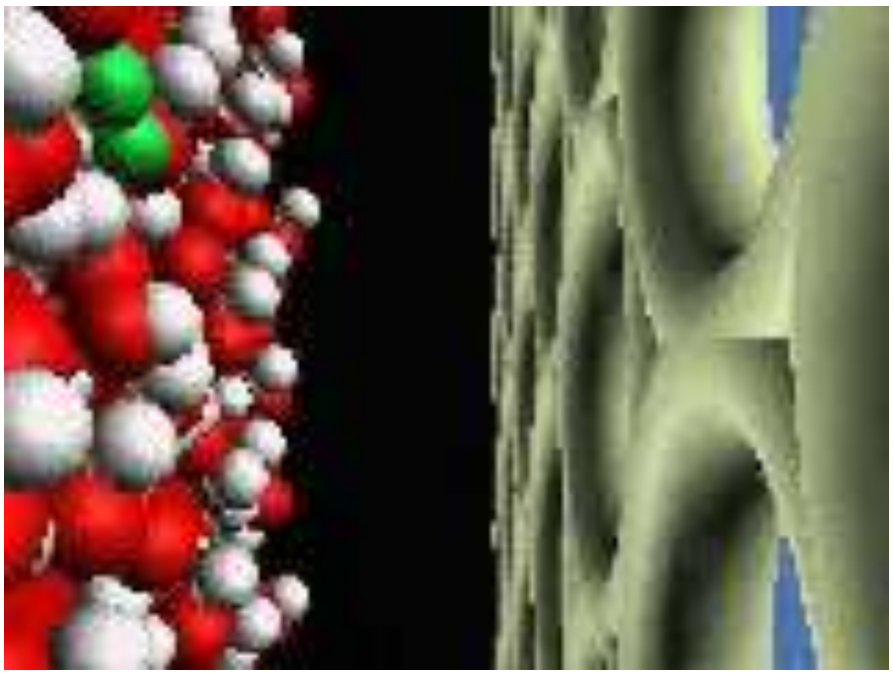
Modular Treatment Systems

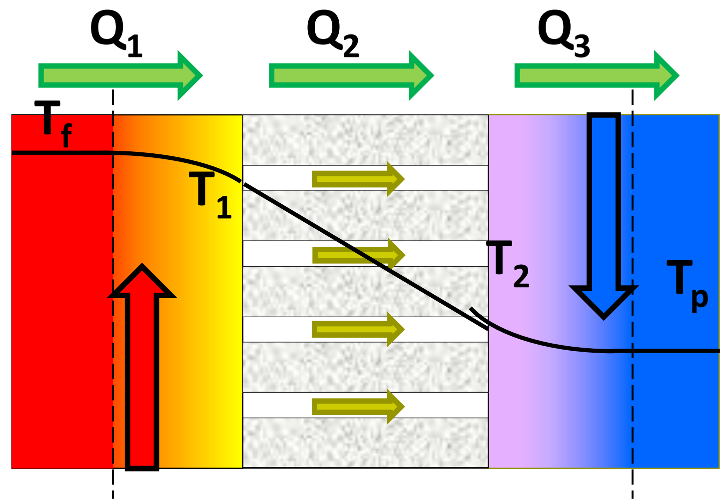
Match treated water quality to intended use



- High Performance Modules
- Lower Chemical Consumption
- Lower Electrical Energy Requirements
- Less Waste Residuals
- Flexible and Adaptive to Varying Source Waters

Example: Enhancing Membrane Distillation





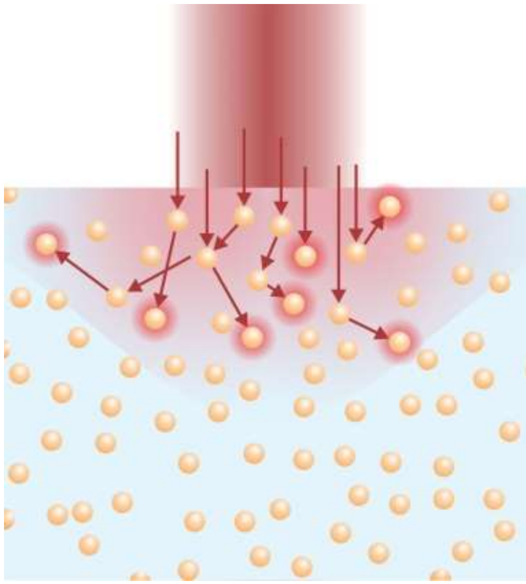
Temperature polarization:

$$a = \frac{T_1 - T_2}{T_f - T_p}$$

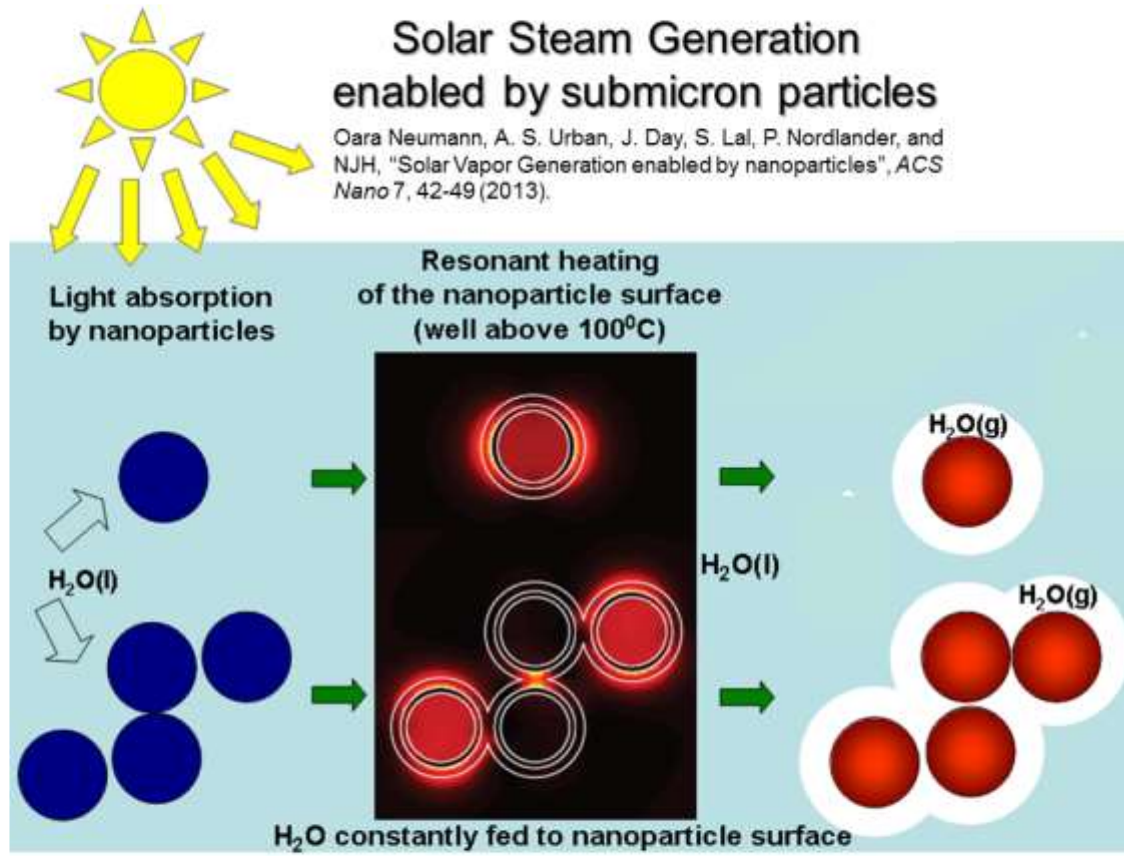
Can reduce transmembrane temperature gradient by up to 70%

www.desalination.biz

Photonics of Nanoparticles for Solar-Thermal Applications

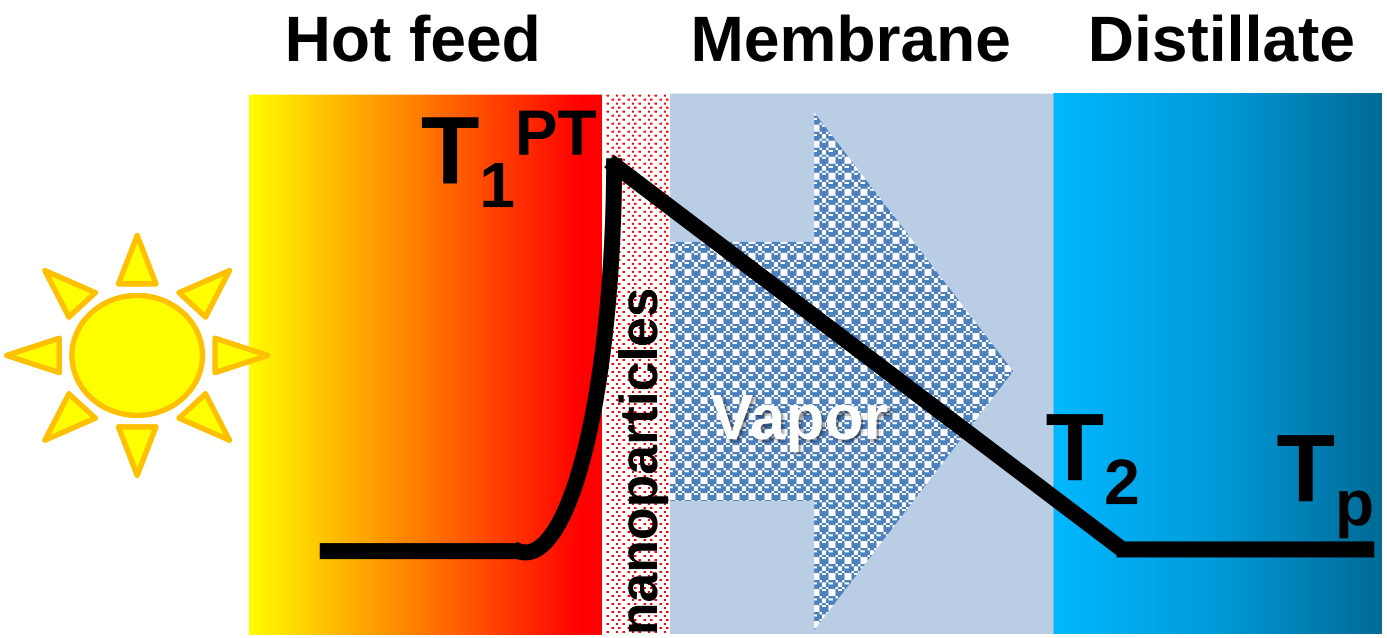


Light localization by multiple scattering confines solar energy, enabling high efficiency heat transfer (Hogan et al., *Nano Lett.* **2014**, *14*, 4640-4645)



Enabling Technology

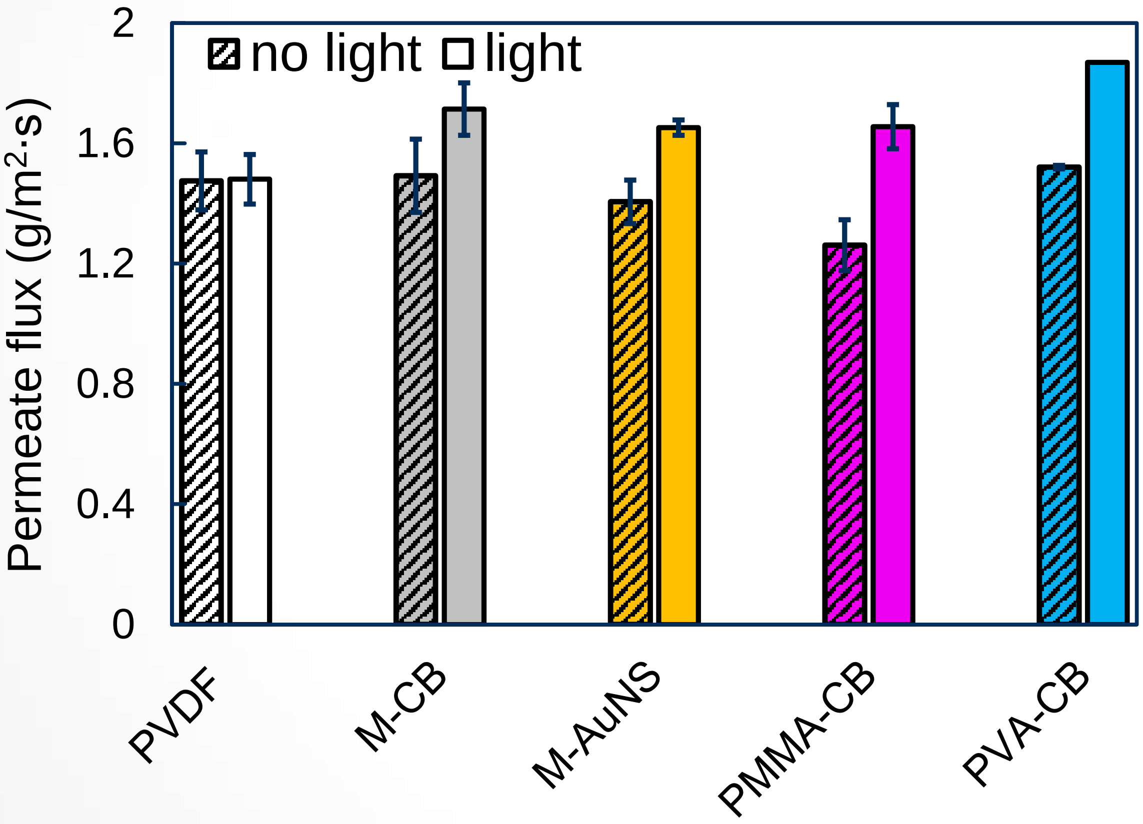
Direct solar membrane distillation for low-energy desalination

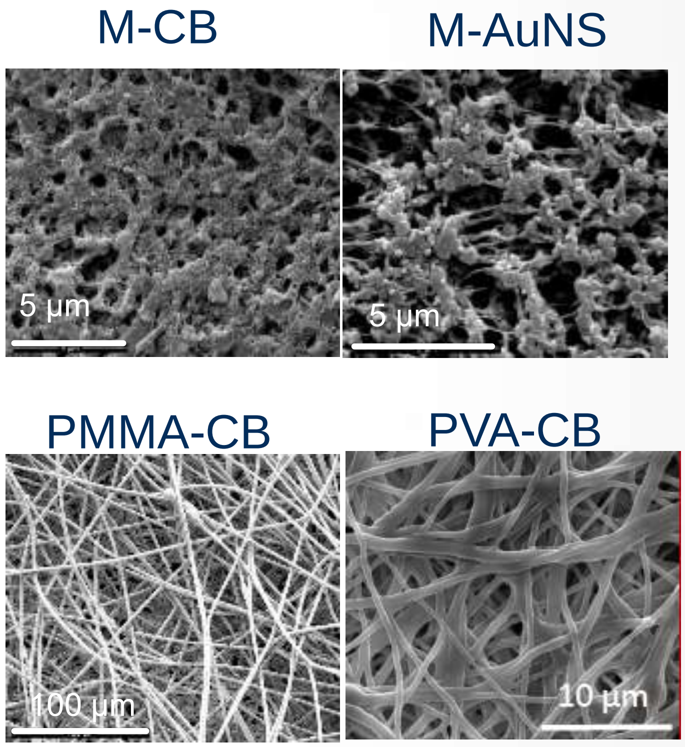


Higher ΔT→ increased efficiency!

Multifunctional membranes: Fouling-resistant, High-flux Self-cleaning

Photothermal Coating Enhances Membrane Permeate Flux





Tf = 35 °C, Tp = 20 °C
Light source: simulated sunlight at 1 sun unit

Potential applications for solar MD

- **Off-Grid drinking water treatment**
  - Portable outdoor treatment units (e.g., camping, army)
  - Single family water purification
  - Commercial drinking water vending station for off-grid communities (solar water station)

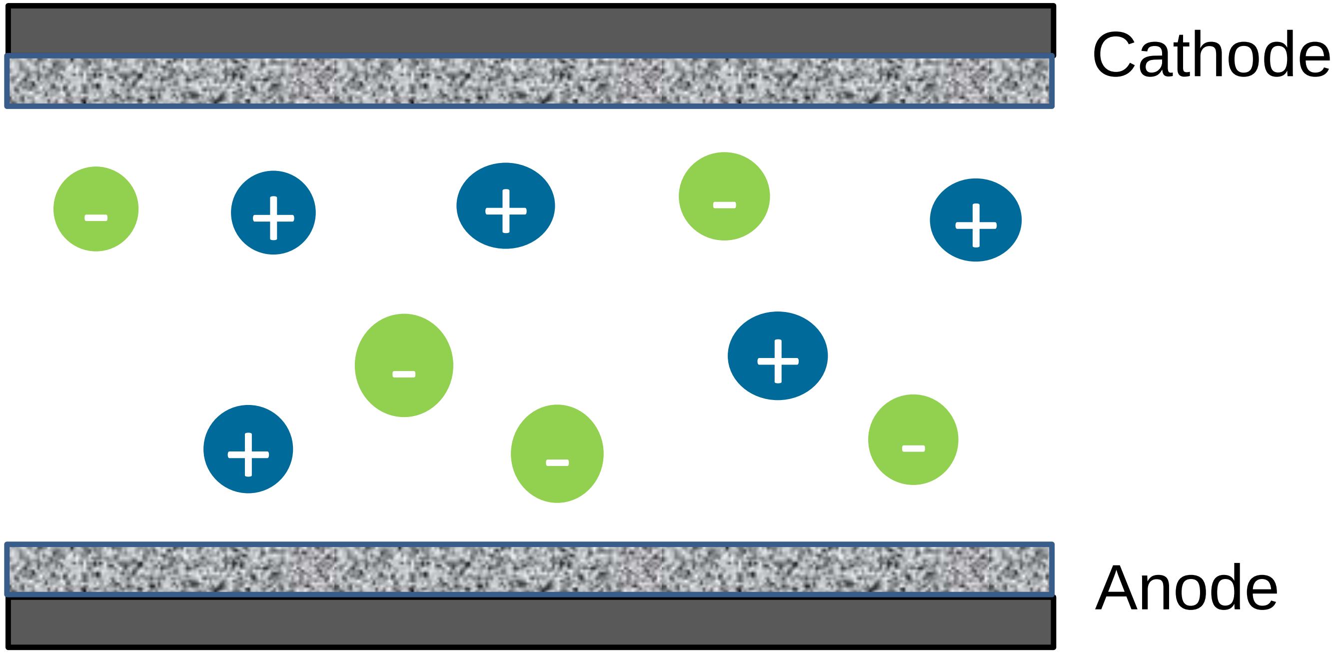
Similar to solar charging station, could build a solar water station

- **Industrial water treatment**
  - Reverse osmosis concentrate treatment
  - Hypersaline wastewater that cannot be handled by reverse osmosis

RO concentrate treatment

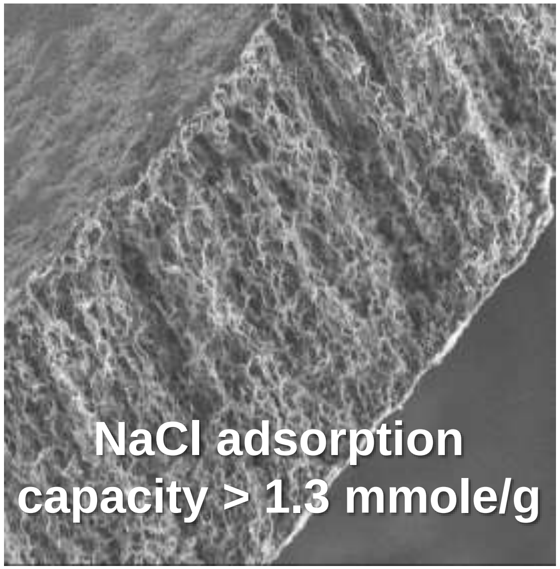
Enabling Technology
Electrosorption for Scaling Control

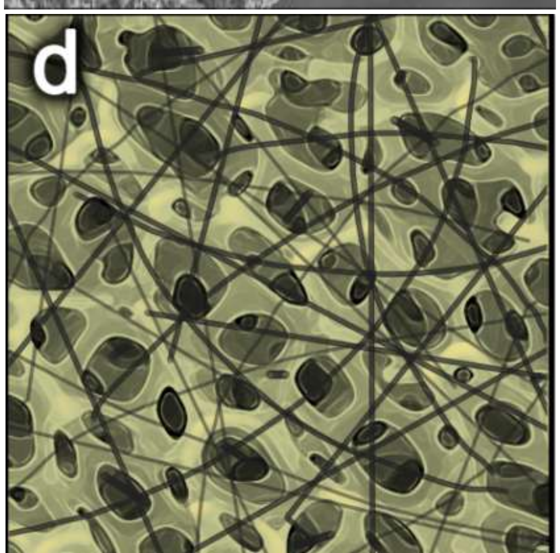
Nanocomposite electrodes to remove multivalent ions from brines, and generate smaller waste streams

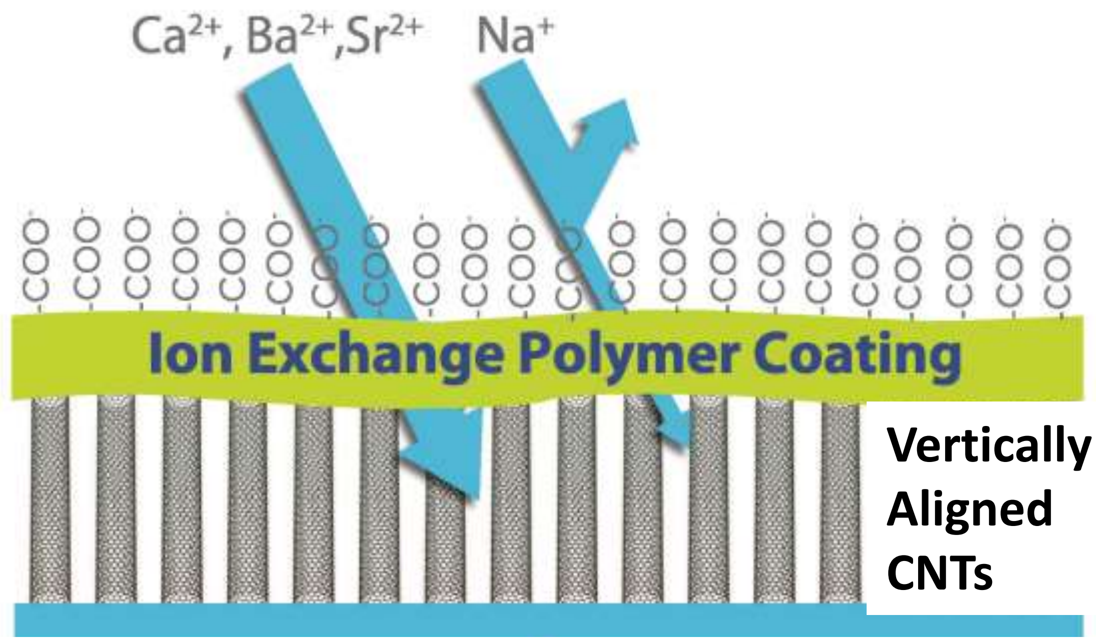


Nano-Enabled CDI for Scaling Control

IX polymers enable preferential removal of divalent cations that cause scaling



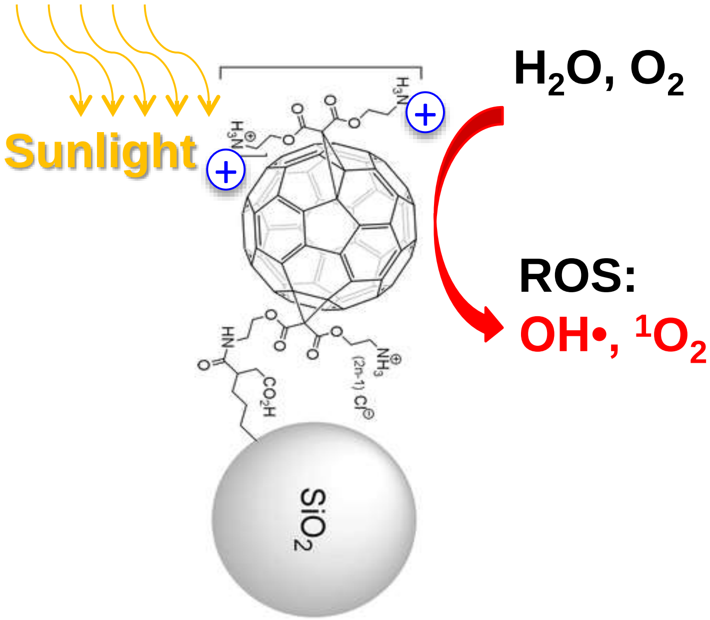




CNTs/graphene enhance sorption capacity, kinetics, mechanical strength and electrical conductivity.

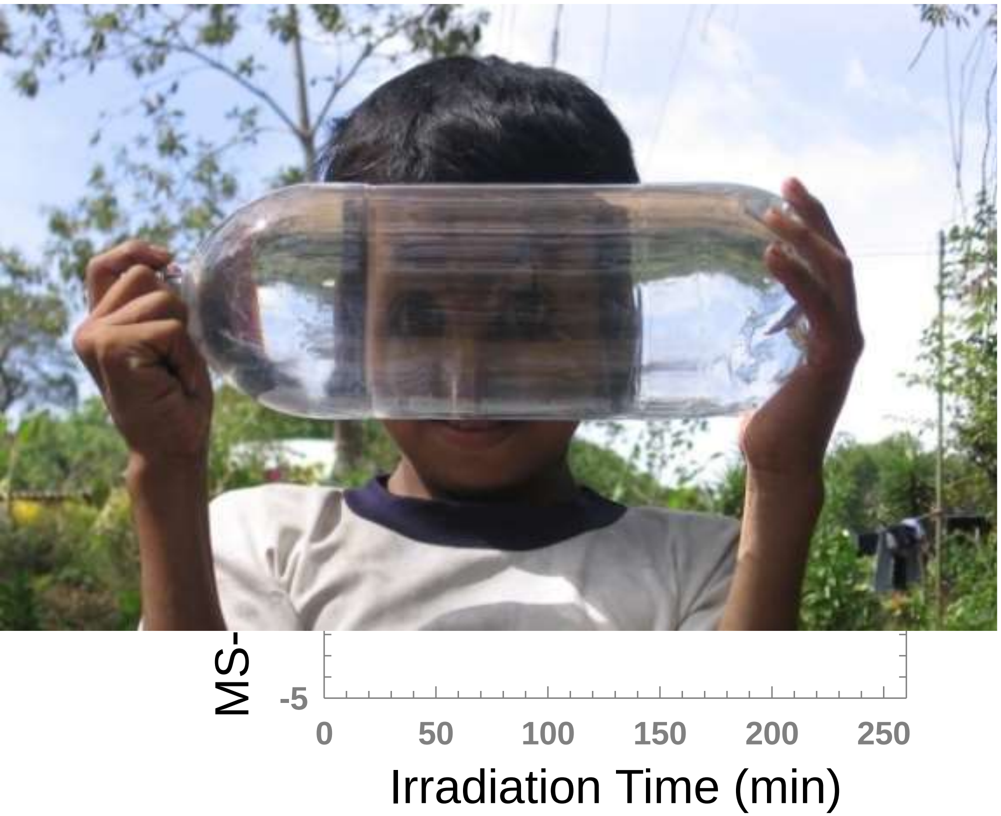
Enabling Technology
(Photo)Disinfection & Advanced Oxidation

Nano(photo)catalysts that use solar radiation to generate ROS that destroy resistant microbes and recalcitrant pollutants without generating harmful disinfection byproducts

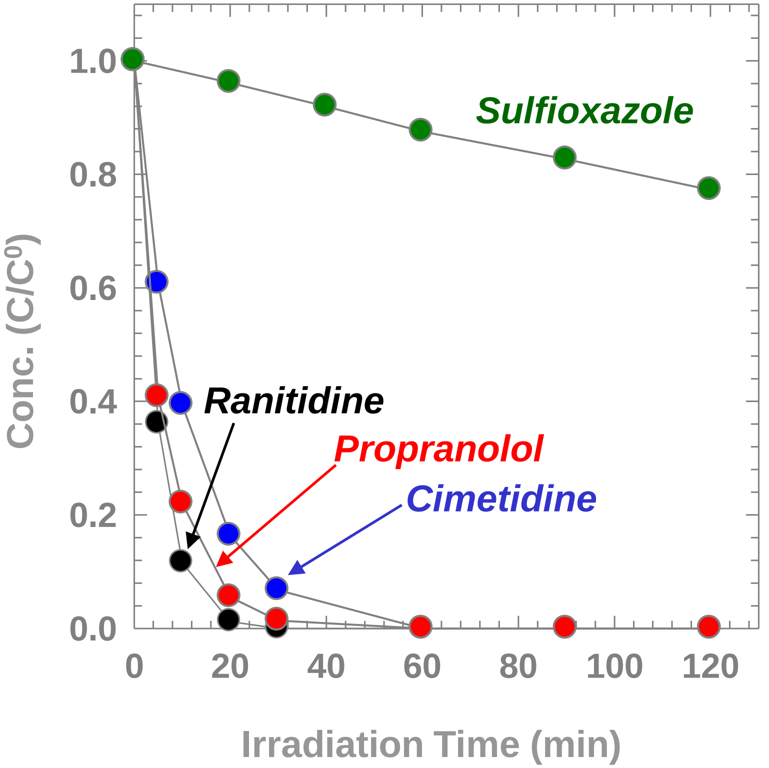


Immobilized Photocatalyst

Advantages of Amino-C_{60} as Photocatalytic Disinfectant

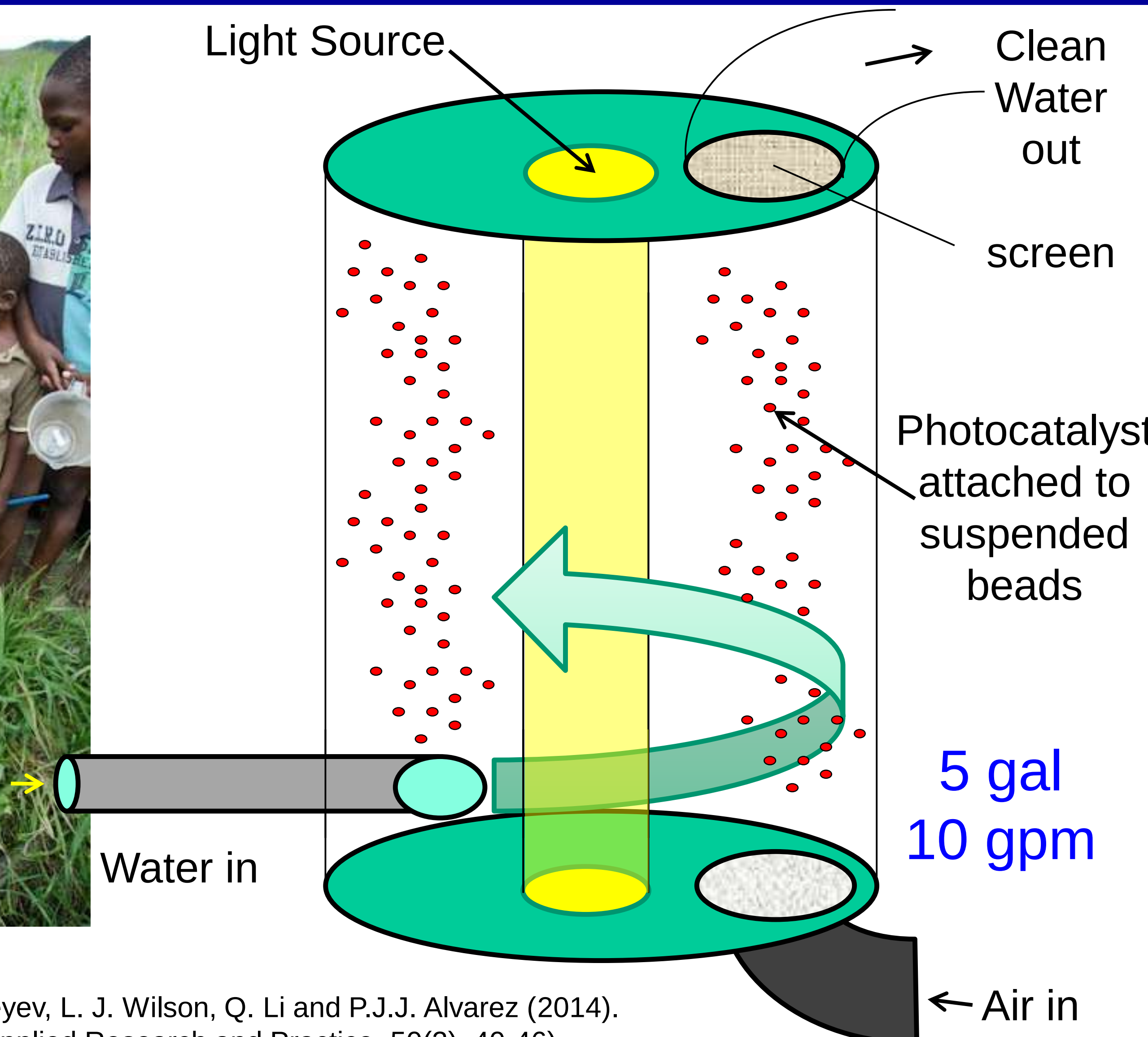


Photocatalytic treatment of emerging contaminants (pharmaceuticals, endocrine disruptors)



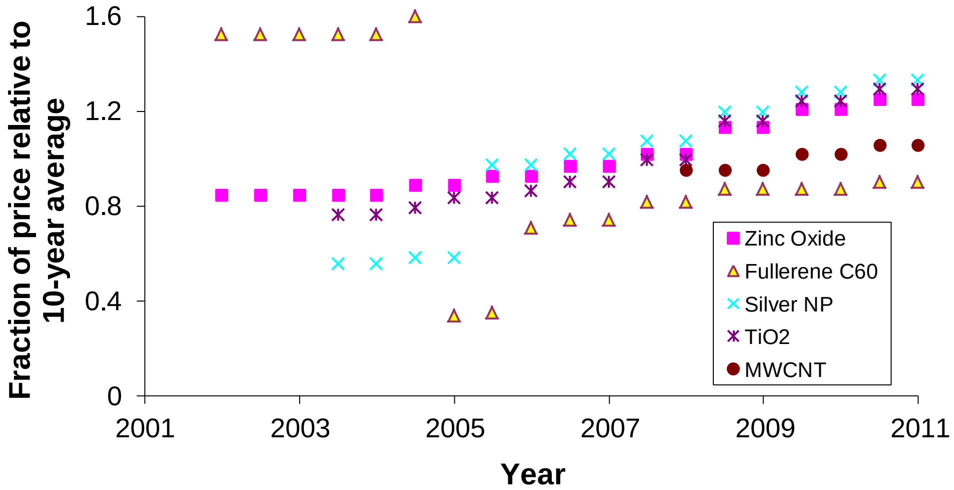
Lee J., S. Hong, Y. Mackeyev, C. Lee, L.J. Wilson, J-H Kim and P.J.J. Alvarez (2011). Environ. Sci. Technol. *45*: 10598–10604.

Fluidized Bed Photocatalytic Reactor for Point-of-Use Disinfection and Pesticide Removal

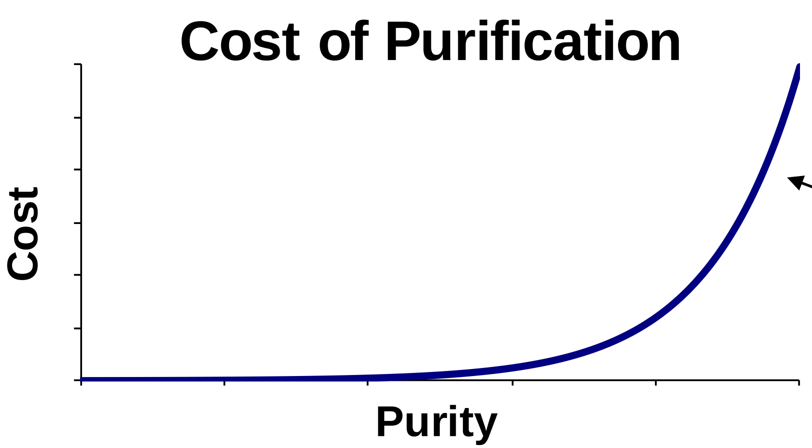


Brame J., V. Fattori, R. Clarke, Y. Mackeyev, L. J. Wilson, Q. Li and P.J.J. Alvarez (2014). Environmental Engineer and Scientist: Applied Research and Practice. 50(2), 40-46).

Need market-driven decrease ENM price



Few commercial applications
= low supply
→ prices stay high

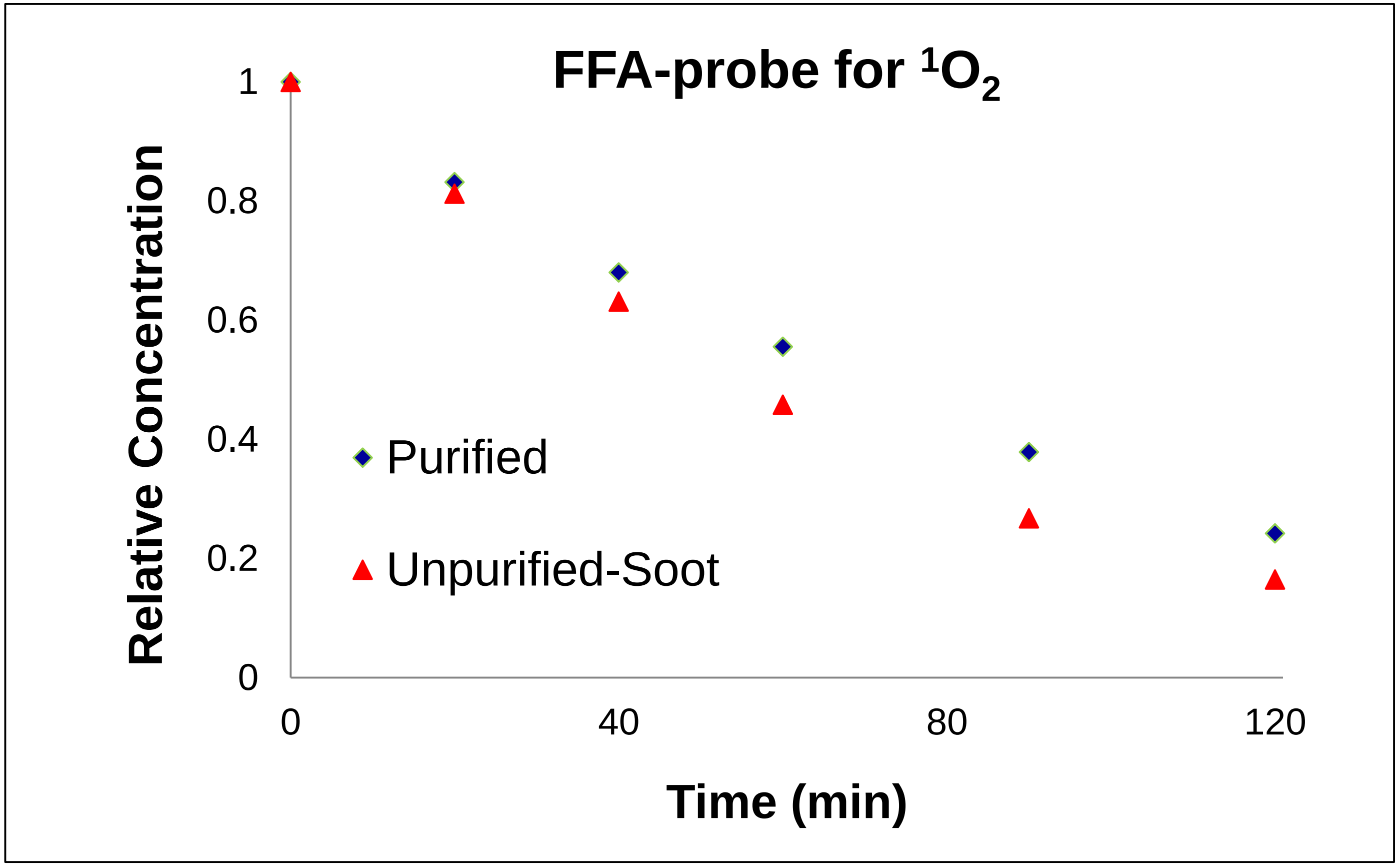


Most production is done for research (small quantities of highly purified material)

High purity requirements increase **separation cost** due to higher energy, solvent, & process time requirements

Avoid the diminishing returns of ultra high purity

Less pure amino-C_{60} cost less (20x) without significantly sacrificing reactivity



SUMMARY OF APPLICATIONS

- Low-energy desalination by nanophotonic MD or electrosorption
- DBP-free disinfection
- Advanced (photo)oxidation
- Selective nano-sorbents
- Multi-functional membranes
- Fouling- & corrosion-resistant surfaces

"People don't know what they want until you show it to them"

– Steve Jobs

Nanosystems Engineering Research Center for

Nanotechnology-Enabled Water Treatment

NEWT

Join Us!

www.newtcenter.org

NSF

RICE ASU UTEP Yale

Safer Use of ENMs

Risk = Hazard x Exposure

Hazard

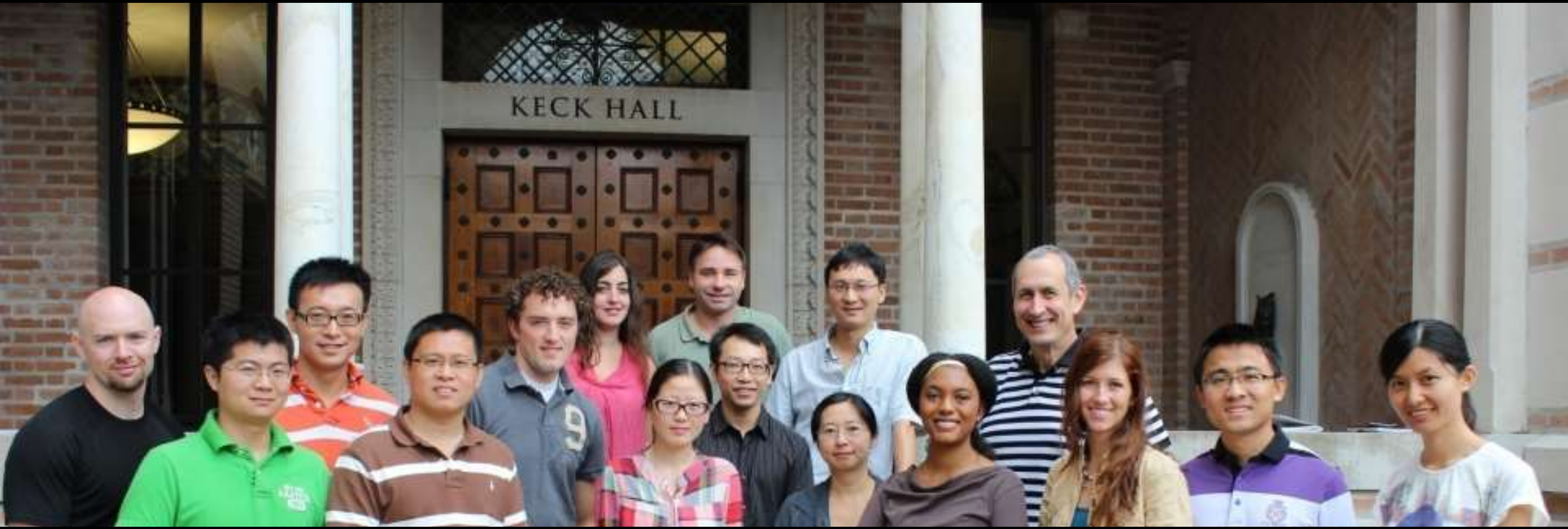
- Prioritize use of ENMs of benign, low-cost, and earth-abundant compositions (GRAS); Green Chemistry and Green Engineering
- Experts panel to select ENMs before incorporation into products
- Interface with TSCA in the US and REACH in the EU

Exposure

- Immobilize ENMs to minimize release and exposure and enable reuse (no free NPs)
- Model & monitor treated water for leaching
- Foster safety in manufacturing by iterating with OSHA on best practices
- Independent certification for meeting health & safety stds.

Thanks! - Graduate Students and Postdocs

NSF



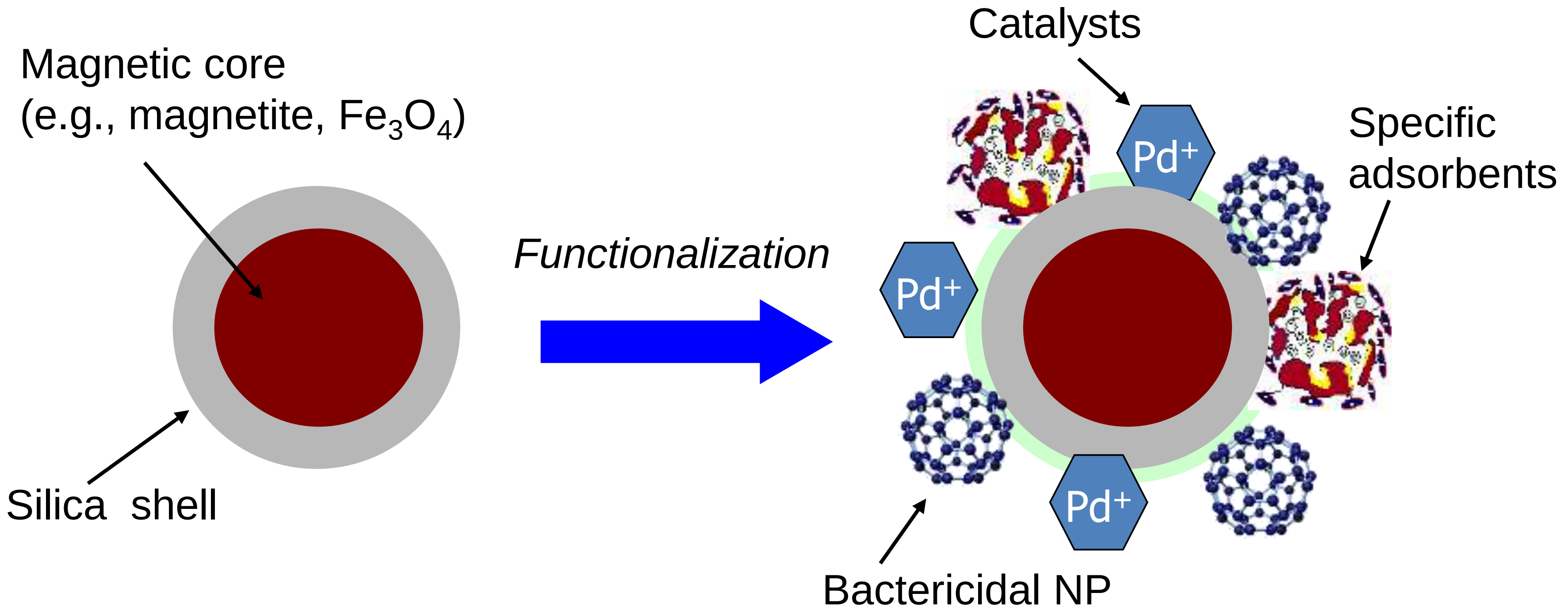
Ph.D. M. Vermace; Craig Hunt; Marcio da Silva; Nanh Lovanh; Alethia Vazquez; Roopa Kamath; Michal Rysz; Natalie Capiro; Delina Lyon; Rosa Dominguez, Dong Li; Diego Gomez, Jacques Mathieu, Leti Vega, Xiaolei Qu, **Jon Brame,** Jiawei Ma, Pingeng Yu, Mengyan Li, Jing Wang, Ana McPhail, O. Monzon

M.S.E. Gary Chesley; Sang-Chong Lieu; Pete Svebakken; Phil Kovacs; Rod Christensen; Marc Roehl; Ken Rotert; Brad Helland; Leslie Cronkhite; Annette Dietz; Bill Schnabel; Ed Ruppenkamp; Leslie Foster; Bryan Till; Nahide Gulensoy; Rebecca Gottbrath; Matt Wildman; Chad Laucamp; Todd Dejournet; Sascha Richter; Nanh Lovanh; Sara Kelley; Eric Sawvel; Jennifer Ginner; Sumeet Gandhi; Richard Keller; Jennifer Wojcik; Anitha Dasappa; Leslie Sherburne; Brett Sutton; Russ Sawvel; Andrea Kalafut; Roque Sanchez; Amy Monier; Isabel Raciny; **Katherine Zodrow**; Robert O'Callaham; Bill Mansfield

Postdocs Graciela Ruiz; Jose Fernandez; Byung-Taek Oh; D. Kim; Joshua Shrout; Laura Adams, Sufia Kafy; Lena Brunet; **Jaesang Lee**, Jiawei Chen; Shaily Mahendra; **Zongming Xiu; Yu Yang**

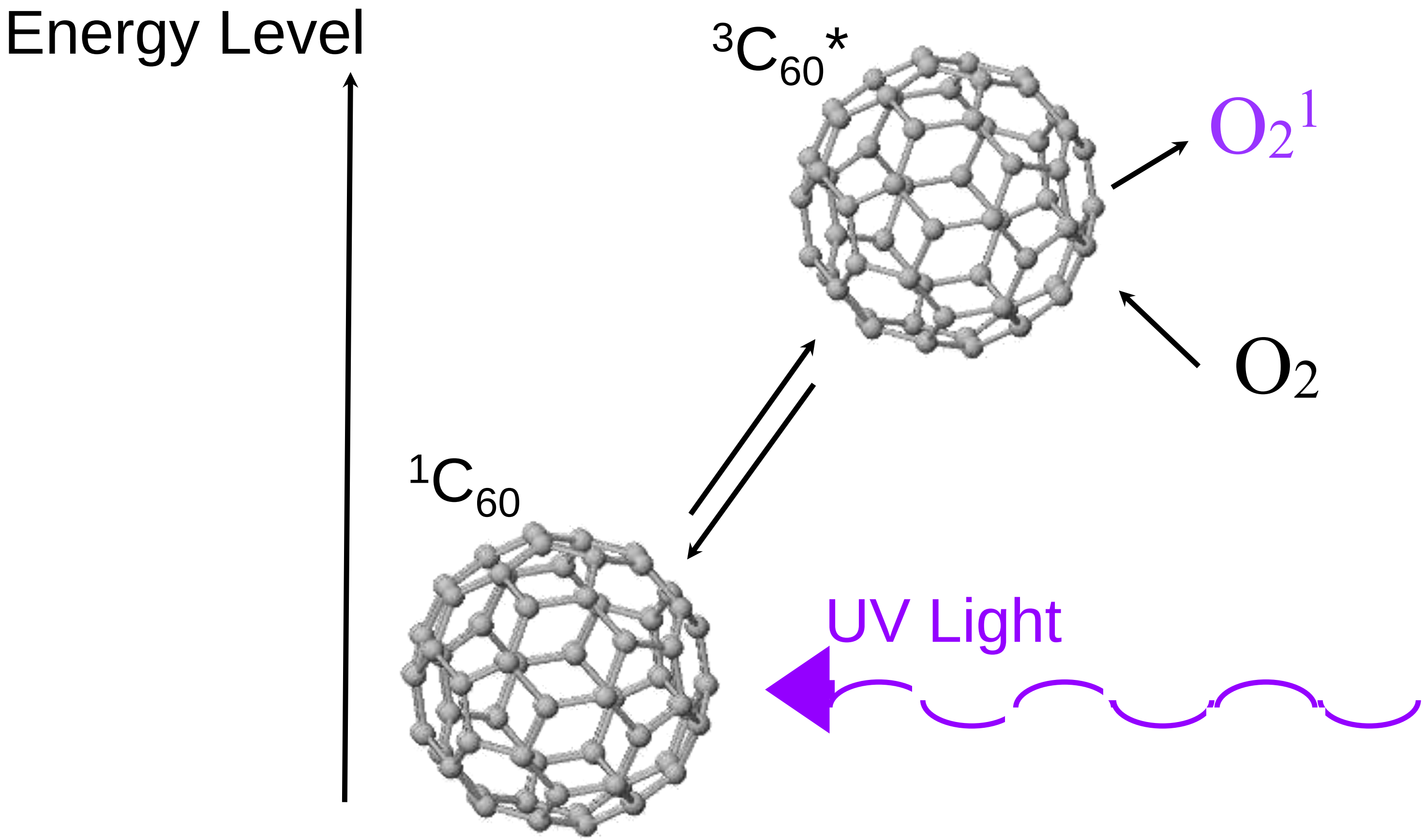
Enabling Technology
Multifunctional nanosorbents

Selective removal of target contaminants by functionalized nanoparticles supported in macroscale structures or subject to (low-energy) magnetic separation for enhanced removal kinetics & reuse



Opportunities for Engineered Nanomaterials (ENMs) in Water Treatment and Reuse

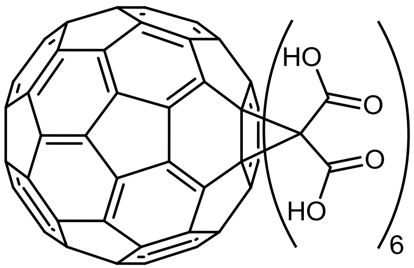
ENM Properties	***Examples of Enabled Technologies***
Large surface area to volume ratio	Superior sorbents (e.g., nanomagnetite or graphene oxides to remove heavy metals and radionuclides)
Enhanced catalytic properties	Hypercatalysts for advanced oxidation (TiO_2 & fullerene-based photocatalysts) & reduction processes (Pd/Au)
Antimicrobial properties	Disinfection and biofouling control without harmful byproducts
Multi-functionality (antibiotic, catalytic)	Fouling-resistant (self-cleaning and self-repairing) filtration membranes that operate with less energy
Self-assembly on surfaces	Surface structures and nanopatterns that decrease bacterial adhesion, biofouling, and corrosion
High conductivity	Novel electrodes for capacitive deionization (electro-sorption) and energy-efficient desalination
Fluorescence	Sensitive sensors to detect pathogens, priority pollutants



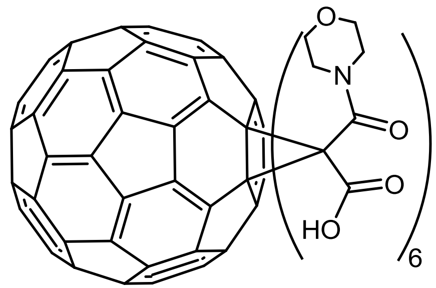
Light excites C_{60} to triplet state. Energy transfer between $^3C_{60}^*$ and molecular oxygen gives rise to singlet oxygen ($^1O_2$)

Hotze M., J. Labille, P.J.J. Alvarez and M. Wiesner (2008). Environ. Sci. Technol. 42, 4175–4180

“Water Soluble” Derivatized Fullerenes

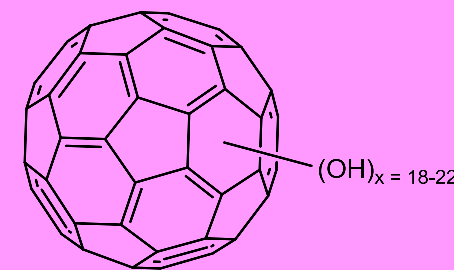


HC1



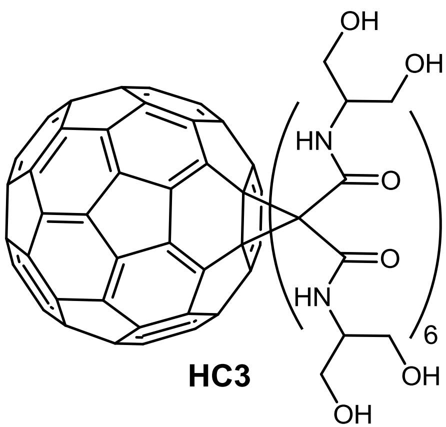
HC2

vs

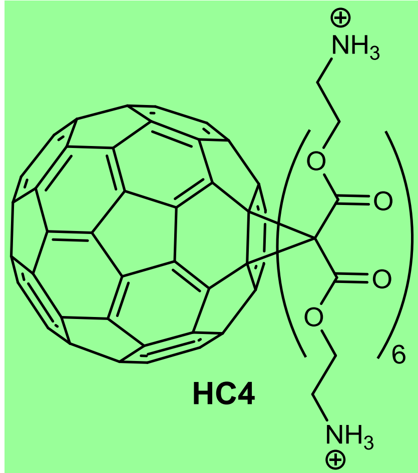


Fullerol

* Commercially Available, MER Corp.



HC3

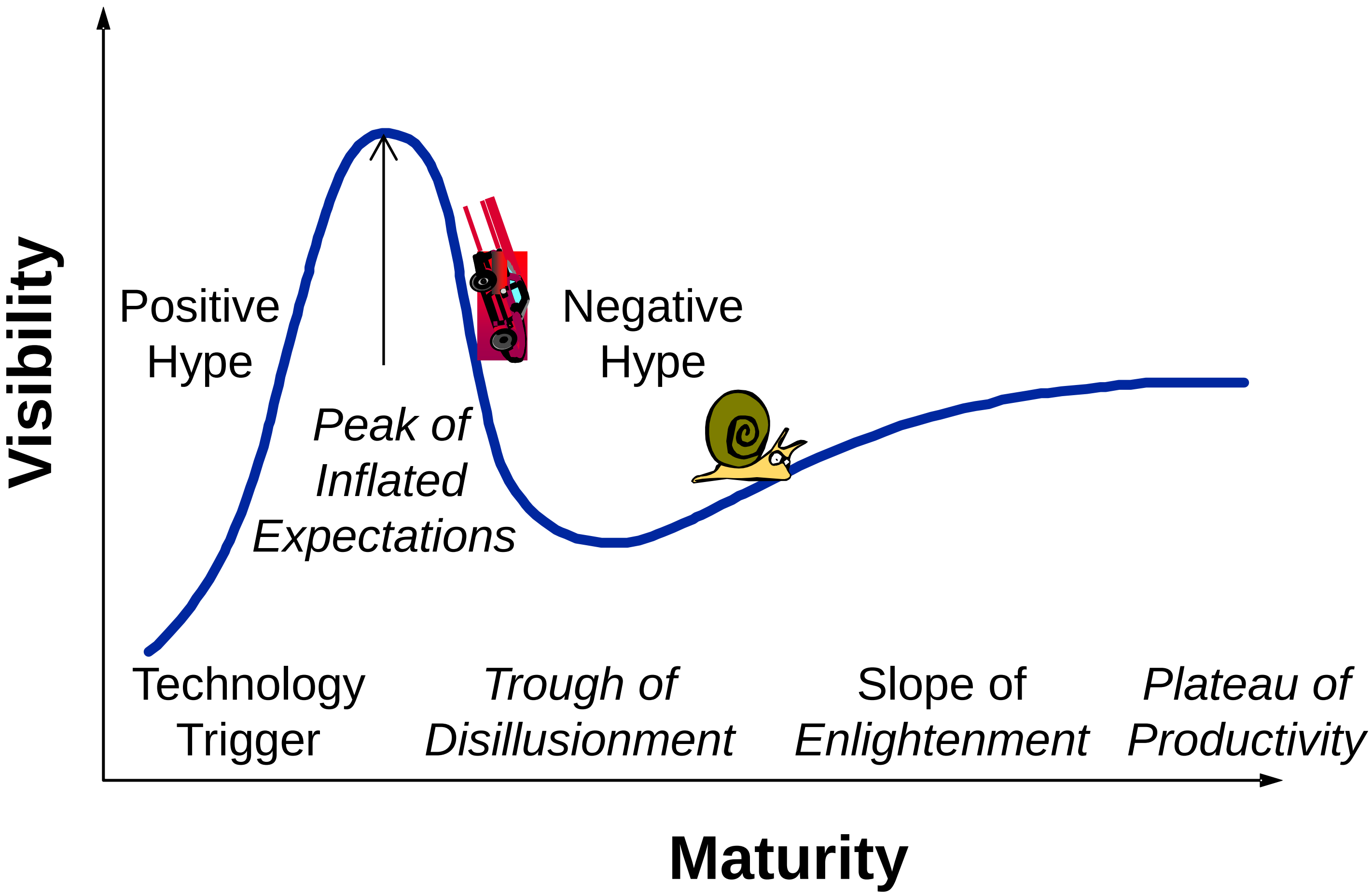


HC4

* Synthesized in Lon Wilson’s lab, Dept of Chemistry, Rice University (Bingel reaction)

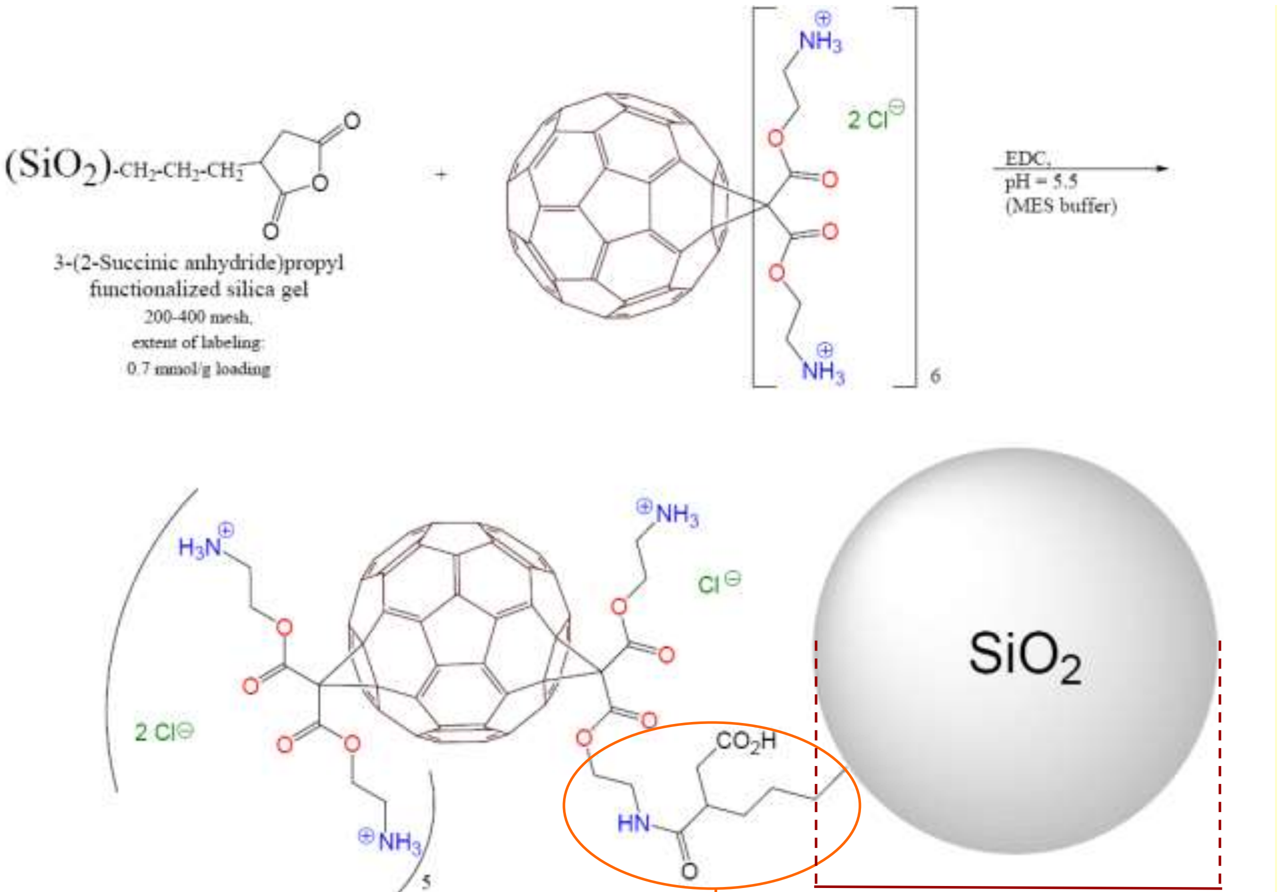
Superior $^{1}O_2$ Production confirmed by EPR & Laser Flash Photolysis

Quo Vadis, Nano?



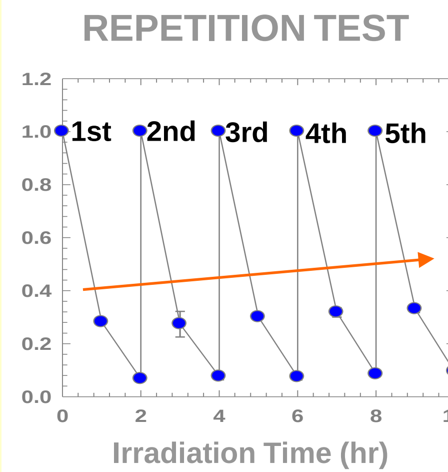
“Nanohype” - Berube

Immobilization of aminofullerene onto silica beads facilitates separation, reuse and recycling



NO C_{60} AGGREGATION ON THE SILICA SURFACE (HIGHER CATALYTIC AREA)

0.2 - 0.3 mm
EASILY SEPARABLE



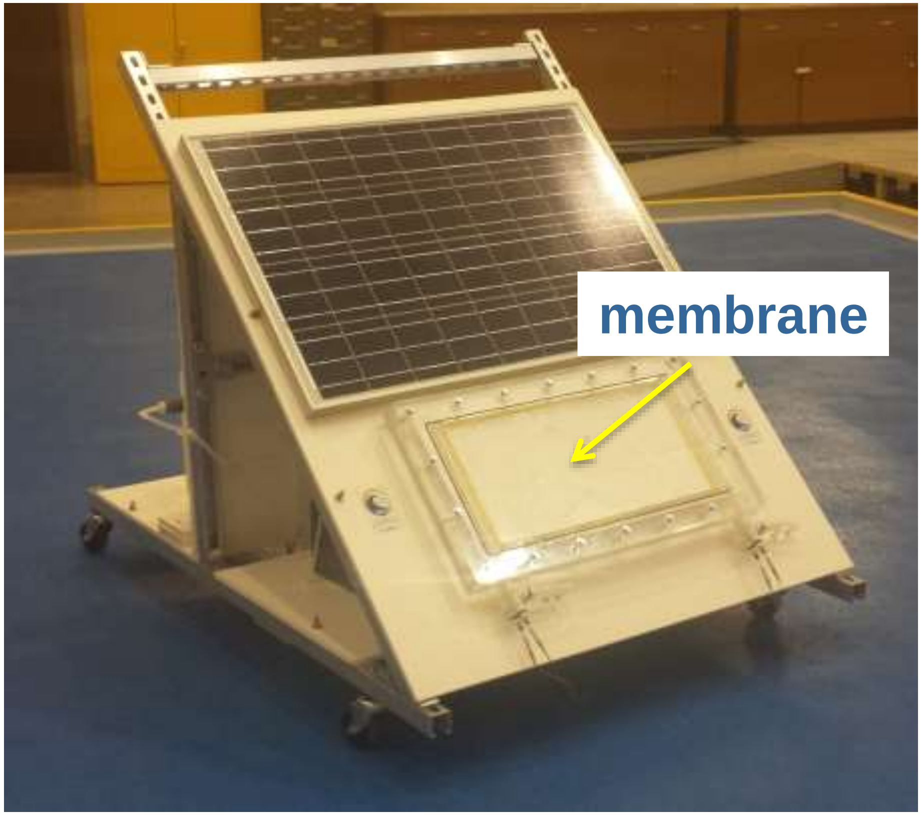
No loss of photo-activity

Lee, Mackeyev, Cho, Wilson, Kim and Alvarez (2010). *Environ. Sci. Technol.* 44: 9488–9495.

Pilot Solar MD

Built by Rice Undergraduates

Desalinates 8 L of seawater in 8 hours (enough DW for 4)



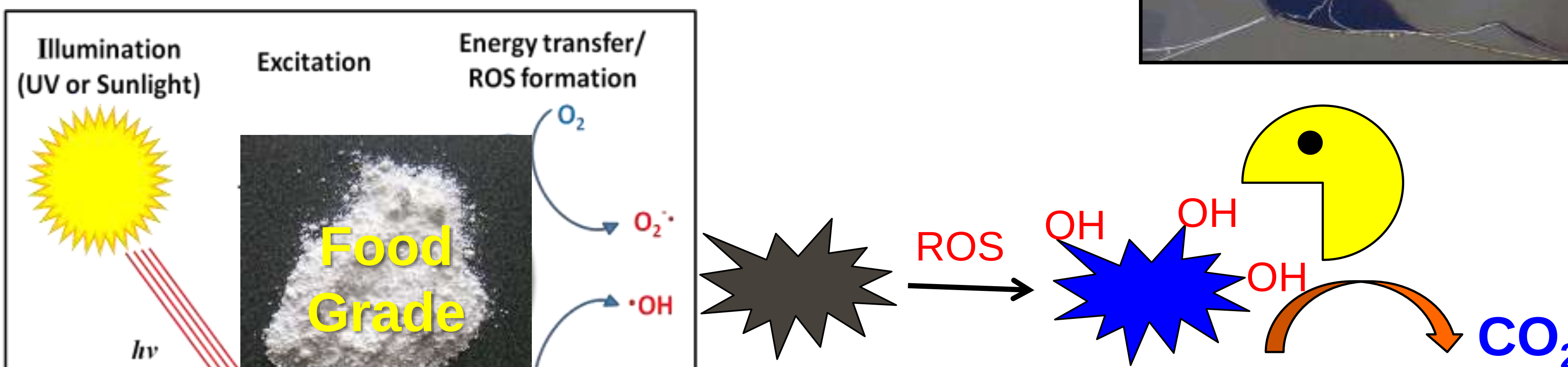
Responsible Nanotechnology

"With Great Power, Comes Great Responsibility”

Uncle Ben to Peter Parker in Spider Man

Paul Hermann Muller
Thomas Midgley

Photocatalytic Hydroxylation of Weathered Oil to Enhance Bioavailability and Bioremediation

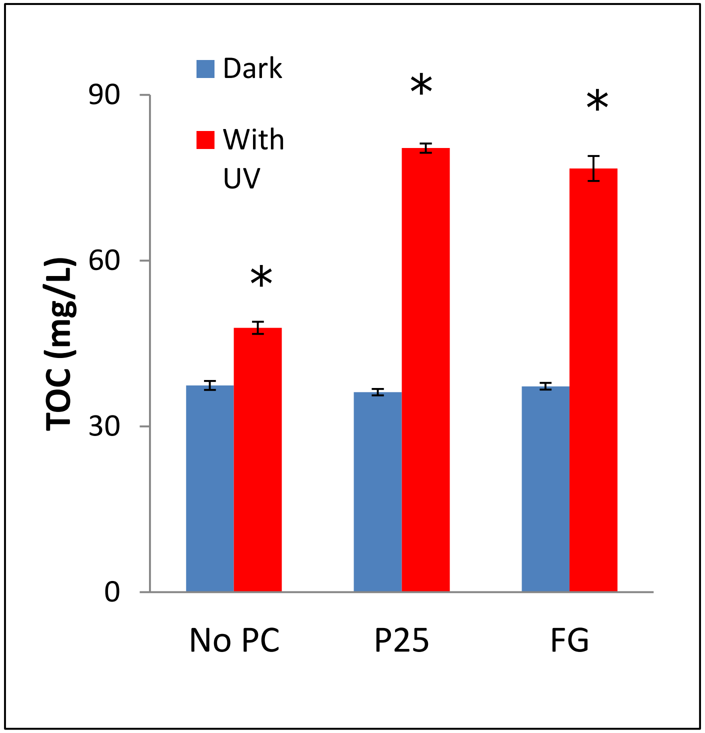


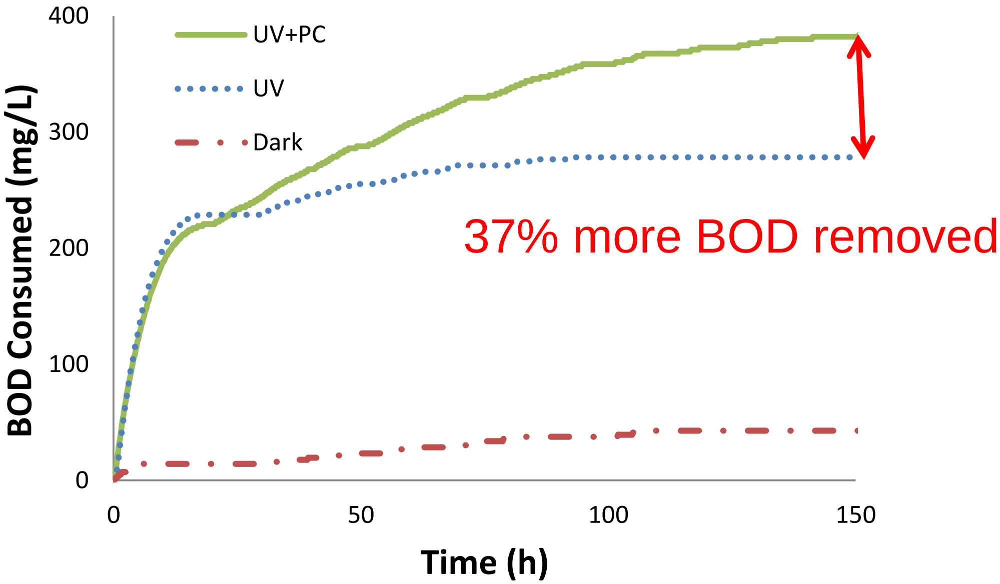
Photocatalyst

Weathered Oil (Recalcitrant)

Hydroxylated or Fragmented Residue (Bioavailable)

Photocatalysis Increased Solubilization and Biodegradation of Weathered Oil

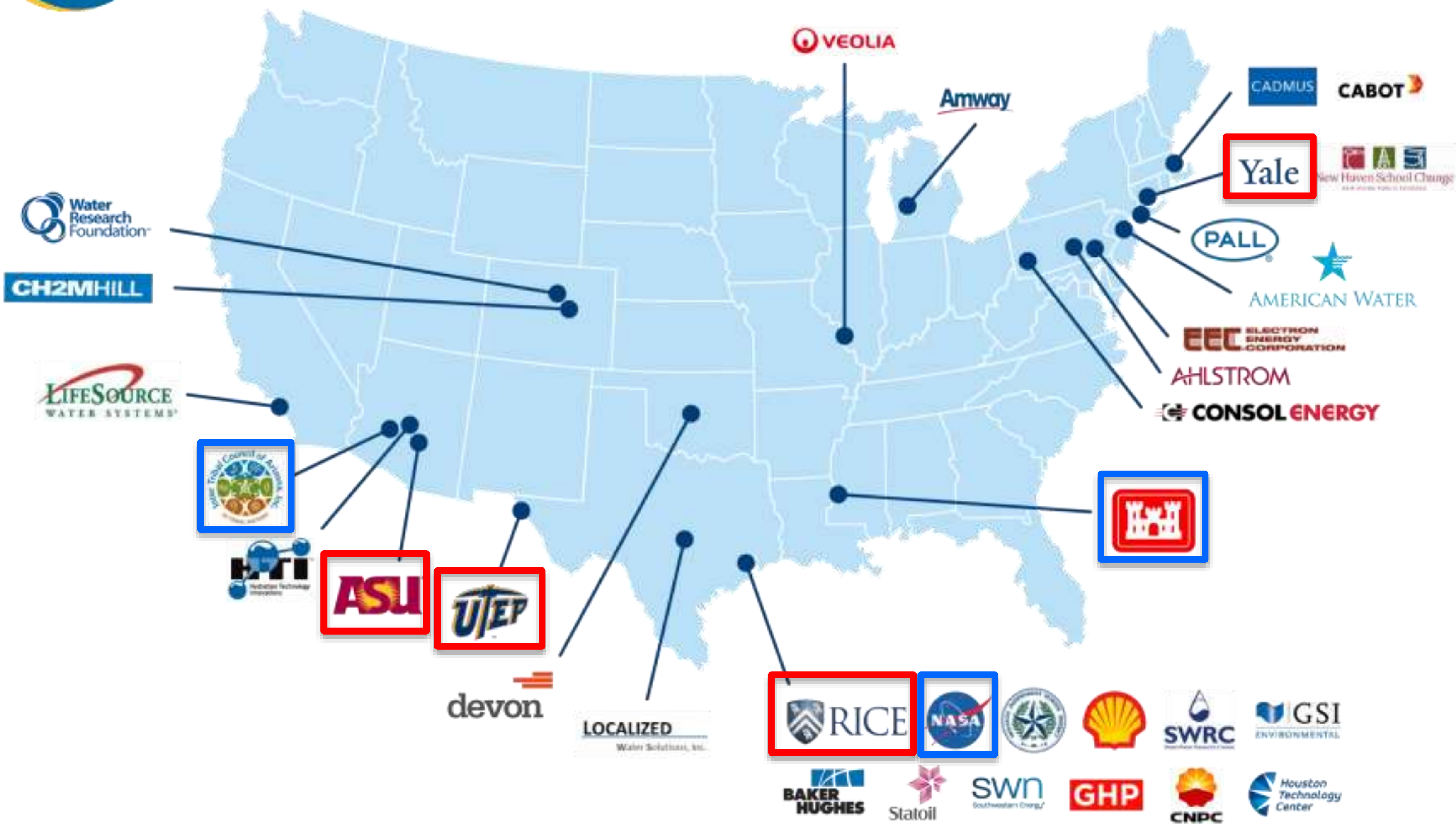




* statistically significant (*p* <0.05) after 1-day exposure

Brame J., S.W. Hong, J. Lee and P.J.J. Alvarez (2013). *Chemosphere* 90: 2315–2319.

Some of Our NEWT Partners



- Innovation across value chain (nanomaterial and equipment manufacturers, service providers, R&D and deployment partners, and users)

NEWT is Supported by Experienced Partners Across the Value Chain

Nanomaterial and advanced material manufacturers	EEC Electron Energy Corporation, CABOT, HTI Hydration Technology Innovations, Purifics
Equipment manufacturers	AHLSTROM, Amway, LifeSource Water Systems, PALL
Research, development and deployment partners	NASA, NSF, CADMUS, GHP, Houston Technology Center, UNESCO, Water Research Foundation, wetsus
Service providers	American Water, Baker Hughes, CH2MHILL, GSI Environmental, Localized Water Solutions, Inc., SWRC, Veolia
End users	CNPC, CONSOL Energy, devon, swn Southwestern Energy, Statoil, Inter Tribal Council of Arizona, Inc.

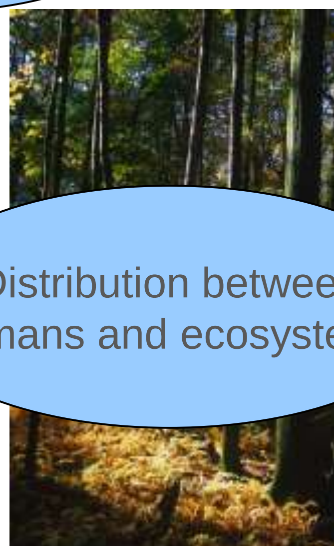
International Partners

- Co-development and production of advanced multifunctional materials
- Globally-relevant research and education experiences for students
- Testbed sites for applications in fast-growing water markets

7 Grand Challenges Related to Water

Safe water quality for a growing population

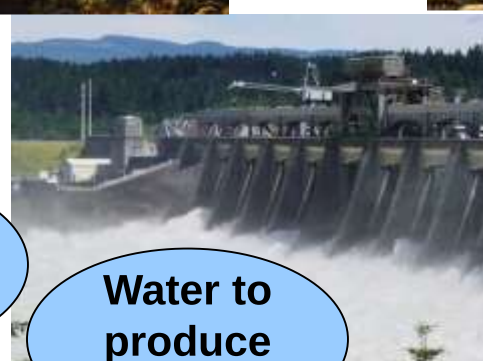
Water infrastructure (distribution & collection)



Distribution between humans and ecosystems

Water induced disasters and flood protection

Enough food for all

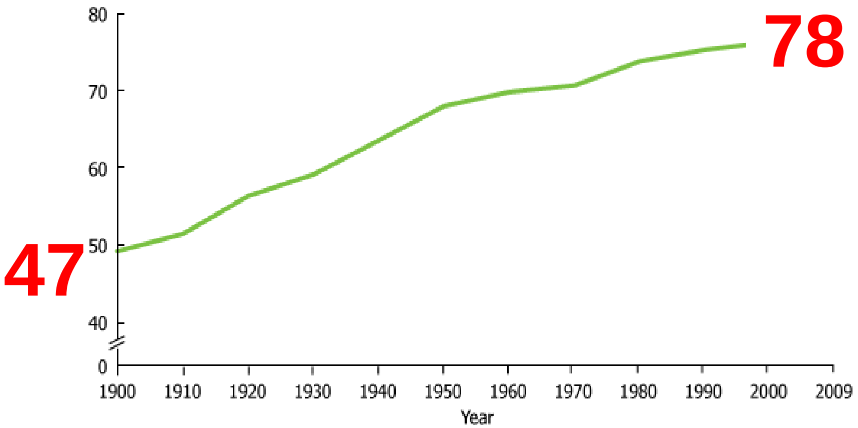


Water to produce energy

Solution for water conflicts and fair water share for all

Clean Water Is Also Critical for Enhancing Human Capacity

American's life expectancy at birth



http://www.prb.org/Publications/Articles/2011/biodemography.aspx

- Public health
- Energy production
- Food security
- Economic development

- 43 million Americans lack access to municipal water; 800 million worldwide lack access to safe water
- Global market for drinking water ~ $700 billion
- Larger market for industrial wastewater reuse