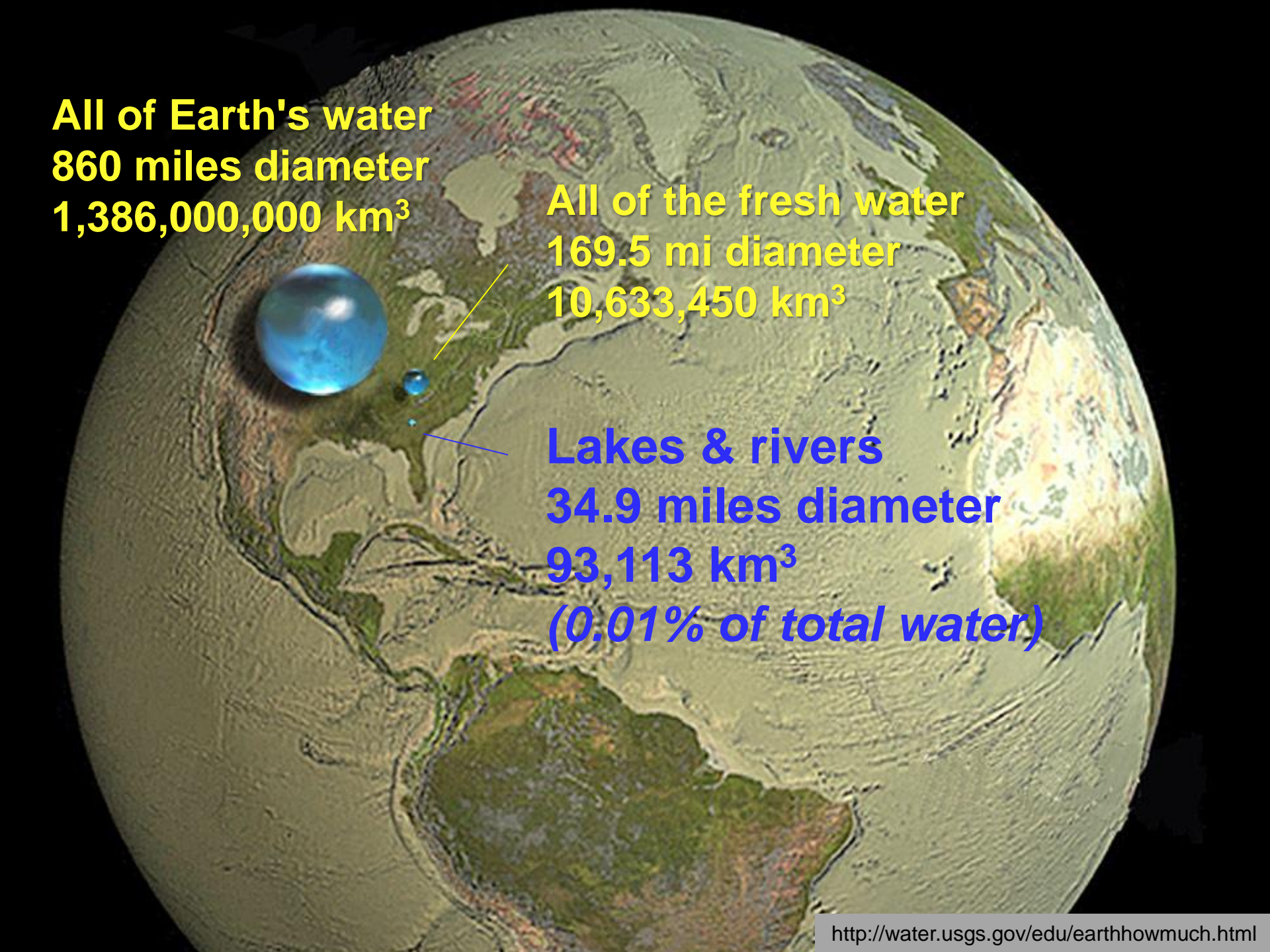


Nanotechnology and Water: Environmental Applications & Implications



Pedro J.J. Alvarez, Rice University
Sustainable Nanotechnology Organization
Marina del Rey, 5 November 2017

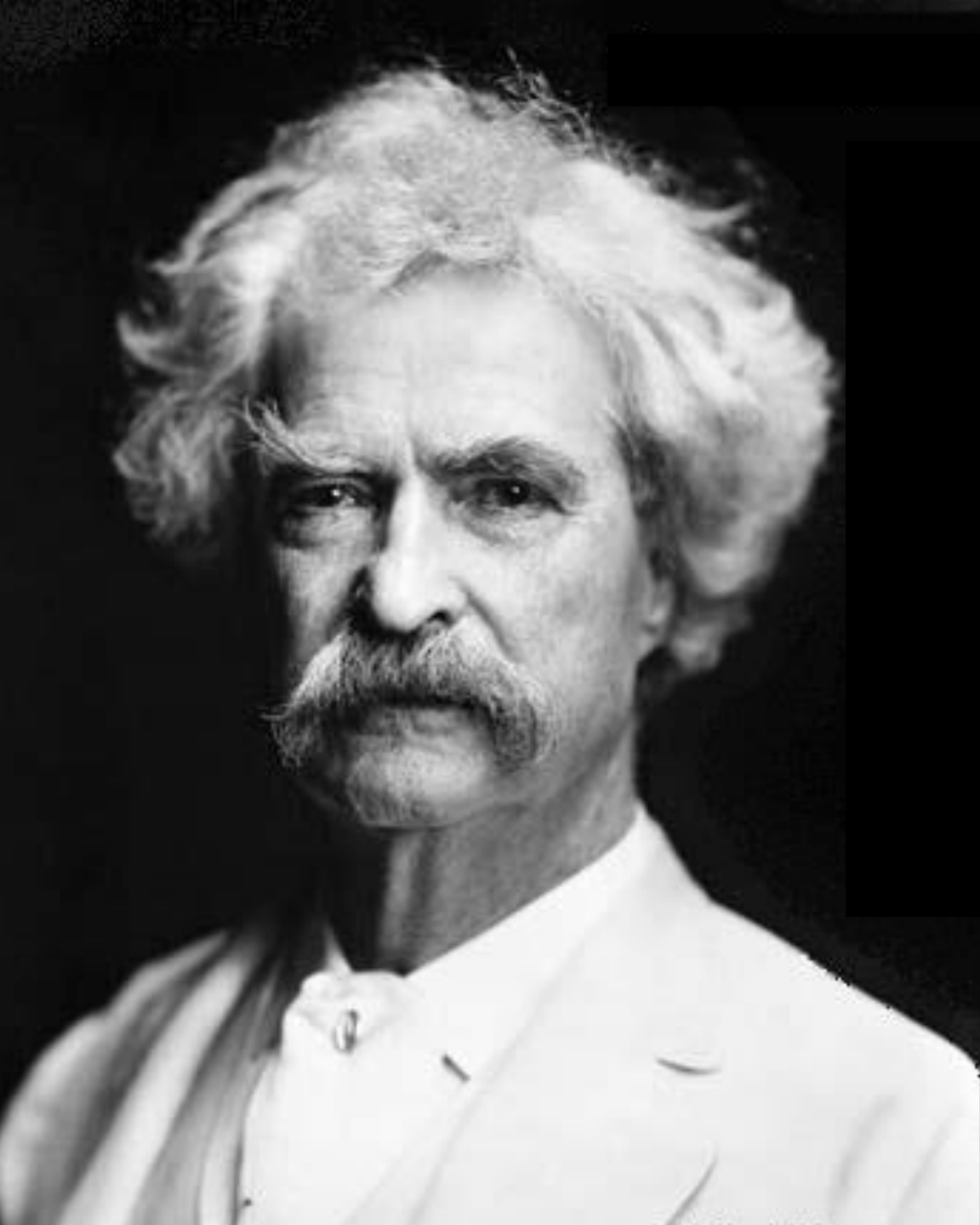




All of Earth's water
860 miles diameter
1,386,000,000 km³

All of the fresh water
169.5 mi diameter
10,633,450 km³

Lakes & rivers
34.9 miles diameter
93,113 km³
(0.01% of total water)

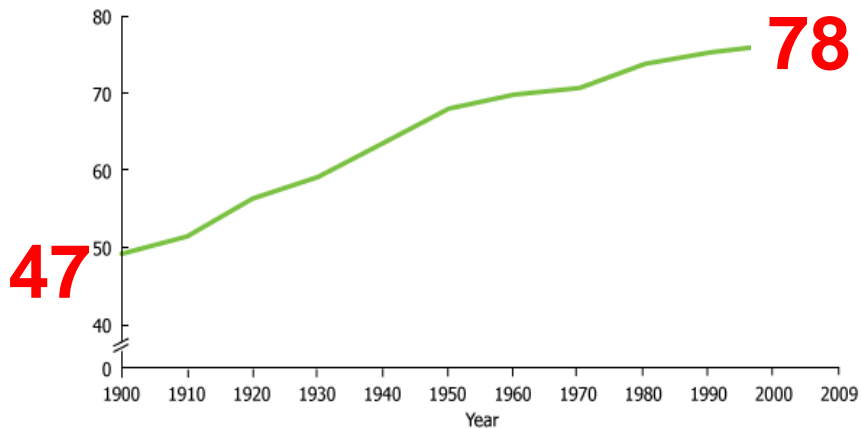


***“Whiskey is for
Drinking;
Water is for
Fighting Over”***

~Mark Twain

Clean Water Is 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



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



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



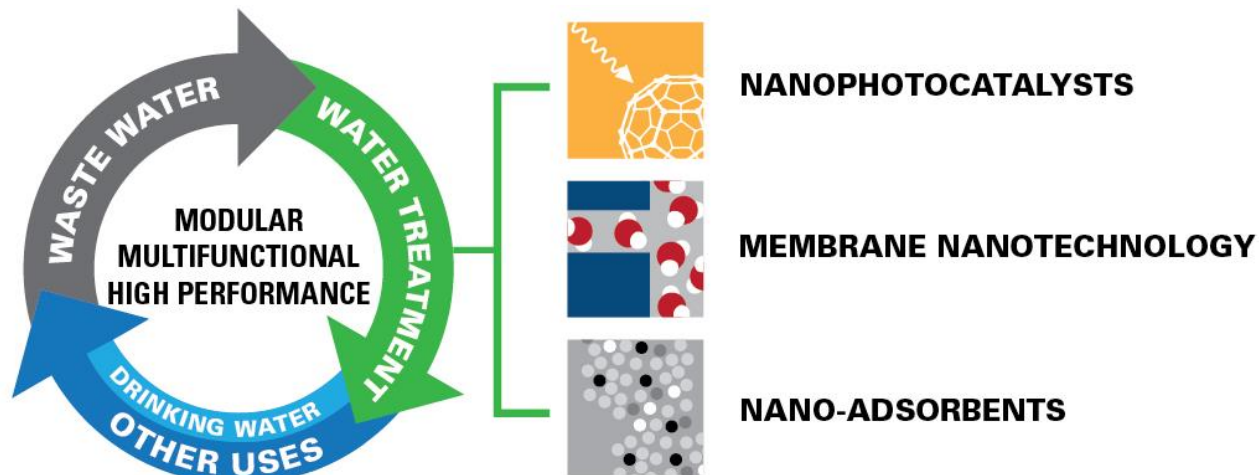
<http://switchboard.nrdc.org/blogs/rhammer/fracking-2.jpg>



Why Nano?

Leap-frogging opportunities to:

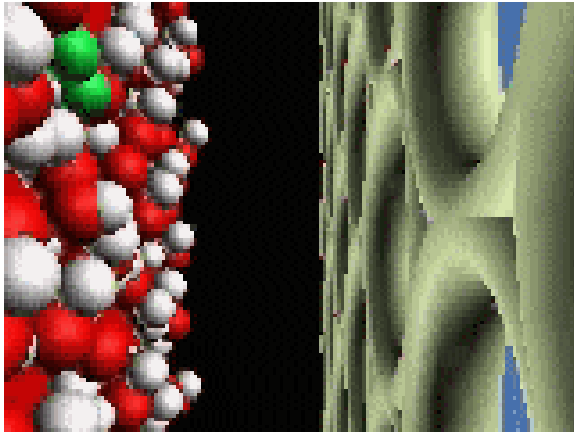
- Tap unconventional water sources, & reduce cost of remote water treatment (*multifunctionality and higher selectivity*)
- Transformative, modular and more efficient chemical treatment processes that harvest solar energy to lower costs and generate less waste





Nanophotonics-Enhanced Membrane Distillation

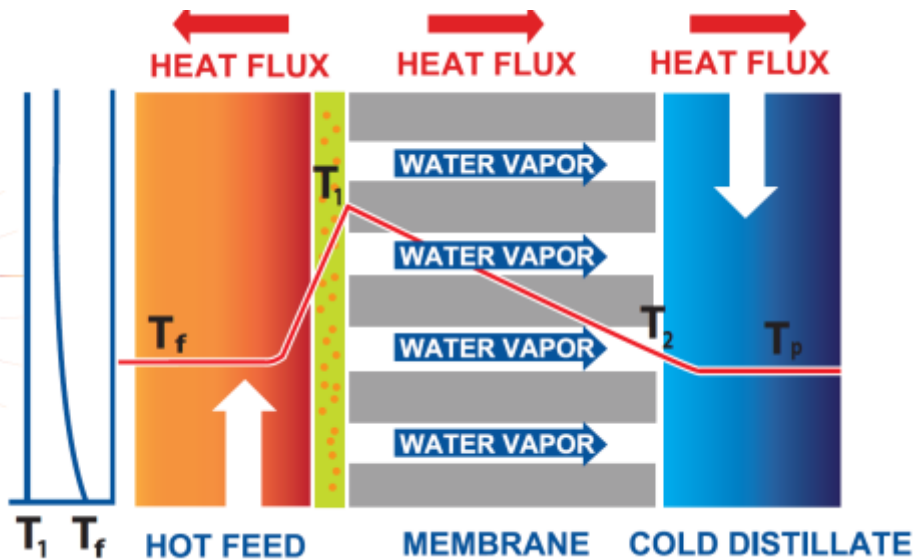
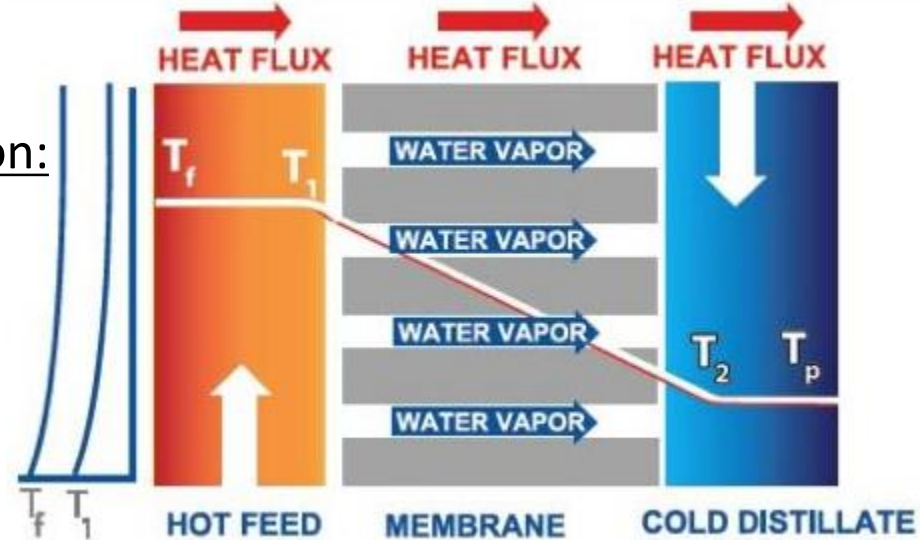
Membrane Distillation



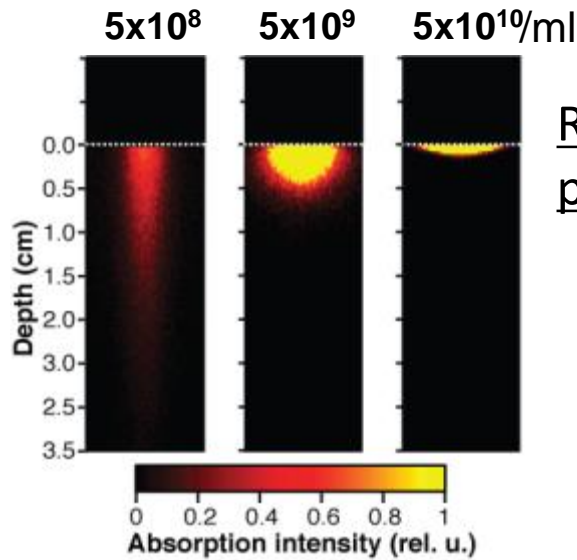
Temp. polarization:

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

Reduces
T gradient
by up to 70%



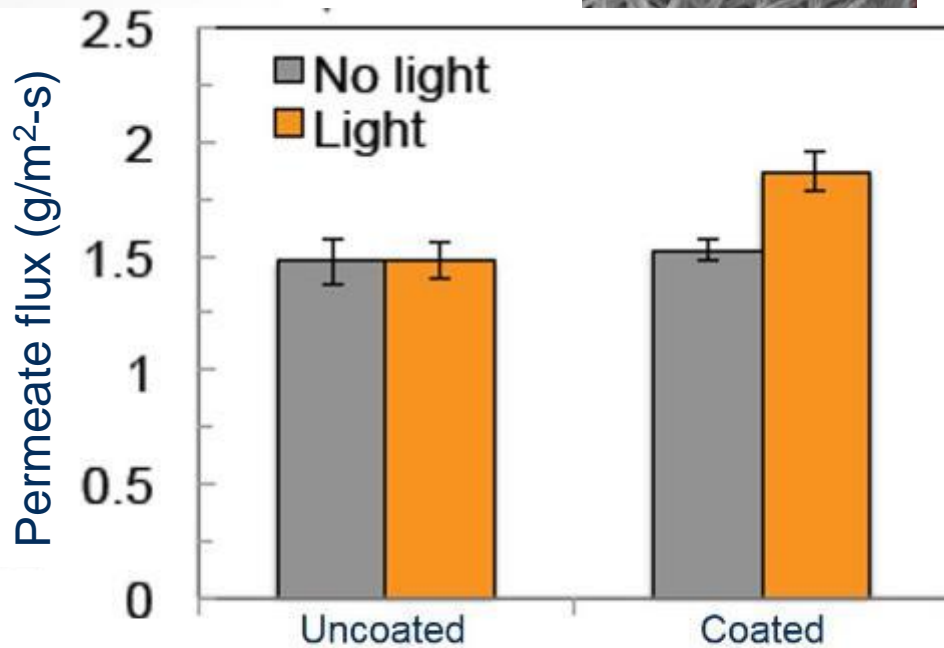
www.desalination.biz



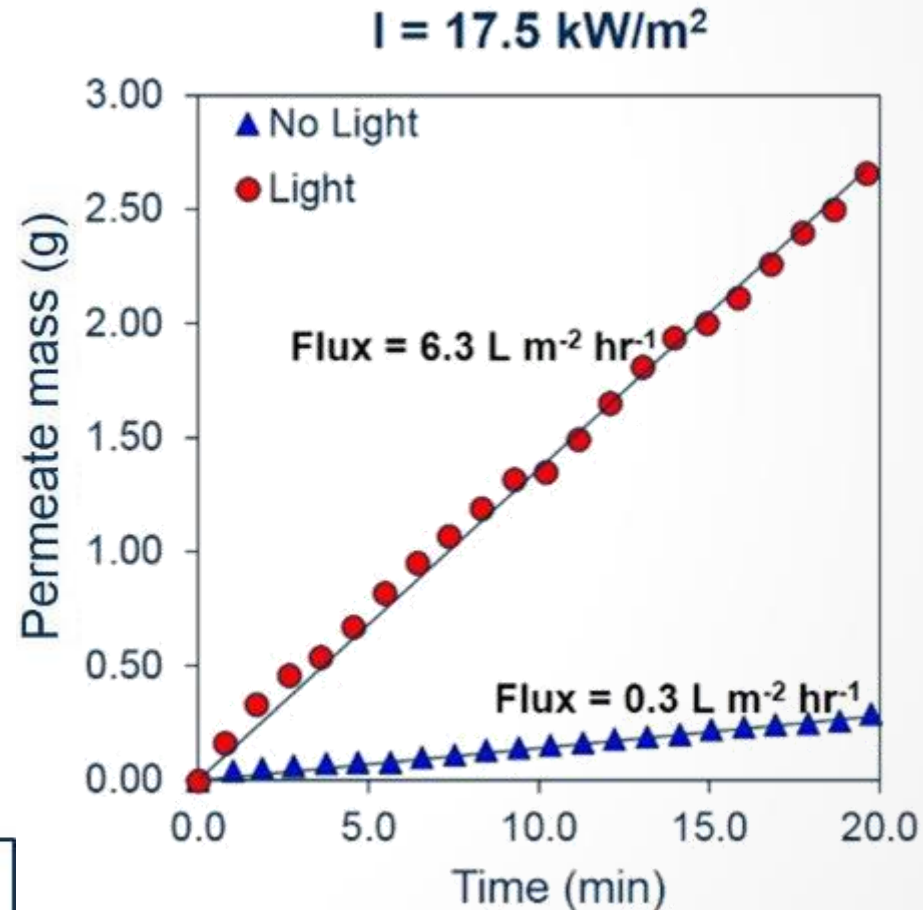
Reverse temp.
polarization:



Photothermal Coating Enhances Membrane Permeate Flux



T_f = 35 ° C, T_p = 20 ° C
Light source: simulated sunlight at 1 sun unit





Pilot Solar MD

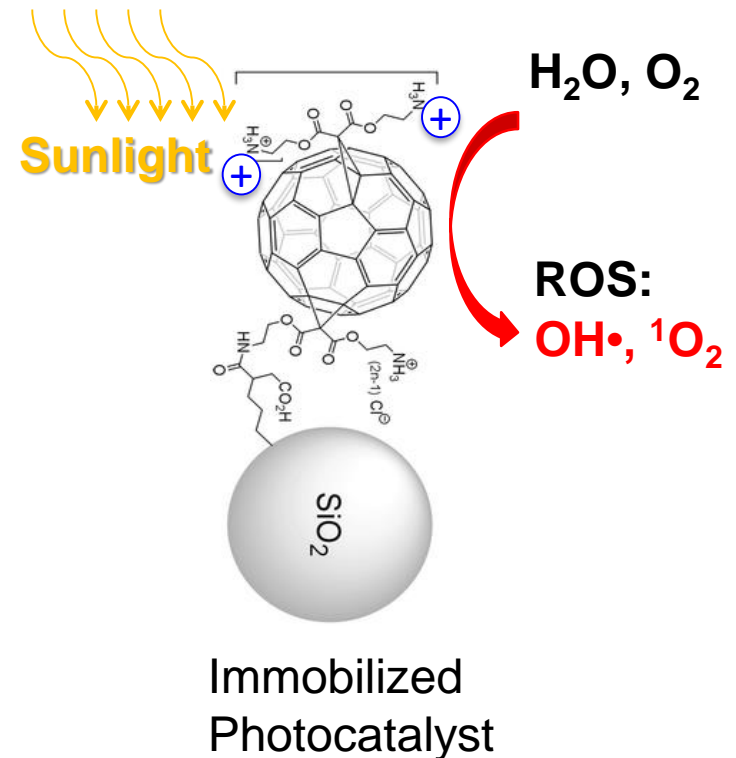
Desalinates 8 L of seawater in 8 hours (enough DW for 4)



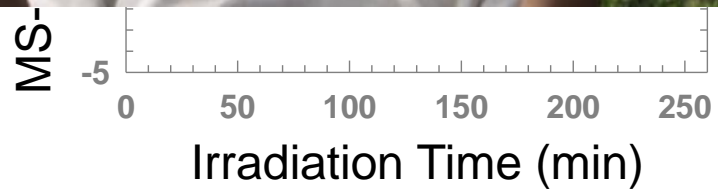


(Photo)Disinfection & Advanced Oxidation

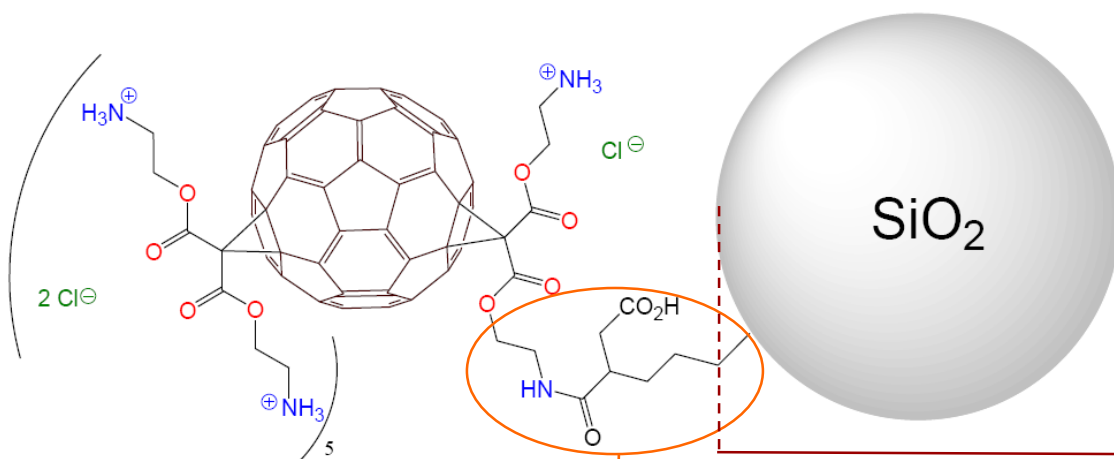
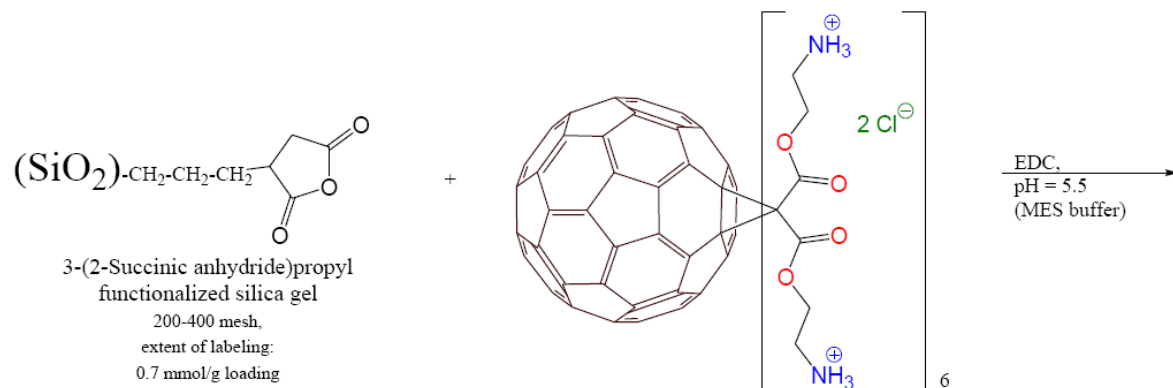
- Nano(photo)catalysts that use solar radiation to generate ROS that destroy resistant microbes and recalcitrant pollutants without harmful disinfection byproducts
- Bait and hook approach to attract pollutant to site of ROS generation



Advantages of Amino-C₆₀ as Photocatalytic Disinfectant



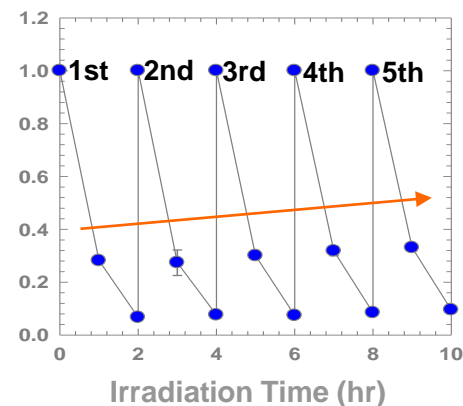
Immobilization of aminofullerene onto silica beads facilitates separation, reuse and recycling



**NO C₆₀ AGGREGATION
ON THE SILICA SURFACE
(HIGHER CATALYTIC AREA)**

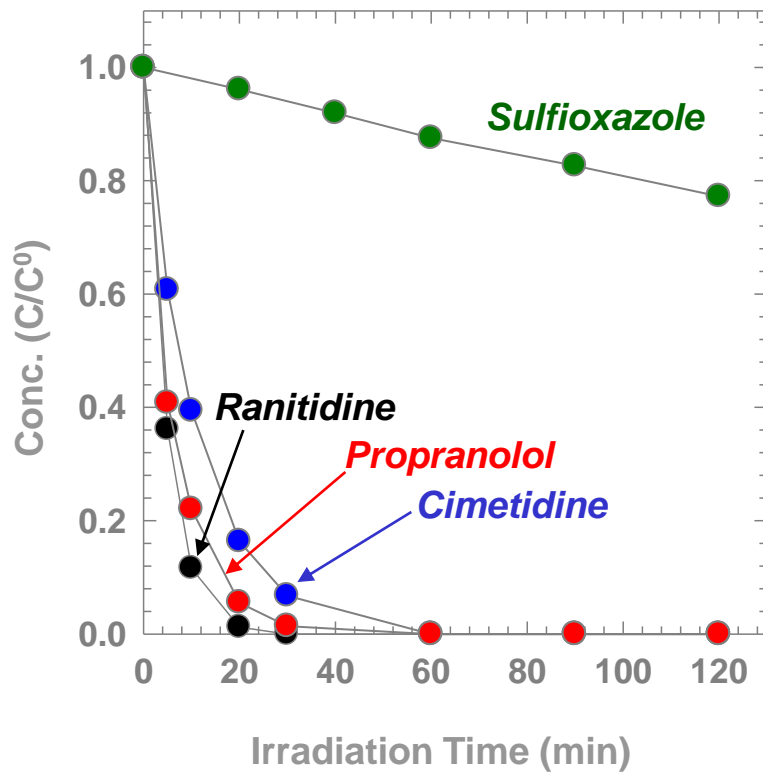
**0.2 - 0.3 mm
EASILY SEPARABLE**

REPETITION TEST



**No loss of
photo-activity**

Photocatalytic treatment could also polish WWTP effluents (pharmaceuticals, endocrine disruptors)

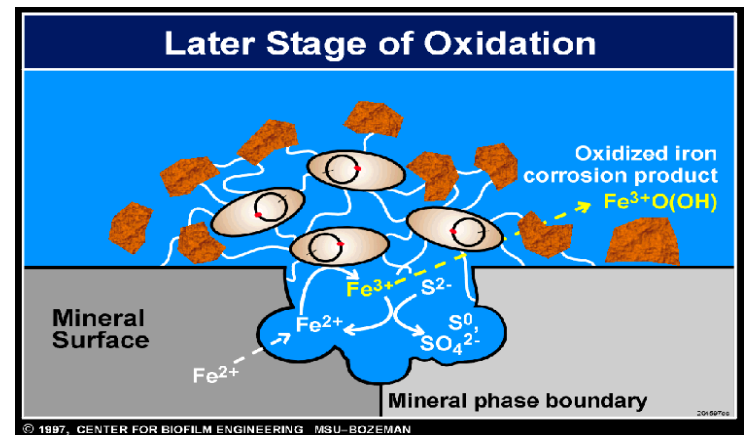




Biofilms

- Surface attached community of microorganisms embedded in a “slimy” matrix
 - Polysaccharides
 - Protein
 - Lipids
- **Can harbor problematic bacteria (pathogens, corrodors)**
- **Difficult to eradicate** (limited penetration by chemical disinfectants)

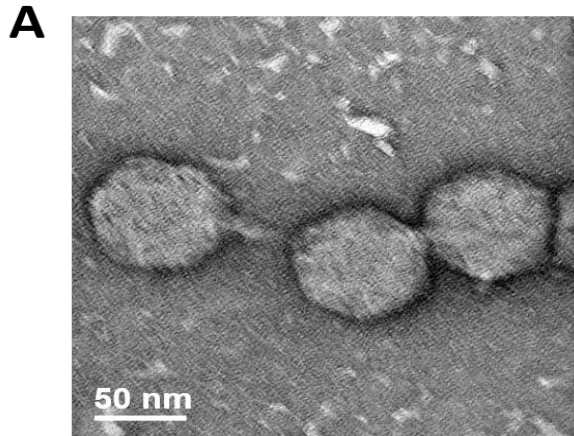
- Can cause corrosion through
 - Production of organic acids
 - Depassivation of surfaces
 - Cathodic depolarization
 - Direct attack of a component



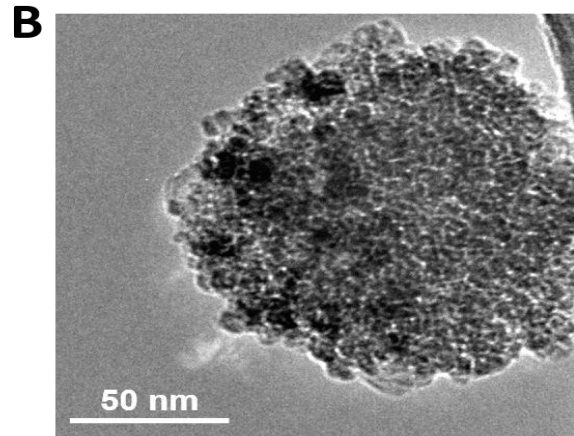
Source: <http://www.biofilm.montana.edu/resources/images/biofilms-nature/oxidation-late-stage.html>



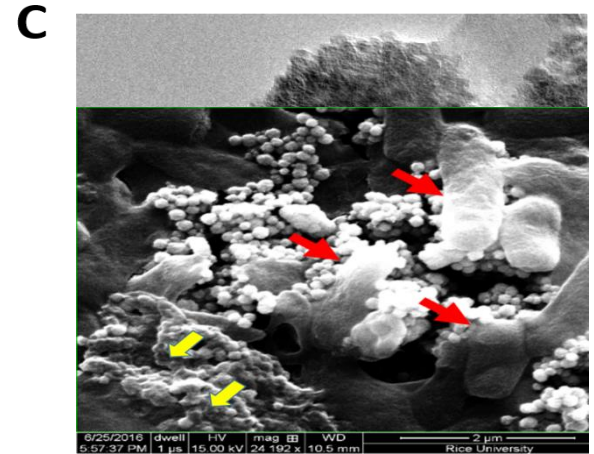
Phage conjugation with magnetic colloidal nanoparticle clusters (CNCs) for enhanced biofilm penetration under a weak magnetic field



Polyvalent phages

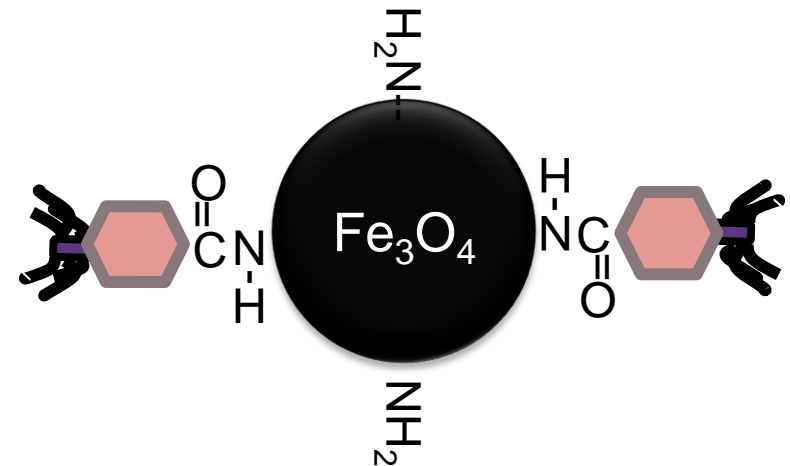


Chitosan-coated Fe_3O_4



CNCs infecting bacteria

Phage tail recognizes target bacteria →





Phage-CNCs complexes are more effective at penetrating & treating biofilms than free phages

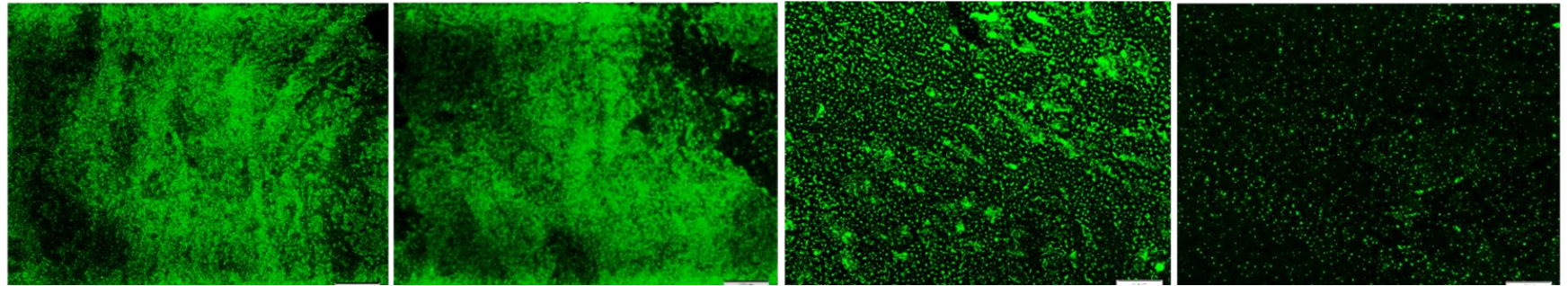
Control

CNCs-only

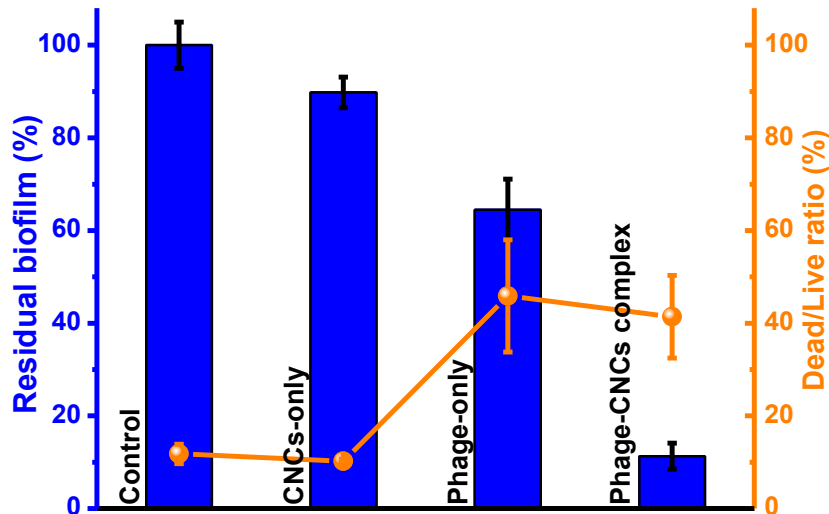
Phage-only

Phage-CNCs

A



B

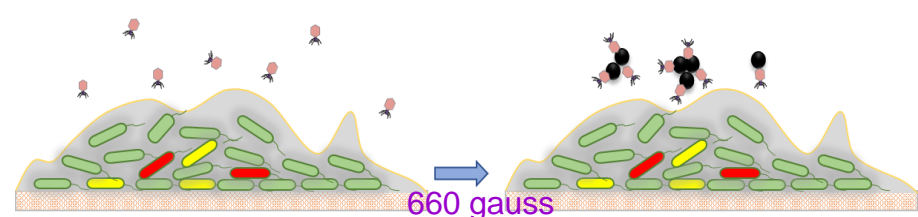


Free phage

Nano-conjugated phage

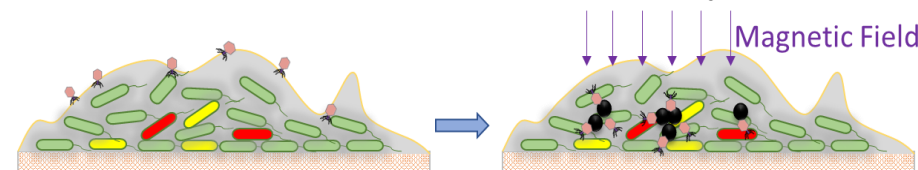
X Phage diluted

✓ Phage concentrated



X Biofilm protection

✓ Enhanced penetration





Summary of Accomplishments

- Low-energy (solar-driven) desalination by nanophotonic MD or electrosorption
- Disinfection without harmful byproducts and selective advanced (photo)oxidation
- Selective nano-sorbents
- Fouling-resistant membranes



*“People don't know what they want
until you show it to them”*

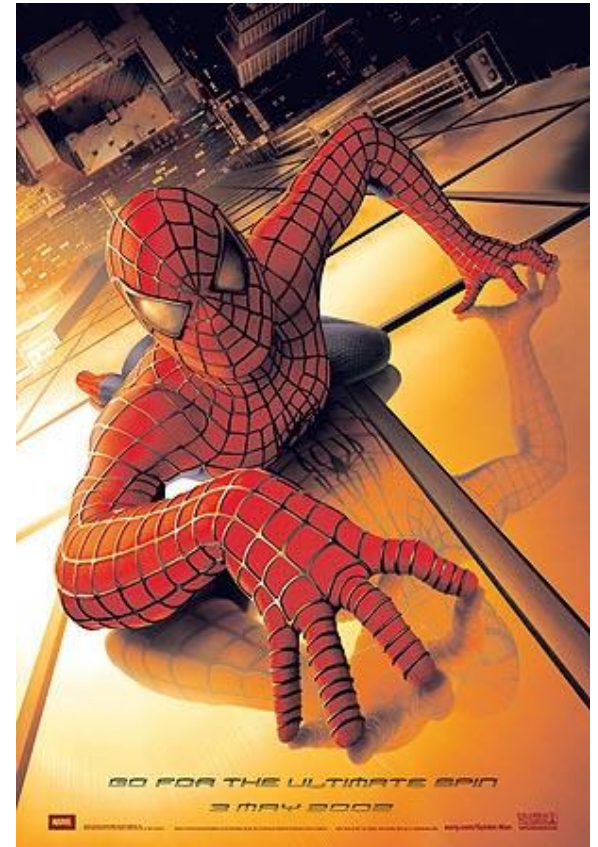
– Steve Jobs

Responsible Nanotechnology

"With Great Power, Comes Great Responsibility"

Uncle Ben to Peter Parker in Spider Man

Paul Hermann Muller
Thomas Midgley



Silver Nanoparticles (AgNPs): Toxicity Mechanisms & Unintended Consequences

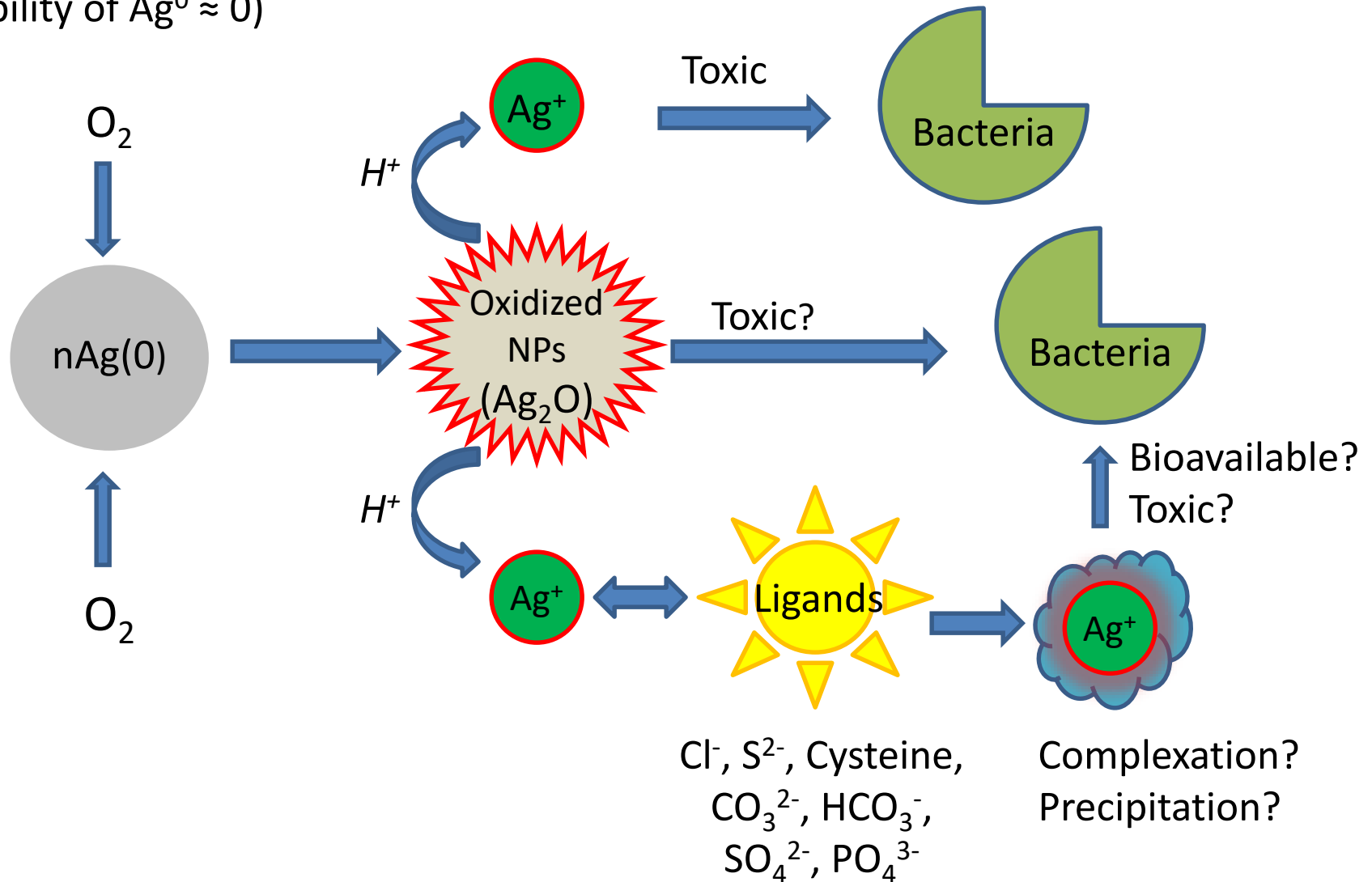


Is the antimicrobial activity of silver due to the nanoparticles themselves, or to the released Ag⁺ ions, or both?

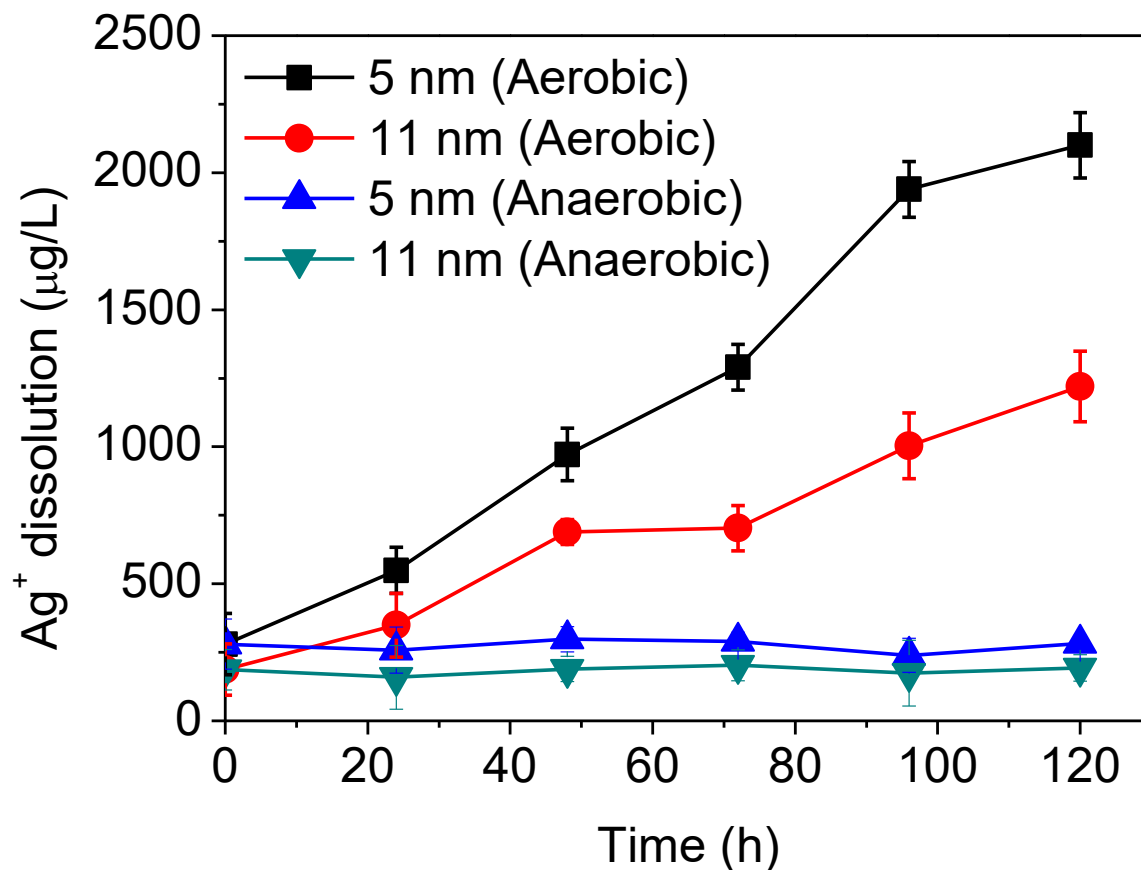
- And how do environmental conditions and water chemistry affect their relative influence?

Bioavailability and Toxicity of nAg

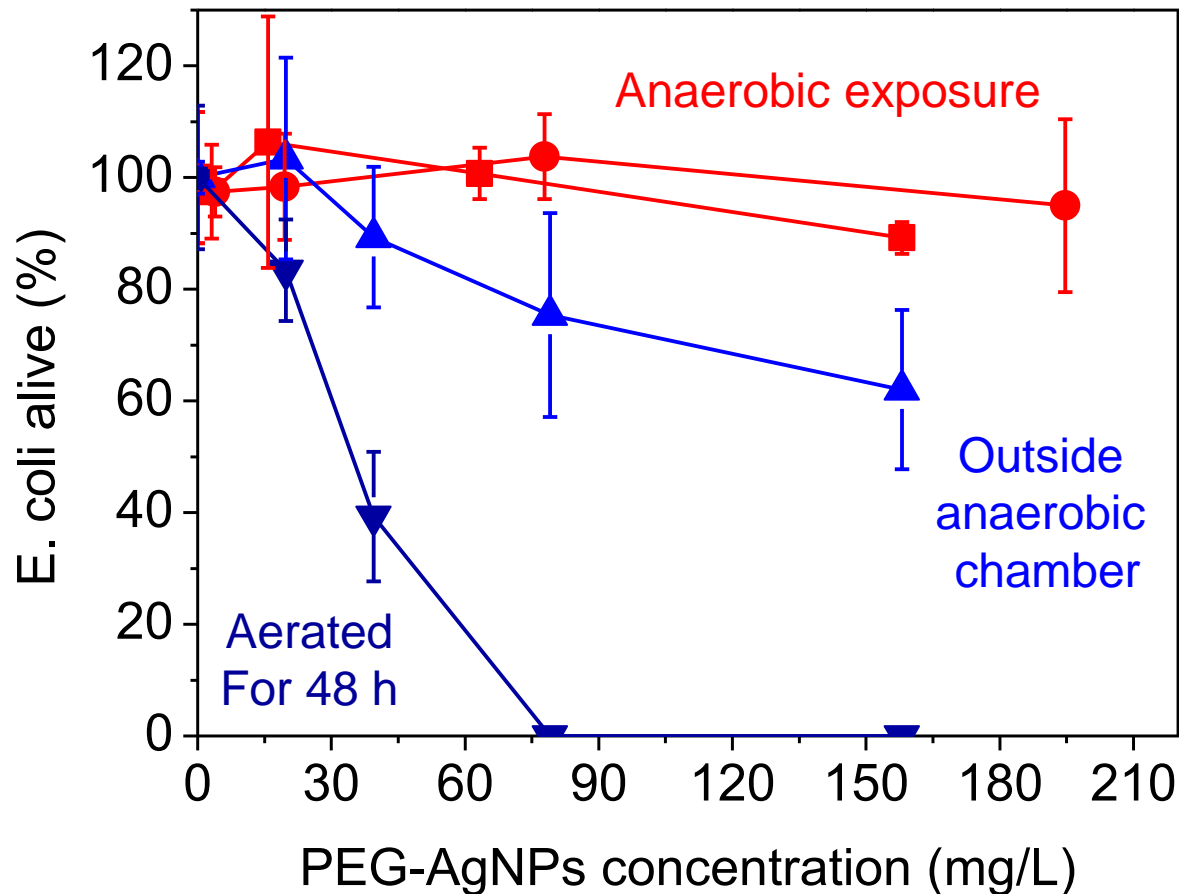
Ag^+ is released only if nAg(0) is oxidized: $4\text{Ag}^0 + \text{O}_2 + 4\text{H}^+ \leftrightarrow 4\text{Ag}^+ + 2\text{H}_2\text{O}$
(Solubility of $\text{Ag}^0 \approx 0$)



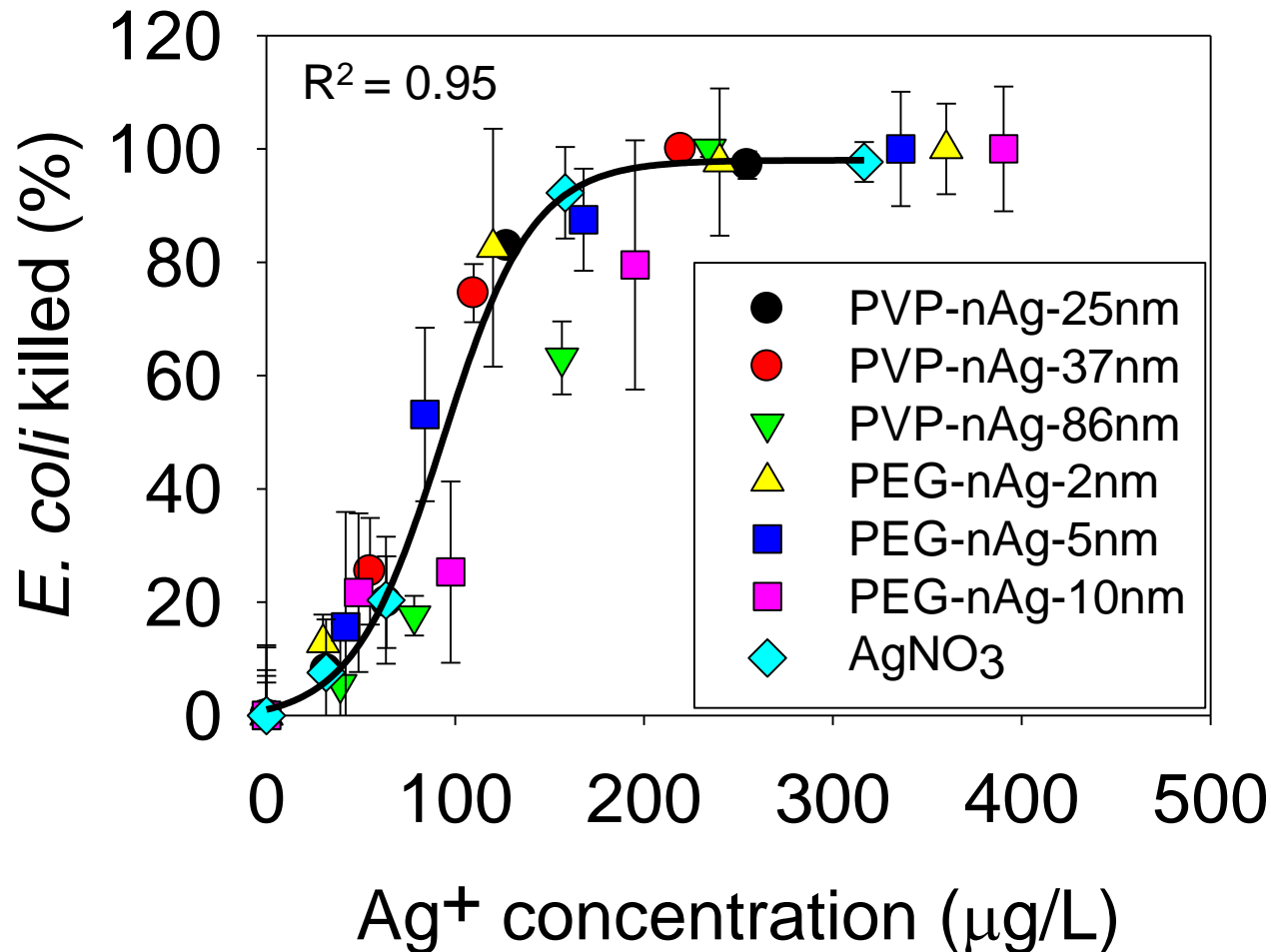
No Ag⁺ release under Anaerobic Conditions (Faster release for air-exposed smaller particles)



No Toxicity Without Ag⁺ Release

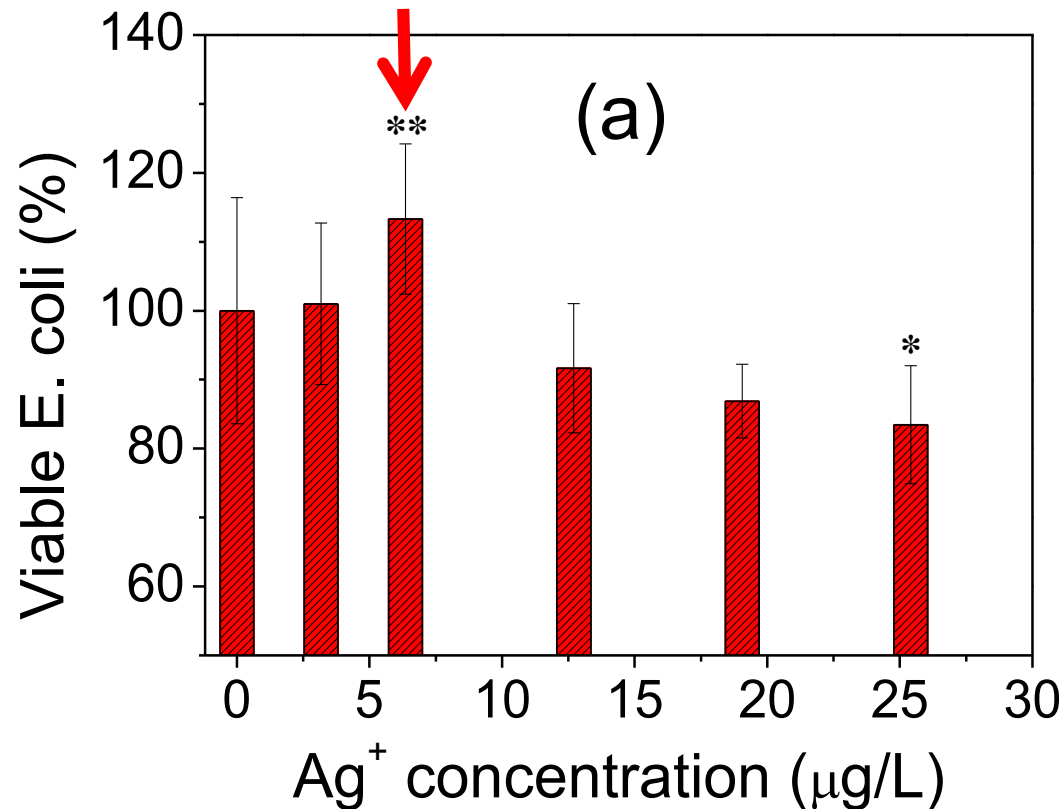


nAg Toxicity Can Be Explained by Dose-Response of Released [Ag⁺]



“What does not kill you makes you stronger”

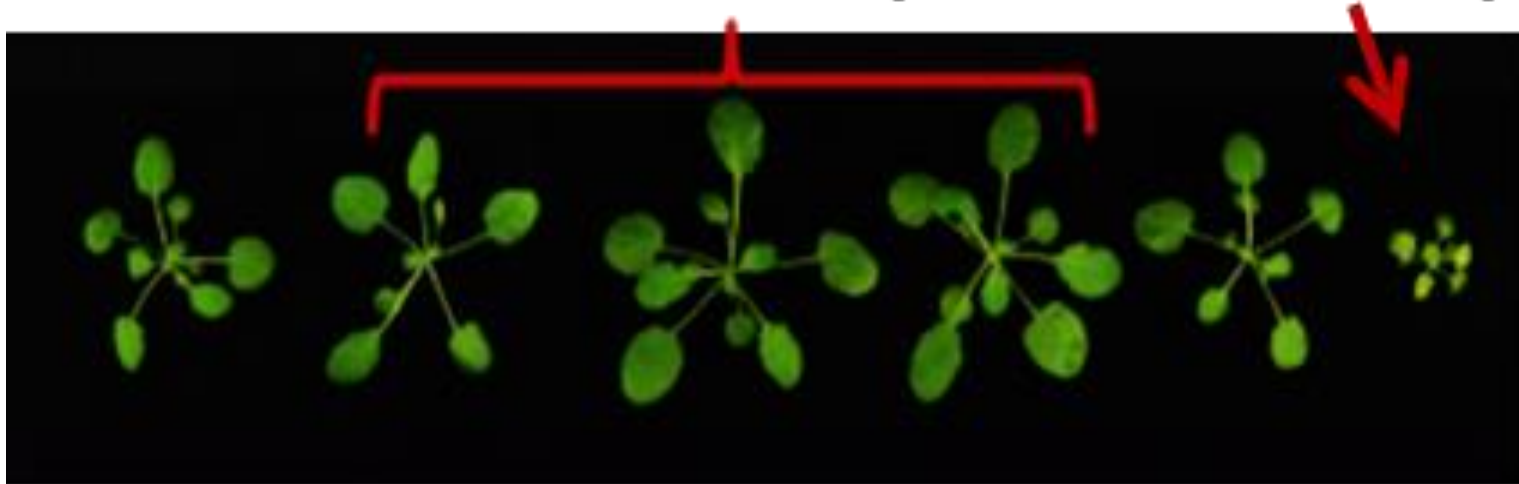
Friedrich Nietzsche



Stimulatory effect after 6 h exposure to sublethal Ag⁺ concentration
(Hormesis?)

Stimulatory

Inhibitory



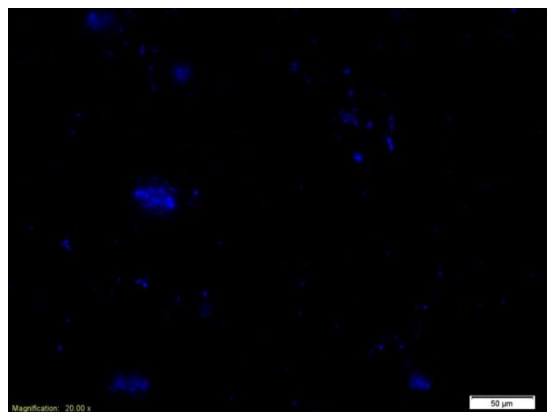
Increasing silver NP concentration



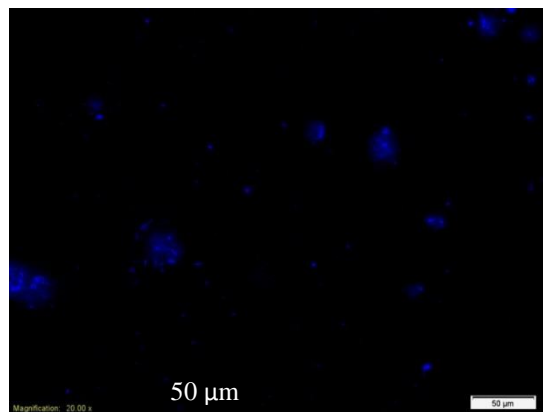
Sublethal Exposure to AgNPs (but not to Ag⁺) stimulated **biofilm** development



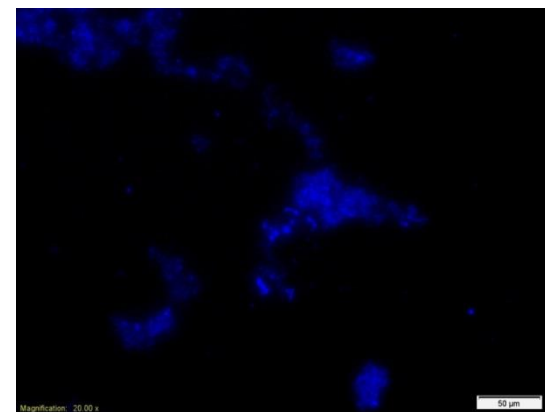
Mixed culture from the effluent of a WWTP, forming biofilm on a glass slide



Control

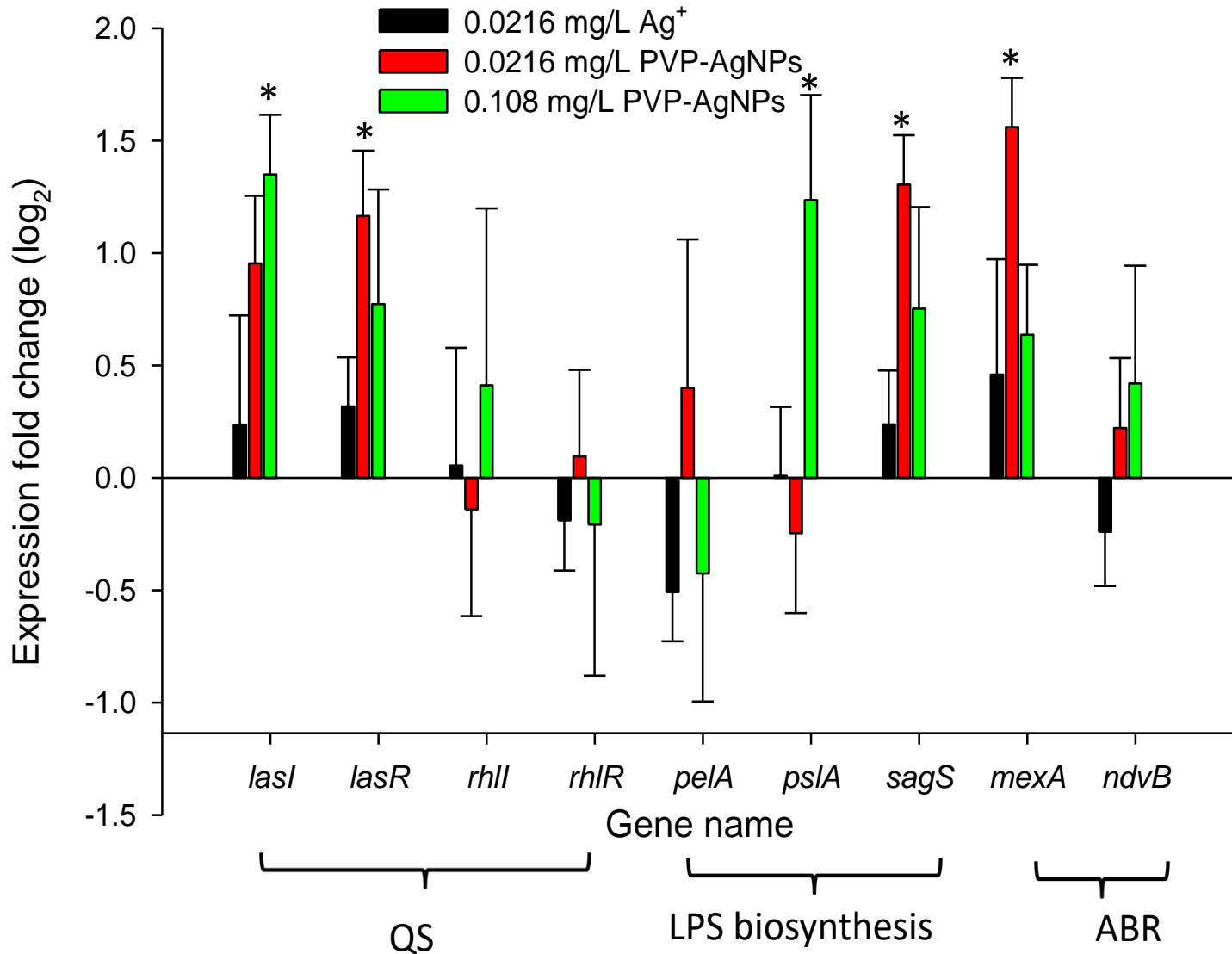


0.02 mg/L of Ag⁺

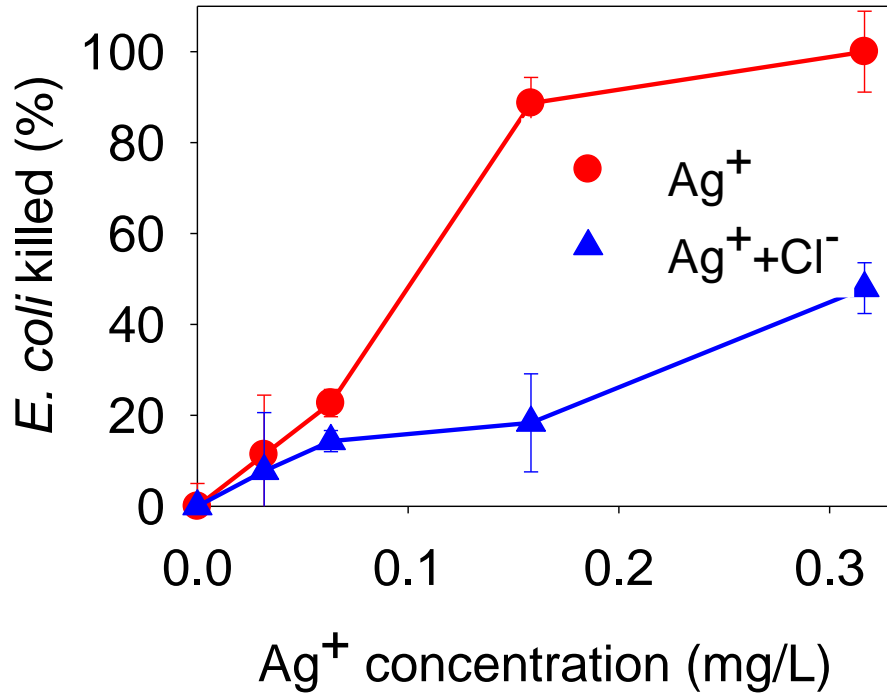


0.02 mg/L of AgNPs

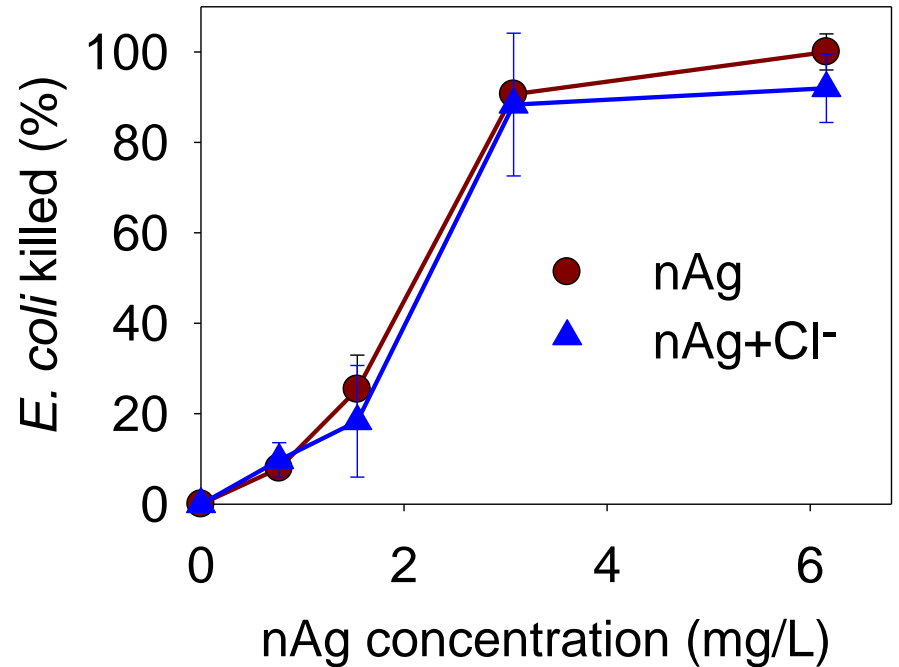
Sub-lethal exposure of *P. aeruginosa* to AgNPs Upregulates Quorum Sensing, LPS, & Antibiotic Resistance Genes



Why is nAg sometimes a stronger bactericide?



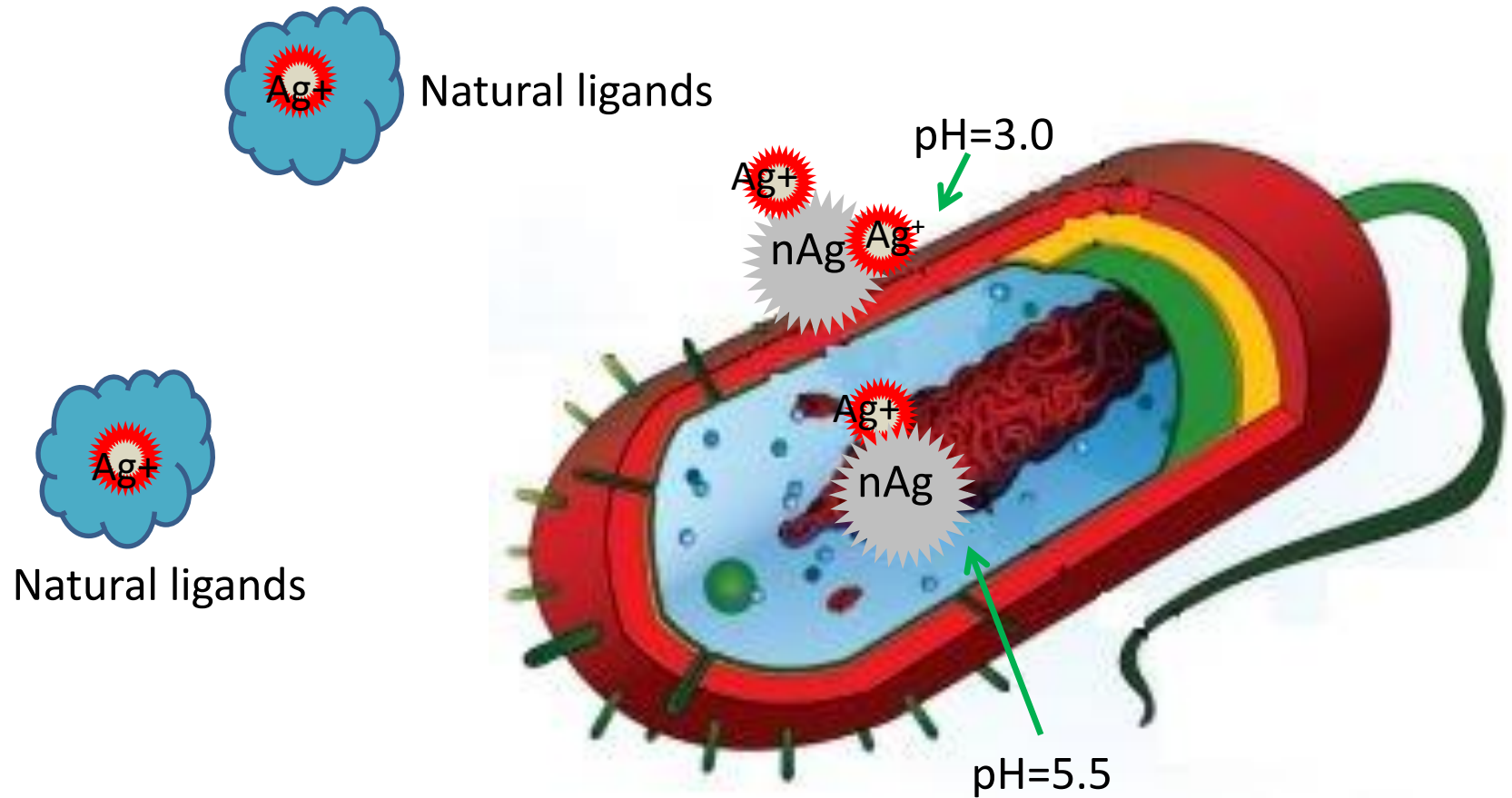
Max [Ag^+]: $3\mu\text{M}$; [Cl^-]: $3\mu\text{M}$



Max [nAg]: $57\mu\text{M}$; [Cl^-]: $57\mu\text{M}$

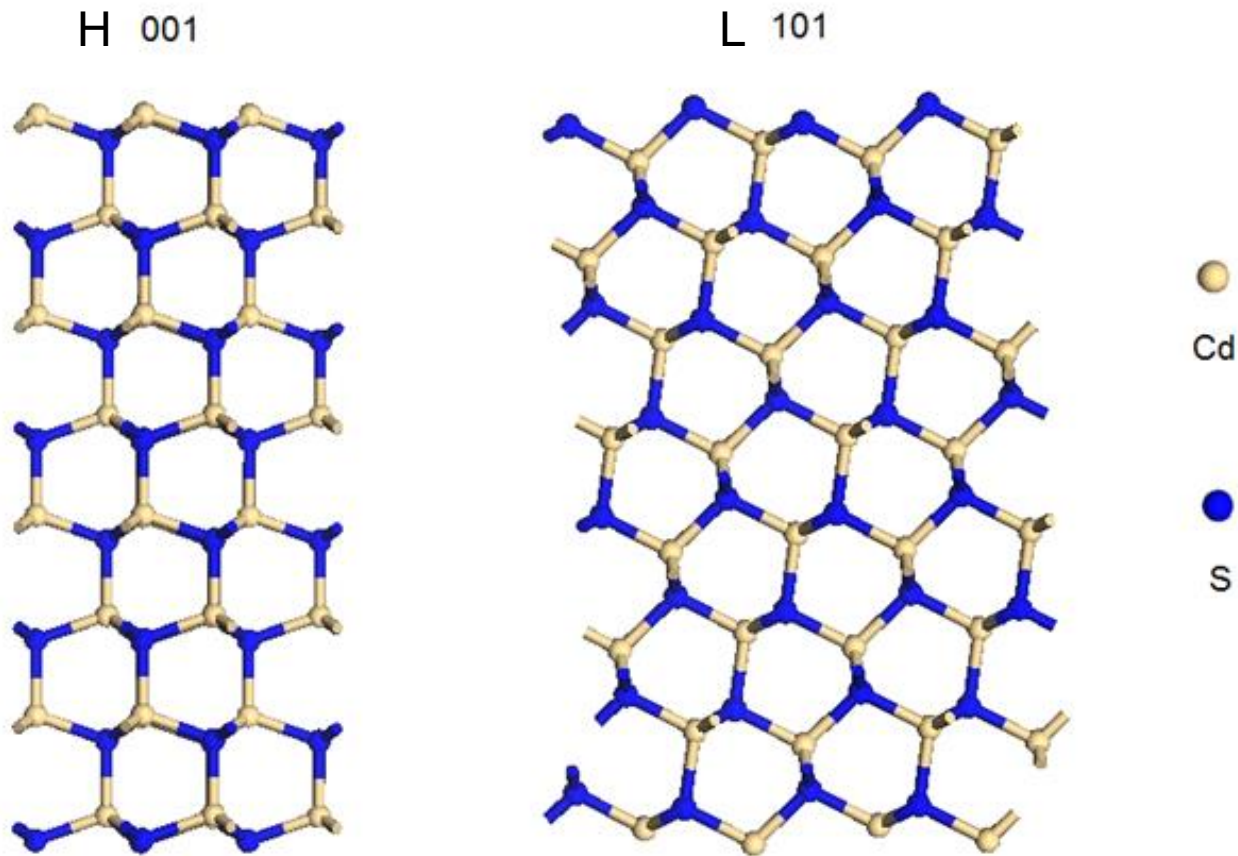
- Cl^- (& other ligands, NOM) reduce Ag^+ bioavailability and preferentially decrease its toxicity, even without precipitation
- nAg may then be more bioavailable & effectively deliver Ag^+

More Effective Delivery of Ag^+ to Membrane and Cytoplasm



How does surface energy affects NP reactivity and toxicity?

The surprising behavior of CdS nanorods



{001} facet (CdS-H) has **higher surface energy** than {101} facet (CdS-L)

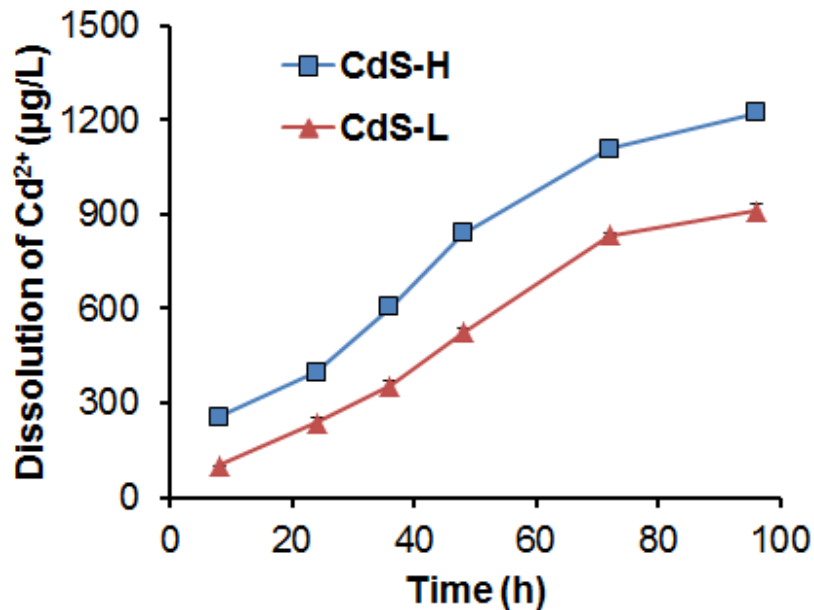
	CdS-H	CdS-L
Length (nm)	110 ± 26	108 ± 11
Width (nm)	25 ± 3	22 ± 4
Surface energy (J/m ²)	0.627	0.451
Surface area (m ² /g)	42.6	49.0
ζ potential (mV)	-12.3 ± 1.6	-9.9 ± 1.2

But similar other properties (size, charge etc.)

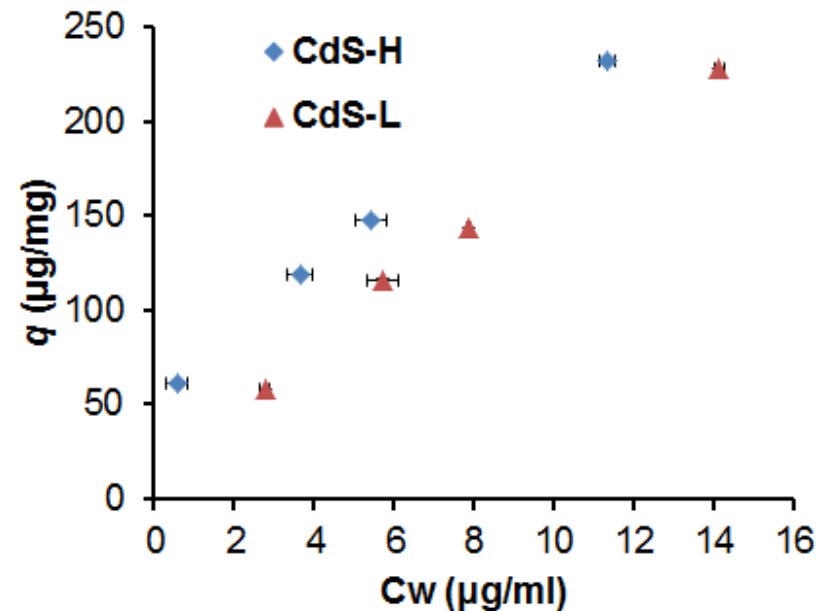
CdS-H is more reactive:

- Faster release of toxic Cd^{2+} and
- Higher tendency to associate with proteins

(a)



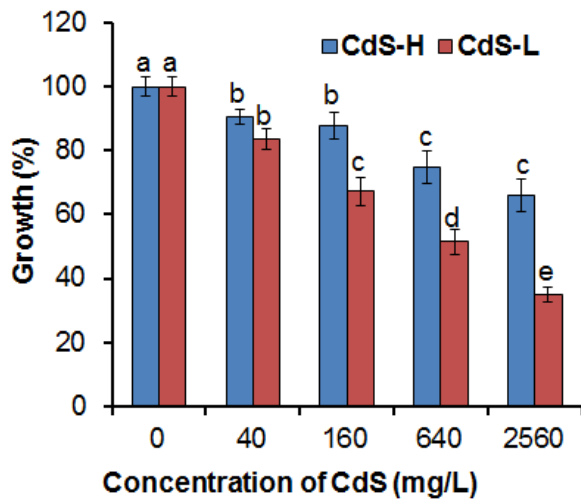
(b)



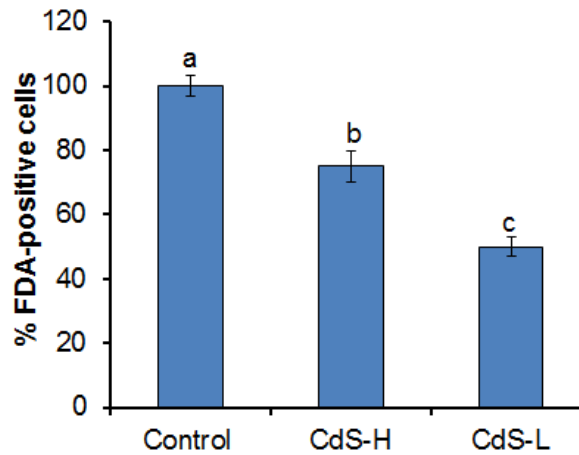
So CdS-H should be more toxic?

But CdS-L was more cytotoxic!

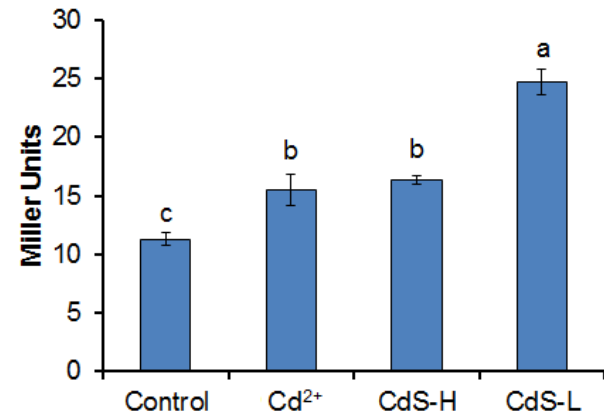
(a) Growth inhibition



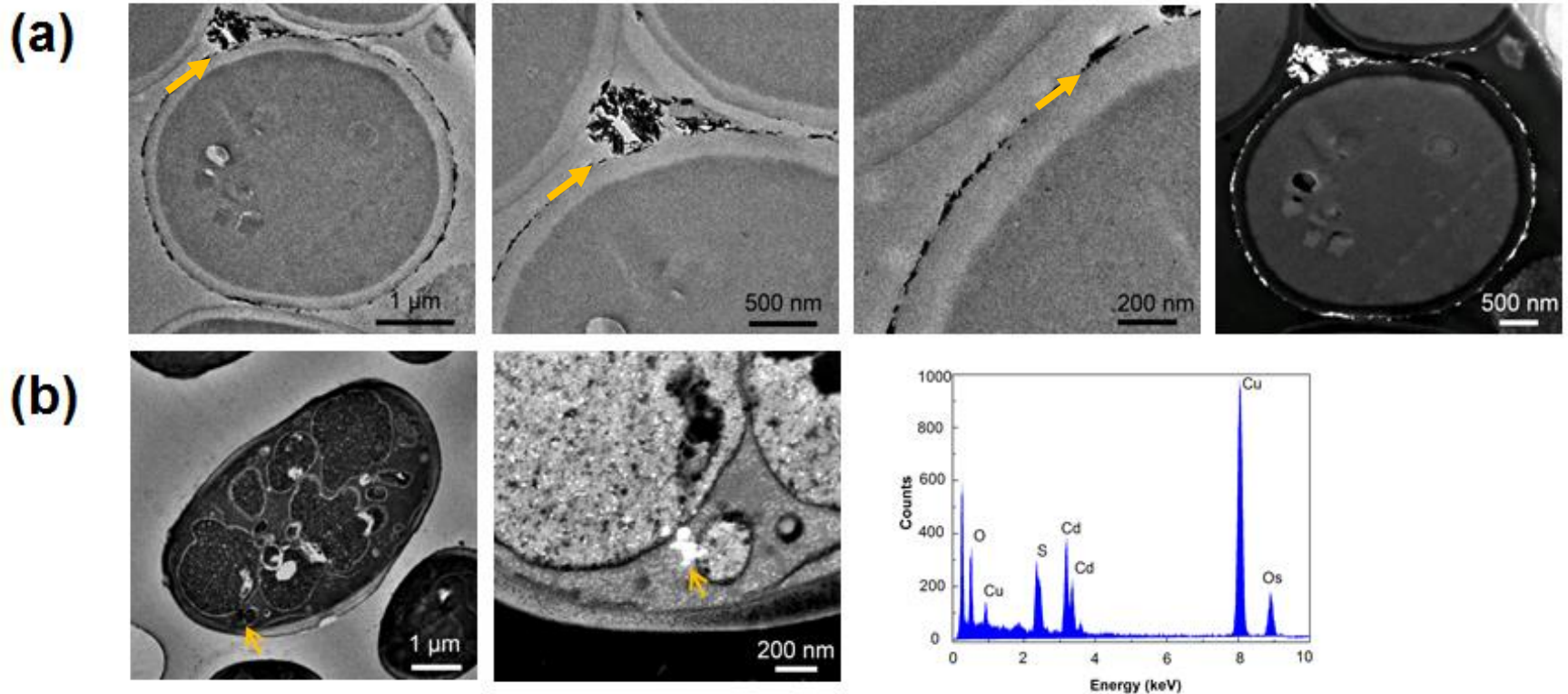
(b) Cell viability



(c) ER Stress

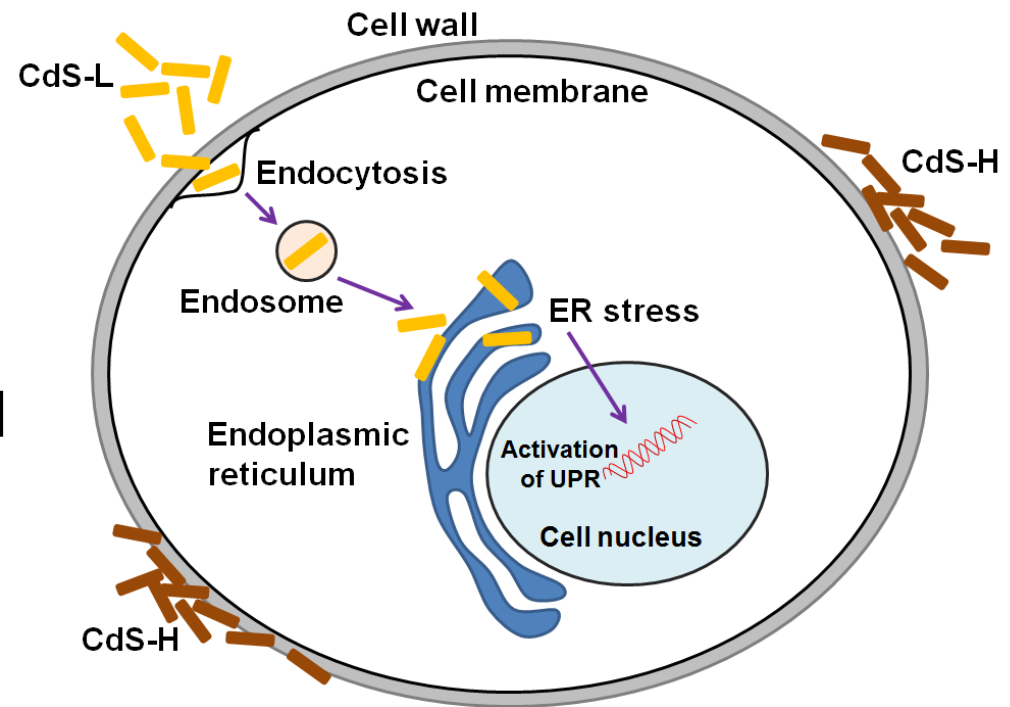


- (a) Accumulation of CdS-H on cell wall.
- (b) Intracellular uptake of CdS-L (confirmed by energy-dispersive X-ray spectroscopy)



Summary of Effect of Surface Energy

- **CdS-H** was less toxic than **CdS-L** (despite similar morphology, aggregate size, & charge).
- **CdS-H** adsorbed to the yeast's cell wall, which decreased endocytosis.
- Higher uptake of **CdS-L** hindered cell viability and increased ER stress despite lower release of toxic Cd^{2+} ions.





Safer Use of ENMs

$$\text{Risk} = \text{Hazard} \times \text{Exposure}$$

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.

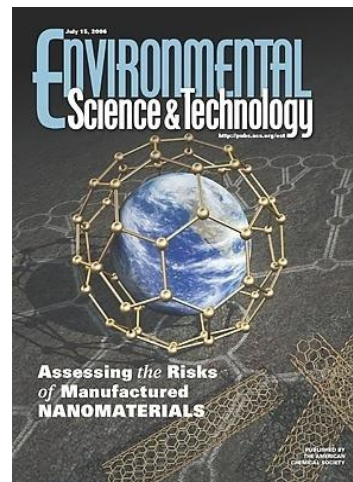


Conclusions

- Implications: Ecotoxicology-Ecosystem services (primary productivity, food webs, nutrient cycling?)

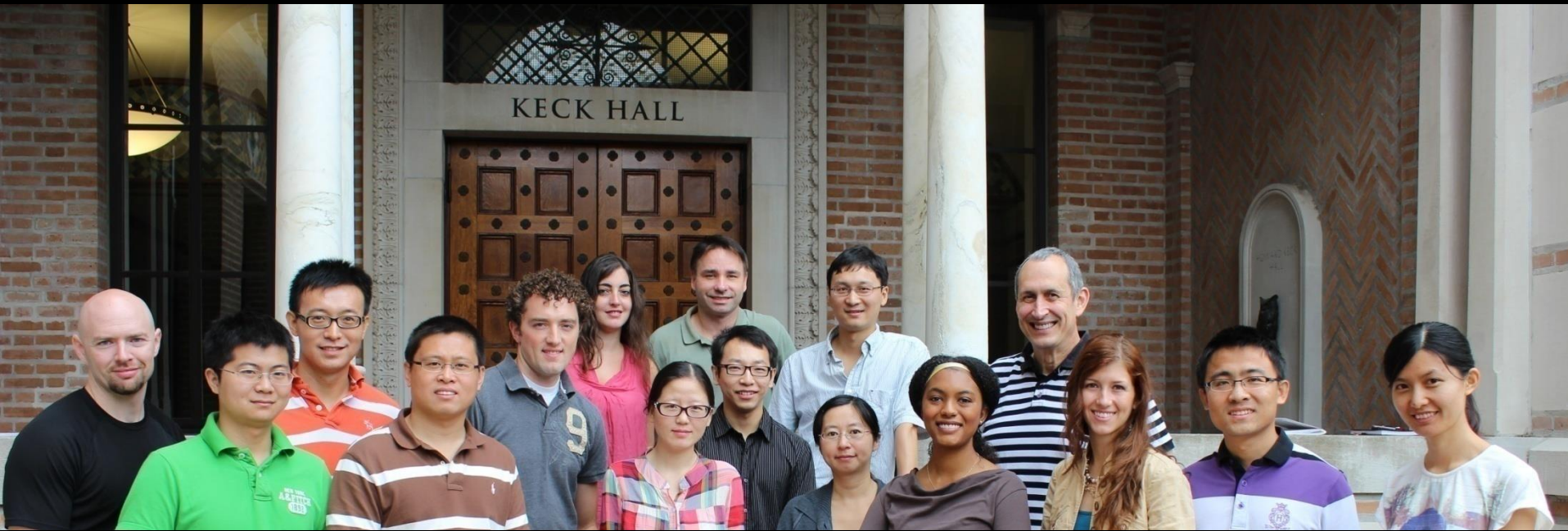
Mitigated by NOM, salts

- Applications: low-energy desalination, selective adsorption and destruction of priority water pollutants, multi-functional membranes, etc.



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, Pinfeng 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 Costura; Matt Wildman; Chad Laucamp; Todd Dejournet; Sascha Richter; 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**; Rachel Carlson; Robert O'Callahan; Bill Mansfield

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

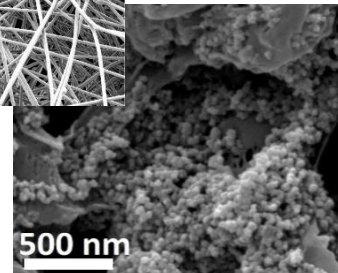
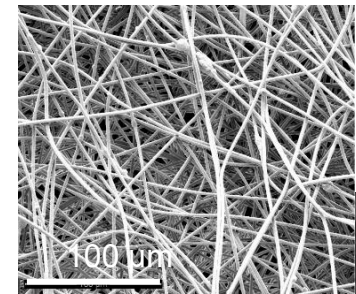
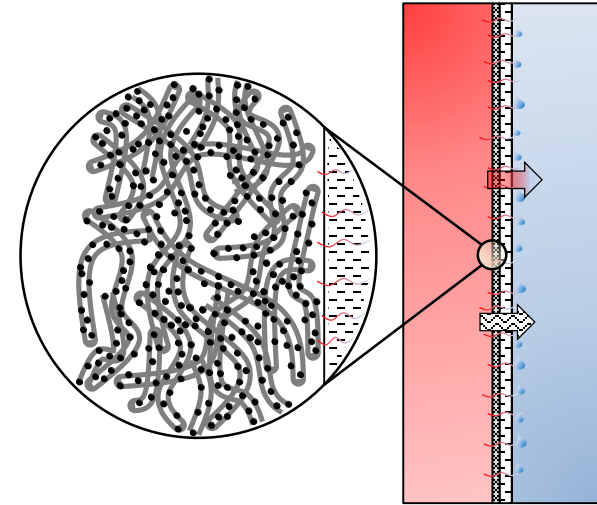
Any Questions?





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?





Potential applications for solar MD

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

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

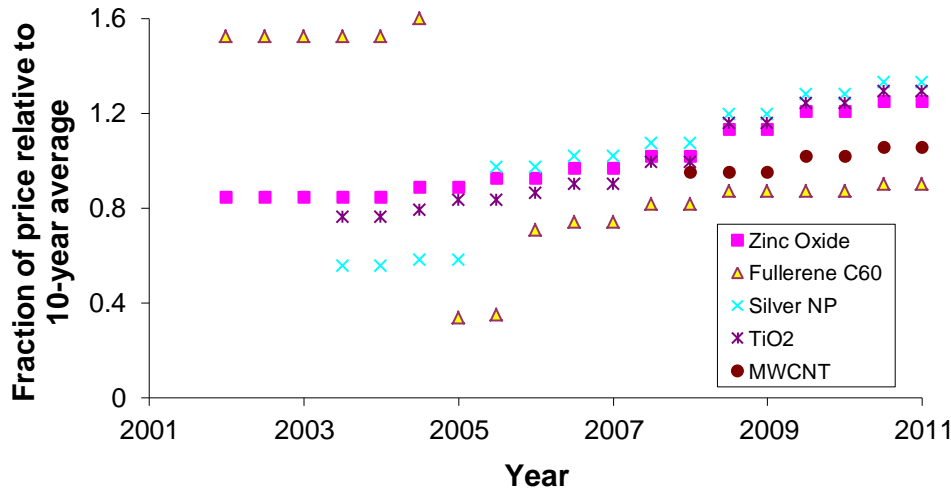


Similar to solar charging station, could build a solar water station

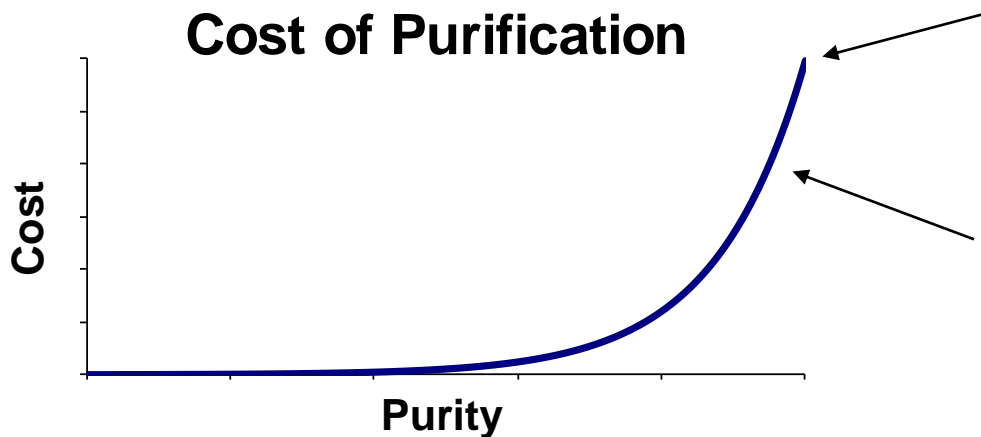


RO concentrate treatment

Need market-driven decrease ENM price



Few commercial applications
= low supply
→ prices stay high

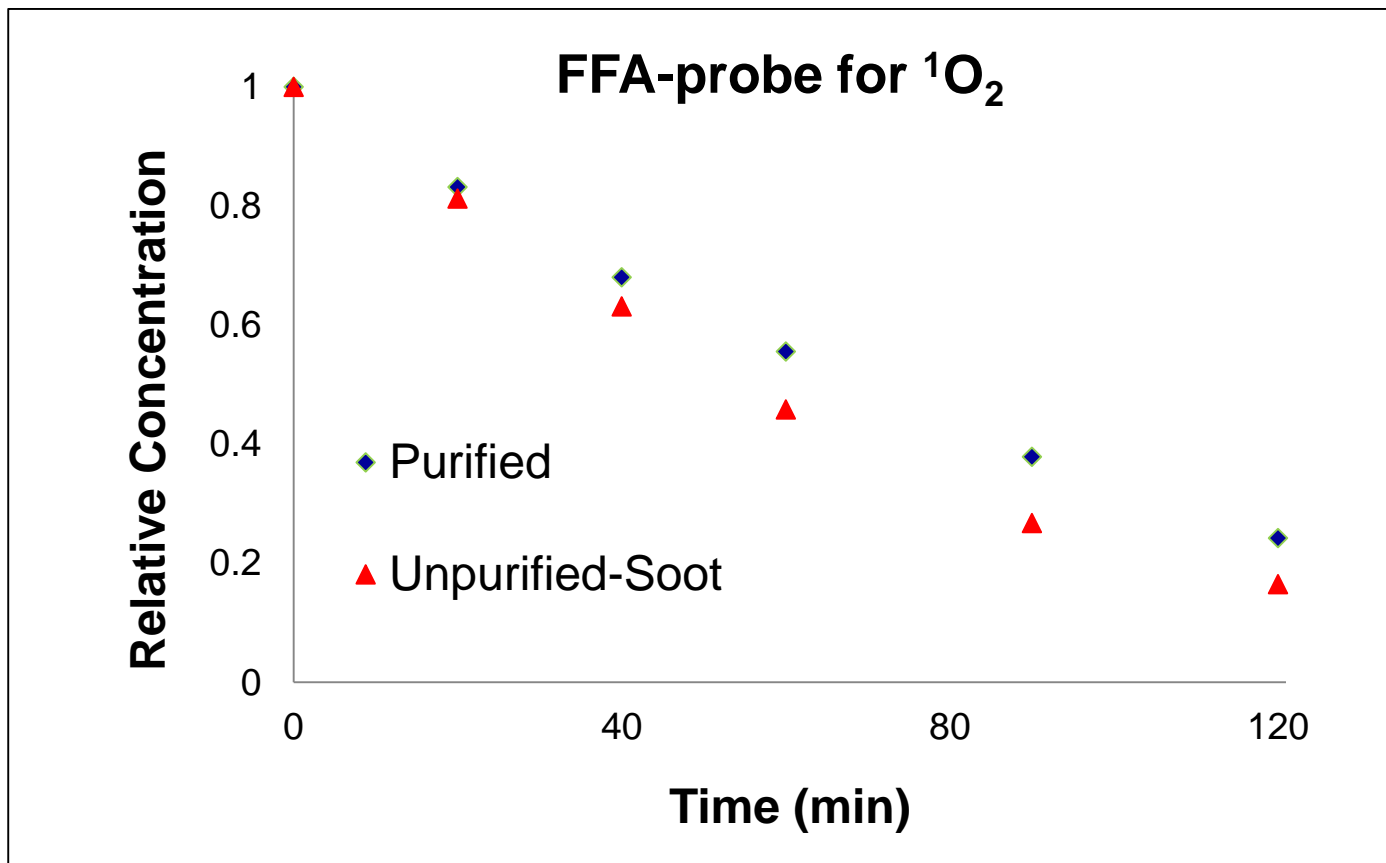


Most production is done for research (small quantities of highly purified material)

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-C₆₀ cost less (20x) without significantly sacrificing reactivity

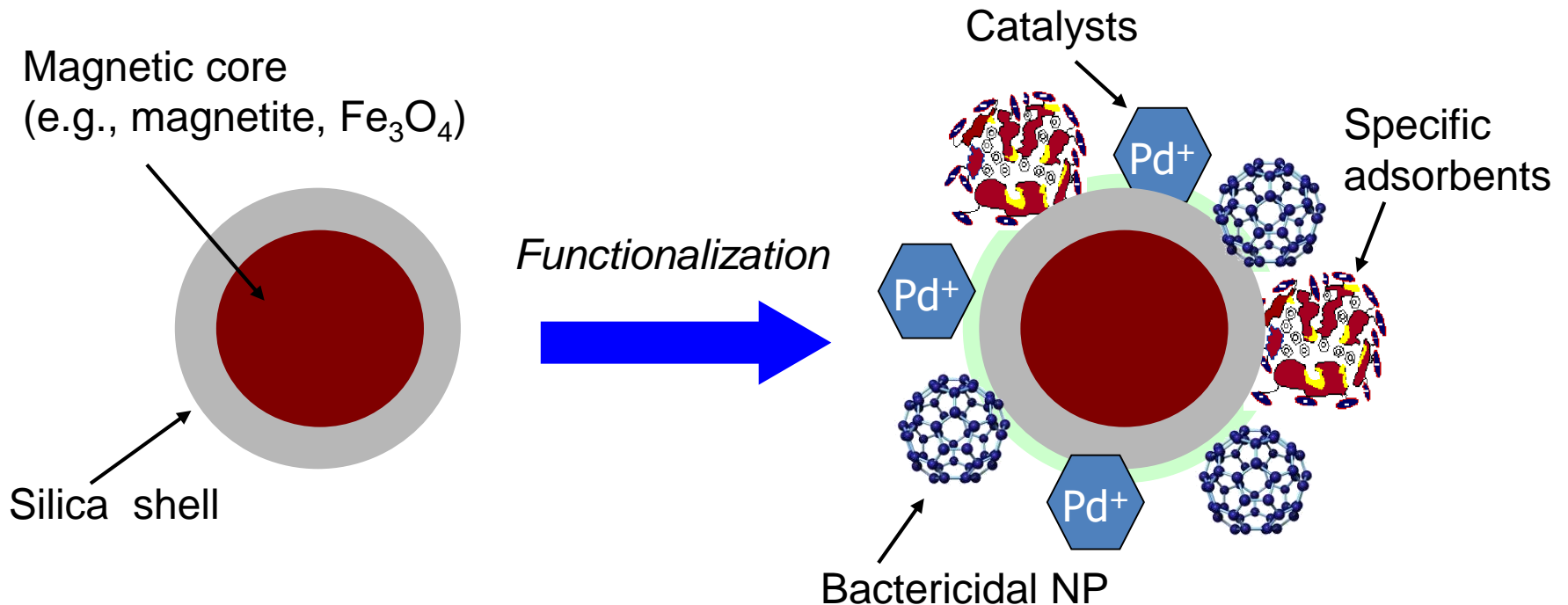




Enabling Technology

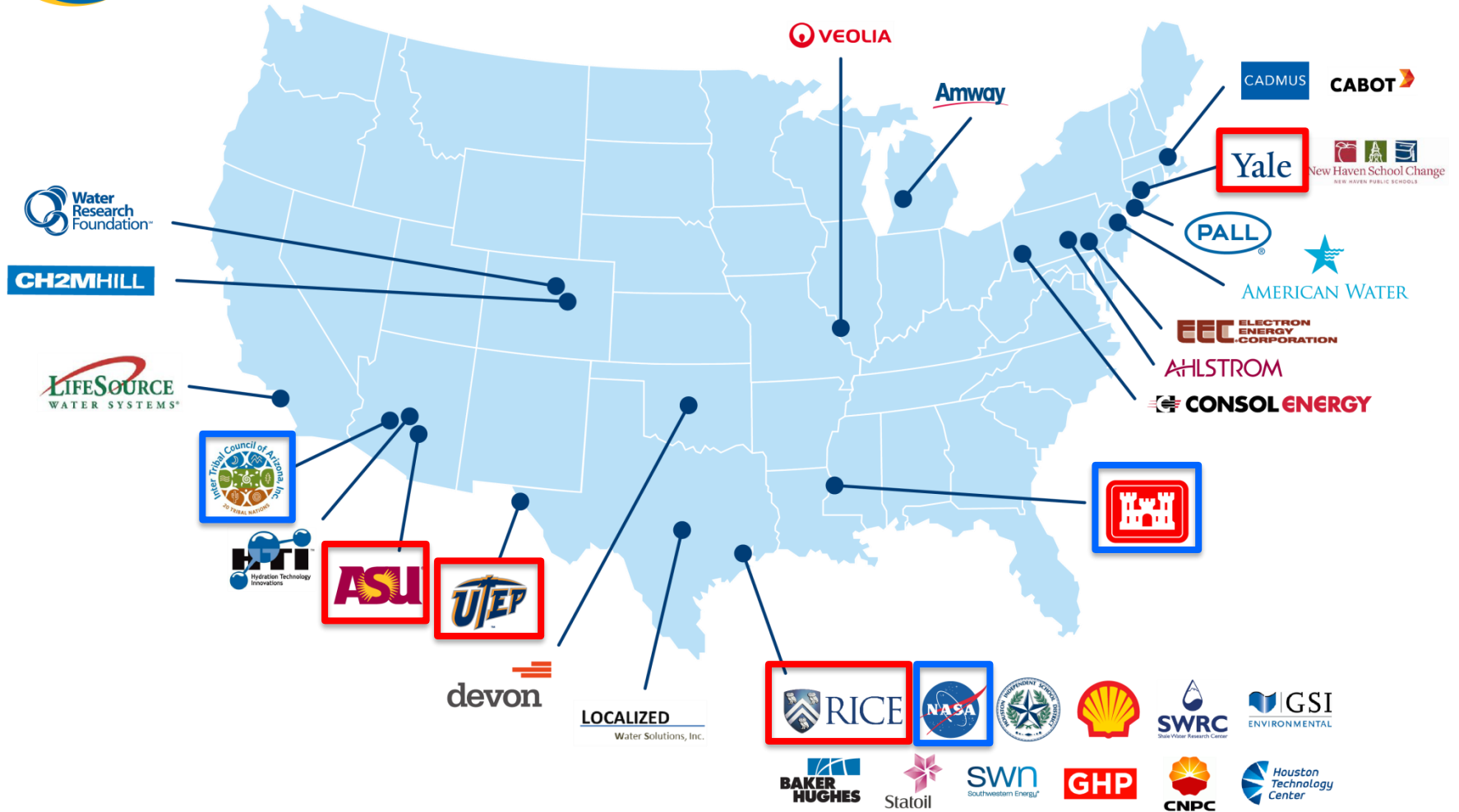
Multifunctional nanosorbents

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





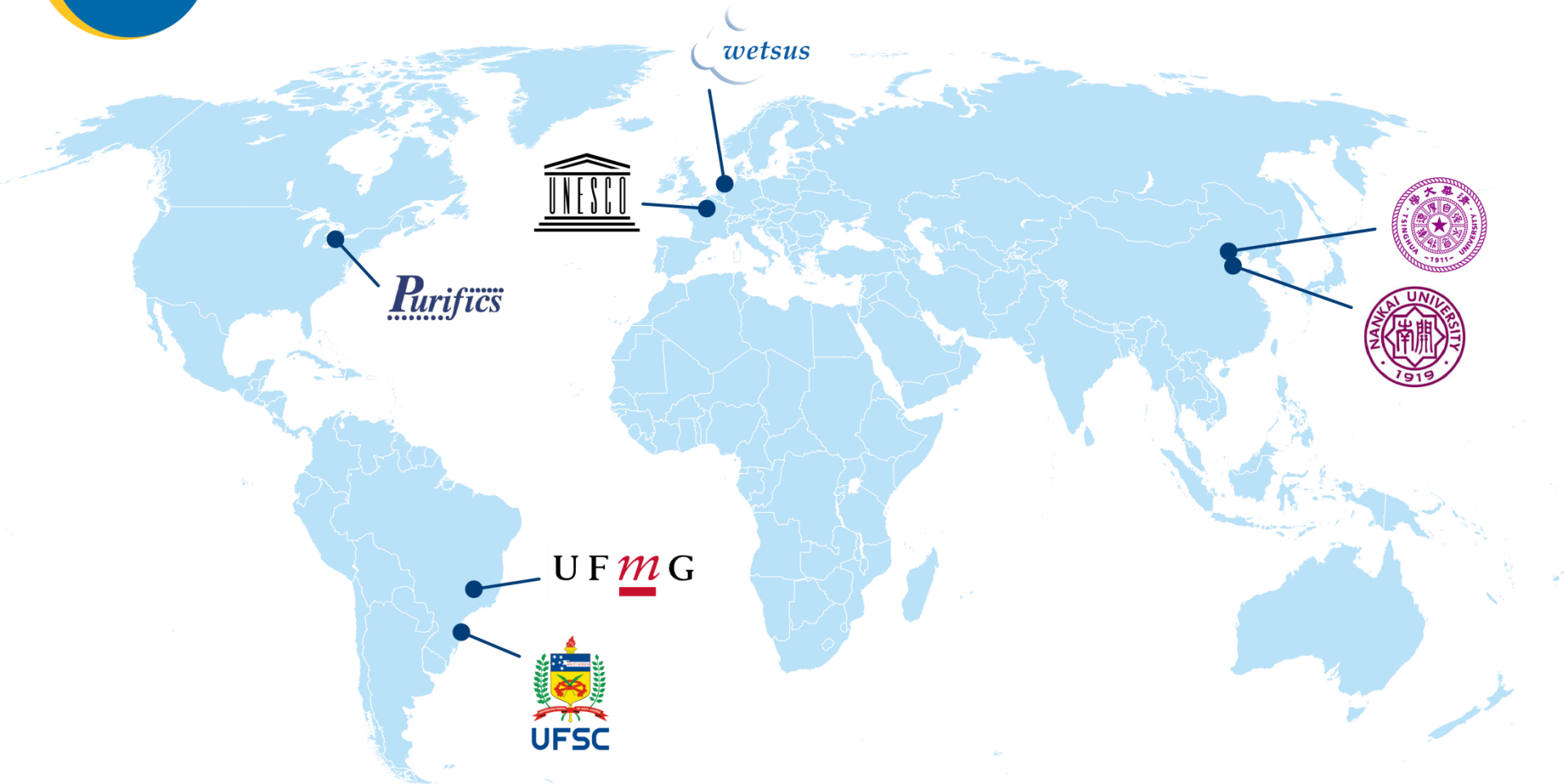
Some of Our NEWT Partners



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




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

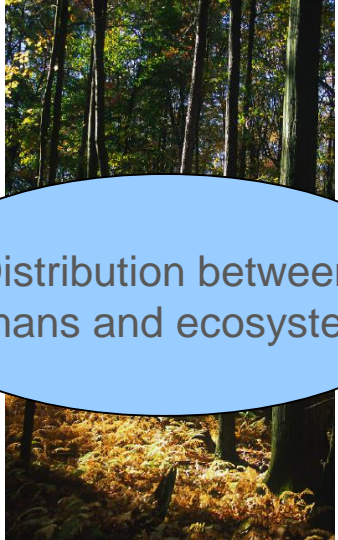
7 Grand Challenges Related to Water




Safe water quality for a growing population




Water infrastructure (distribution & collection)



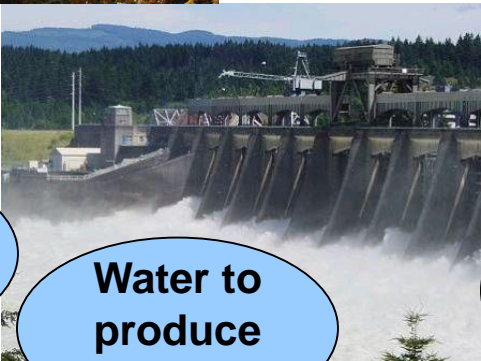
Distribution between humans and ecosystems




Water induced disasters and flood protection



Enough food for all

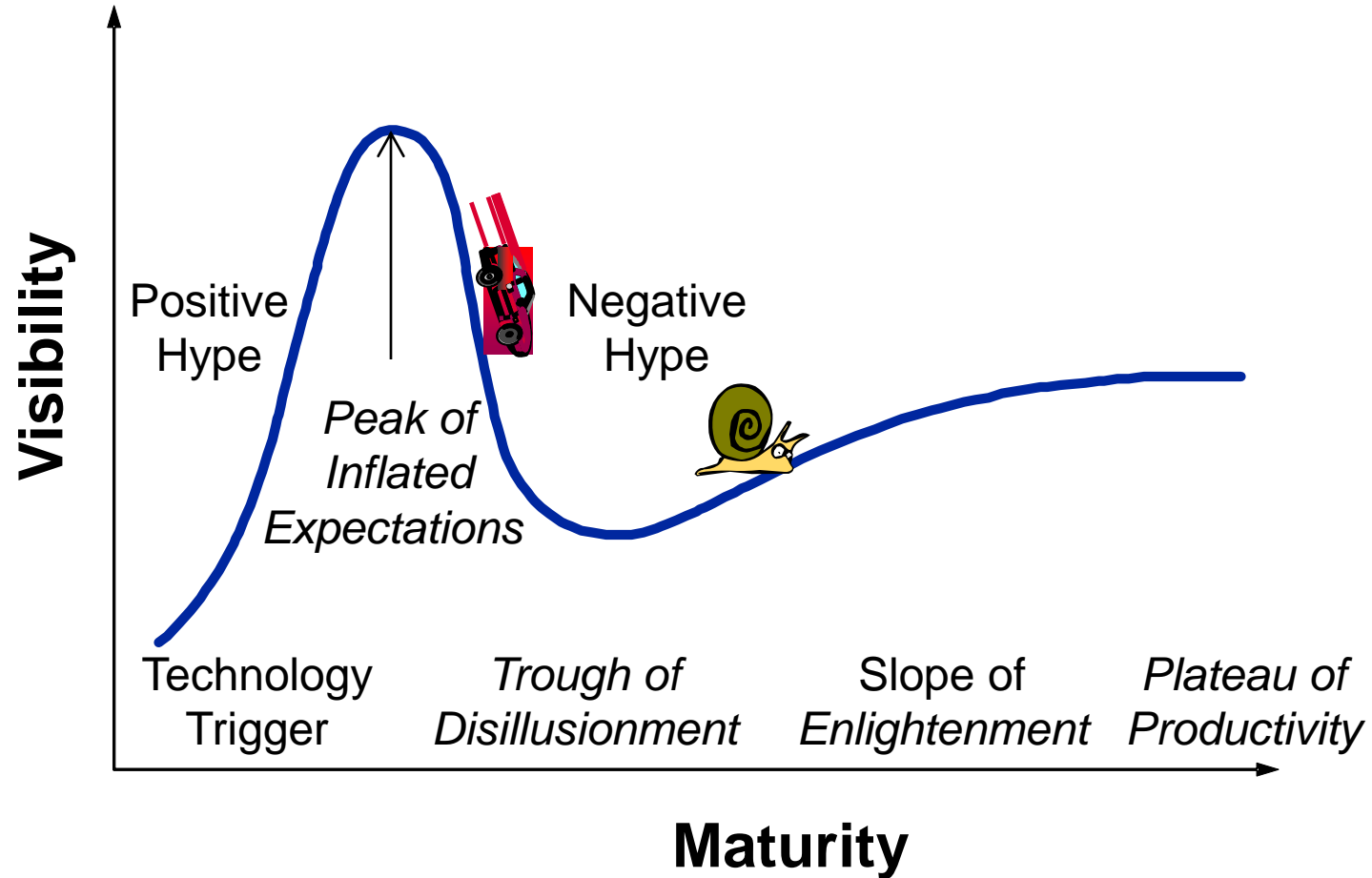


Water to produce energy



Solution for water conflicts and fair water share for all

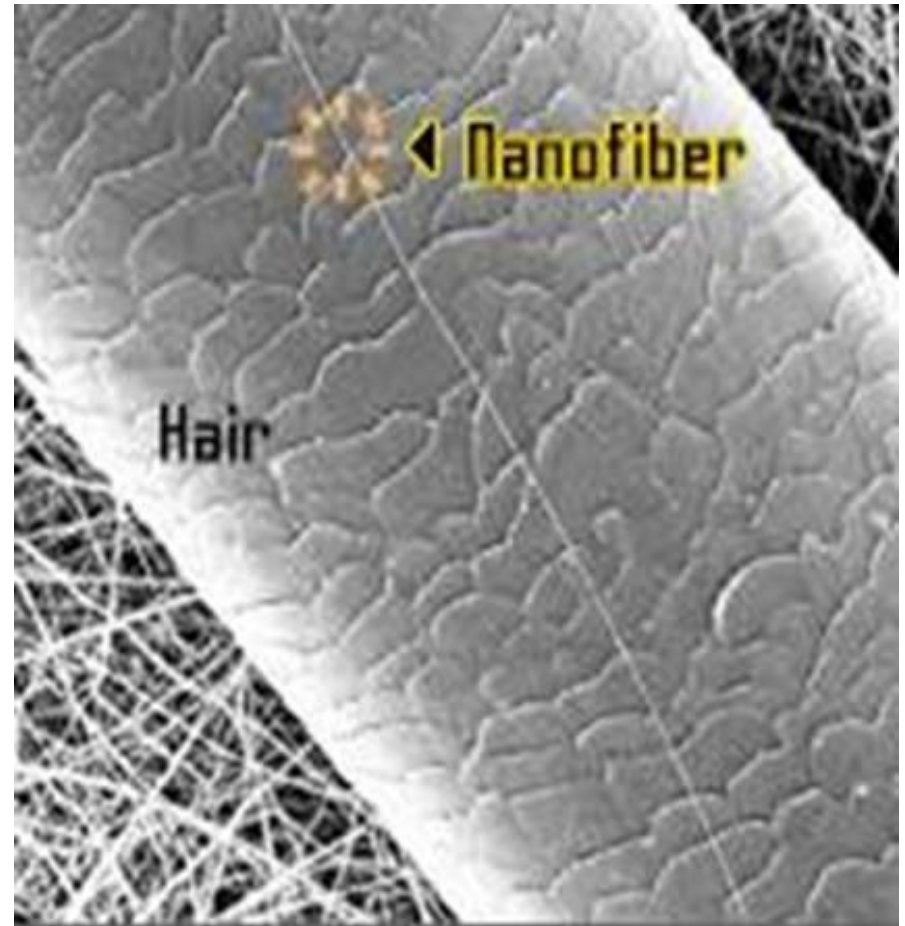
Quo Vadis, Nano?



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

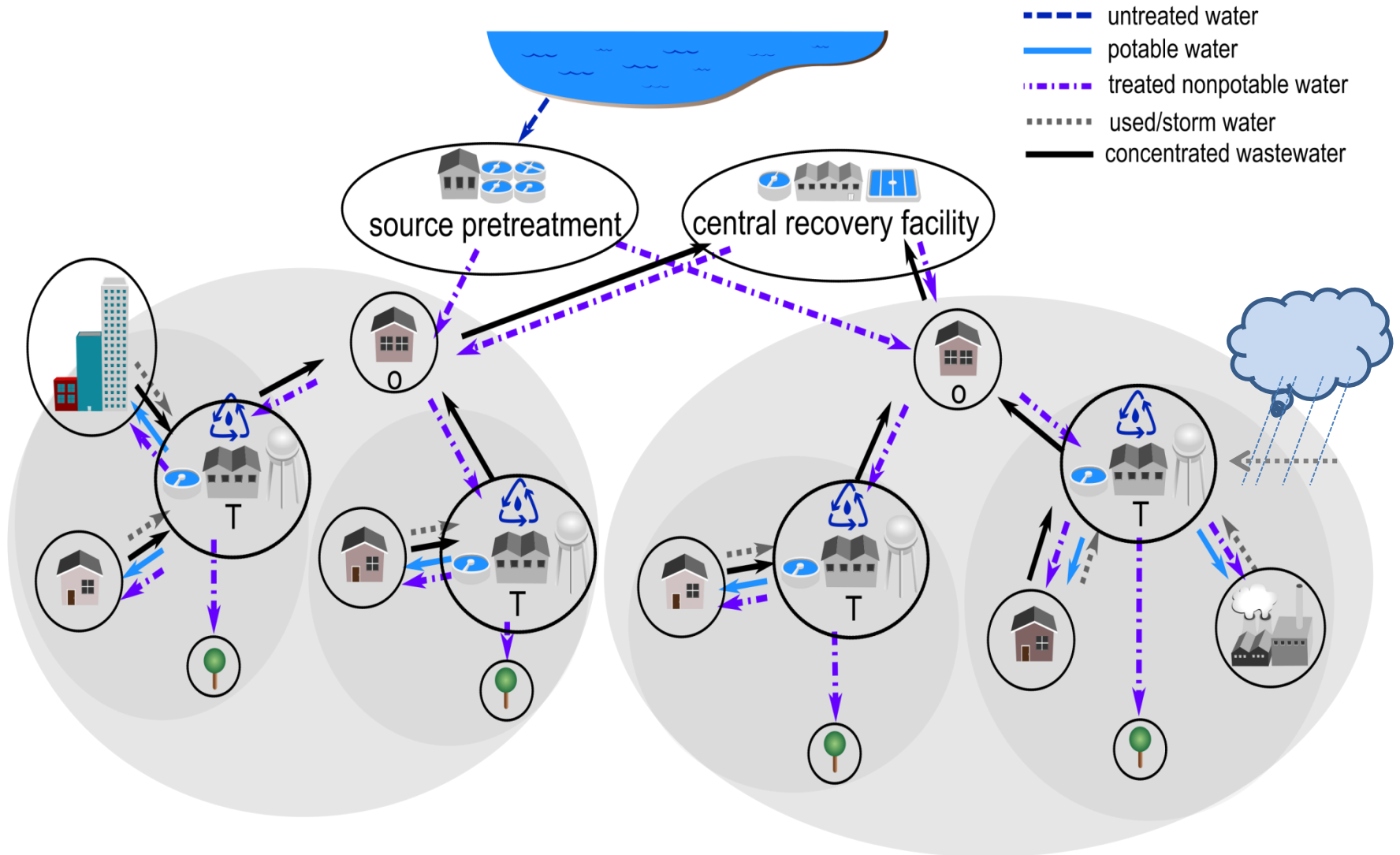
“Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications.”

-National Nanotechnology Initiative

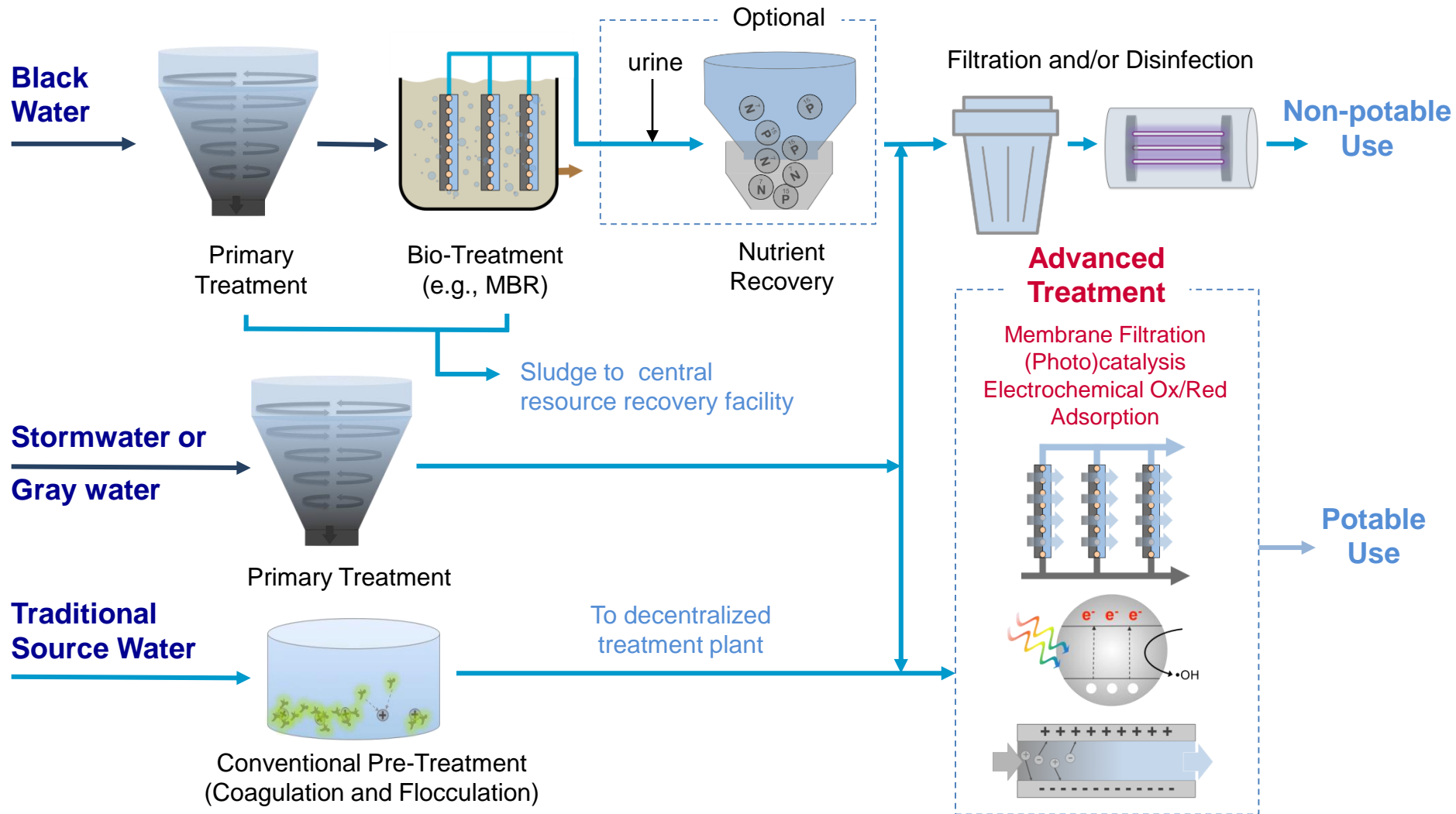




Flows of “fit-for purpose” water in an integrated water management system



Modular Treatment System at Decentralized Facilities that Integrate Various Sources





Houston: 4th largest city in USA
“Energy Capital” of the world

RICE UNIVERSITY

- 3879 undergraduate & 2861 graduate students (6:1 student to faculty ratio)
- Small, but highly ranked
 - USNEWS ranks it #15 overall (highest-ranked in Texas 2017)
 - Leiden ranking (2013): #1 in the world in natural sciences and engineering for the quality and impact of its scientific publications
 - Princeton Review: #1 for best quality of life

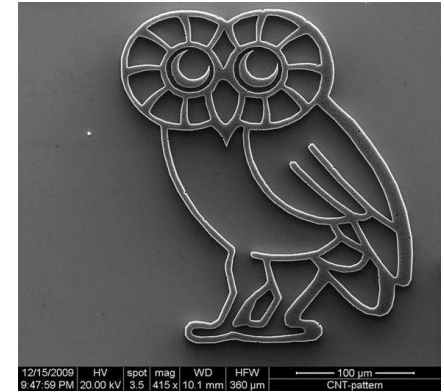
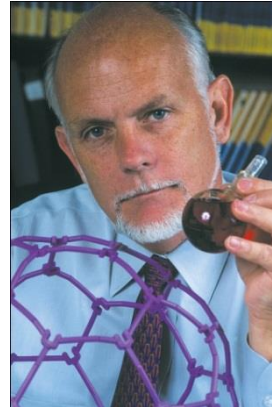
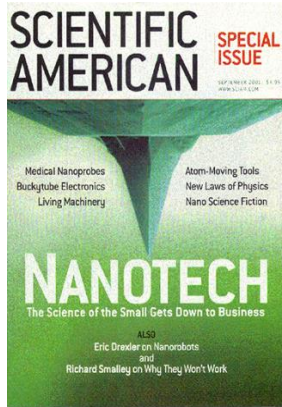
Rice University - Texas Medical Center

***Rice is part of the world's largest medical complex:
Strong Tradition in Bioscience Research***





Rice: A First Mover in Nanotechnology



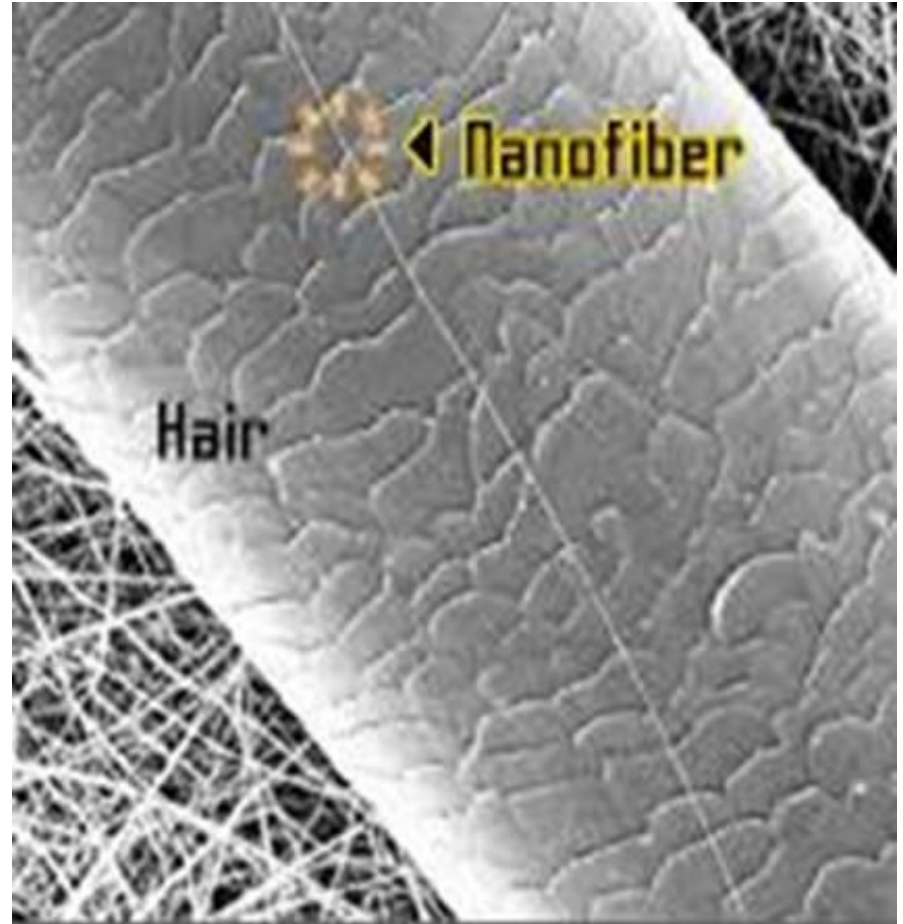
- Ranked among top nanotechnology programs in the world
- The first university-sponsored nanotechnology effort (1994!)
- Nobel prize awarded in 1996 for discovery of C_{60}
- CBEN (2001) was one of the 1st national nanotechnology centers
- Rice faculty are leaders in carbon nanotechnology, nanomedicine, nanophotonics, and environmental nanotechnology

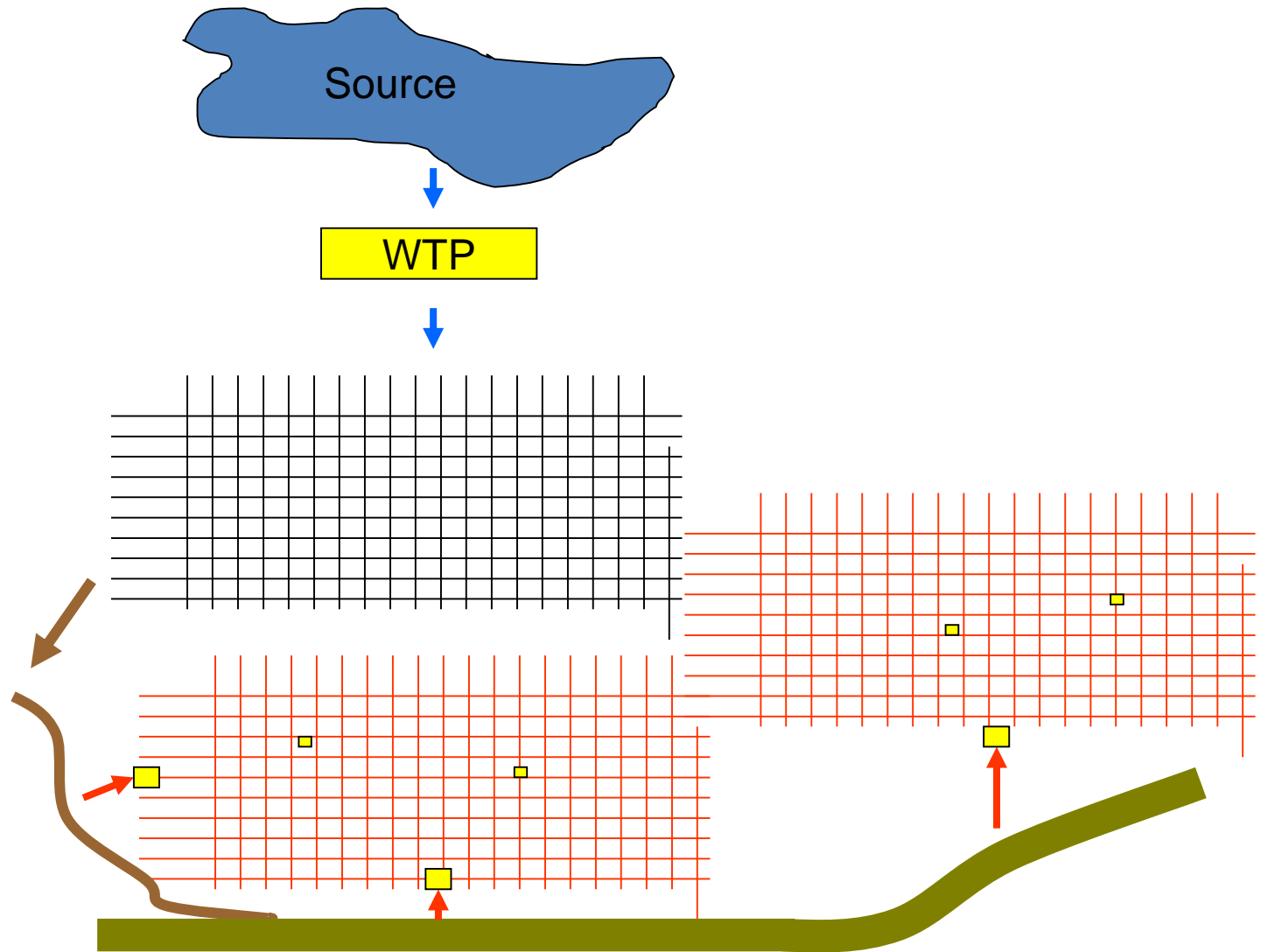


Nano = Dwarf (Greek) = 10^{-9}

“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





Integrate potable water, storm water, and wastewater systems and *(fit-for-purpose) distributed treatment facilities* to minimize freshwater withdrawal and energy consumption for transporting water



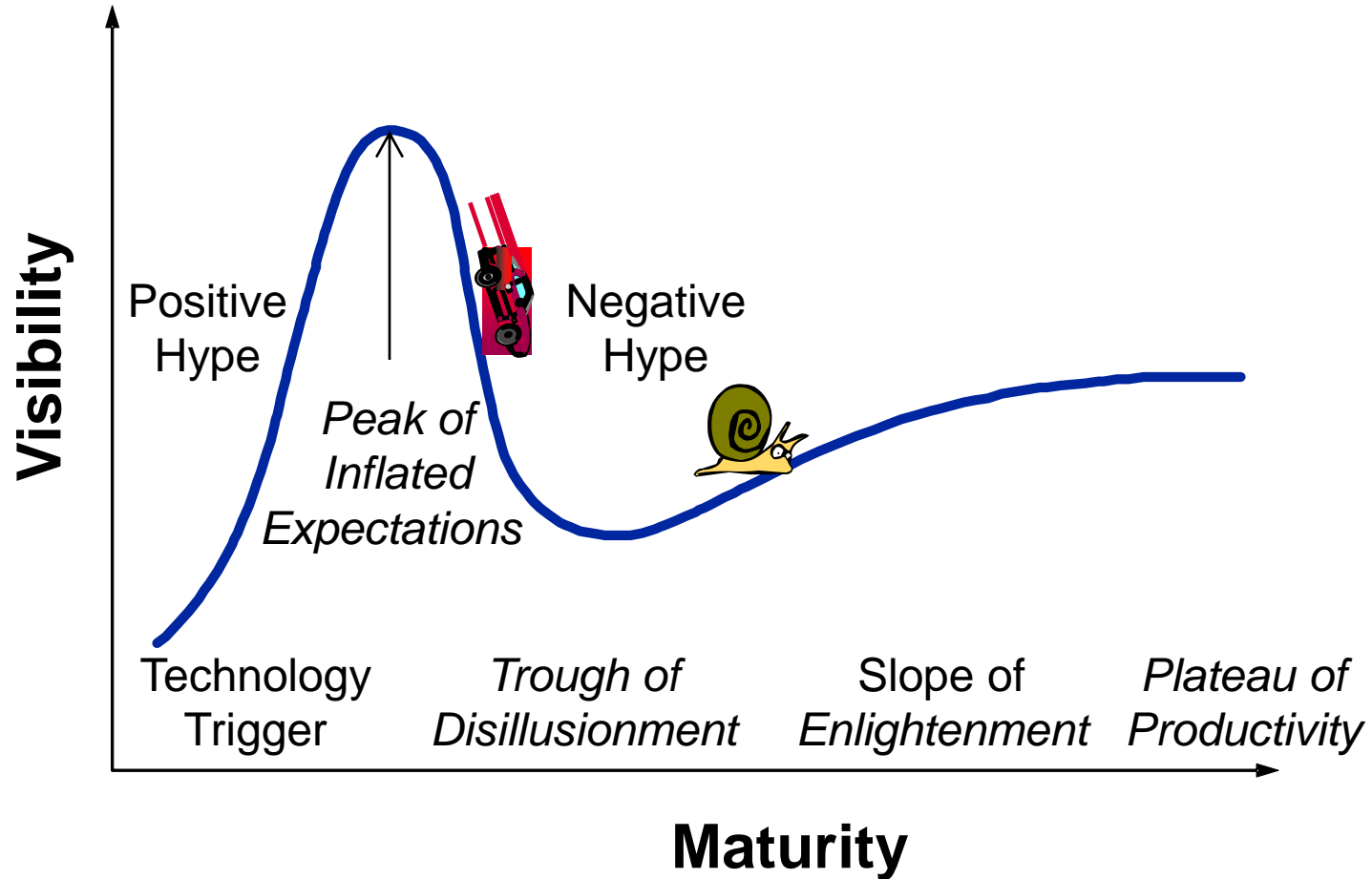
Drivers for Decentralized (Distributed) Modular Treatment

- 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 to the intended use, lowering treatment cost

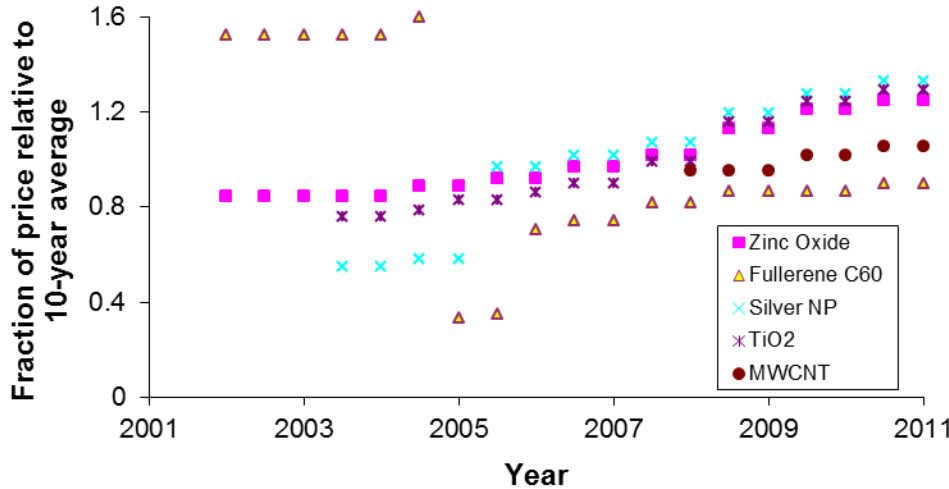
Opportunities for Engineered Nanomaterials (ENMs) in Water Treatment and Reuse

<i>ENM Properties</i>	<i>Examples of Enabled Technologies</i>
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

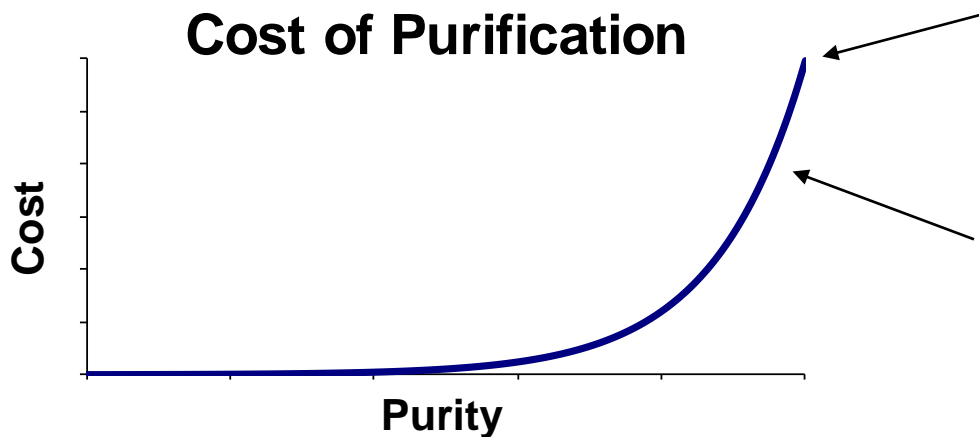
Quo Vadis, Nano?



Need market-driven decrease ENM price



Few commercial applications
= low supply
→ prices stay high

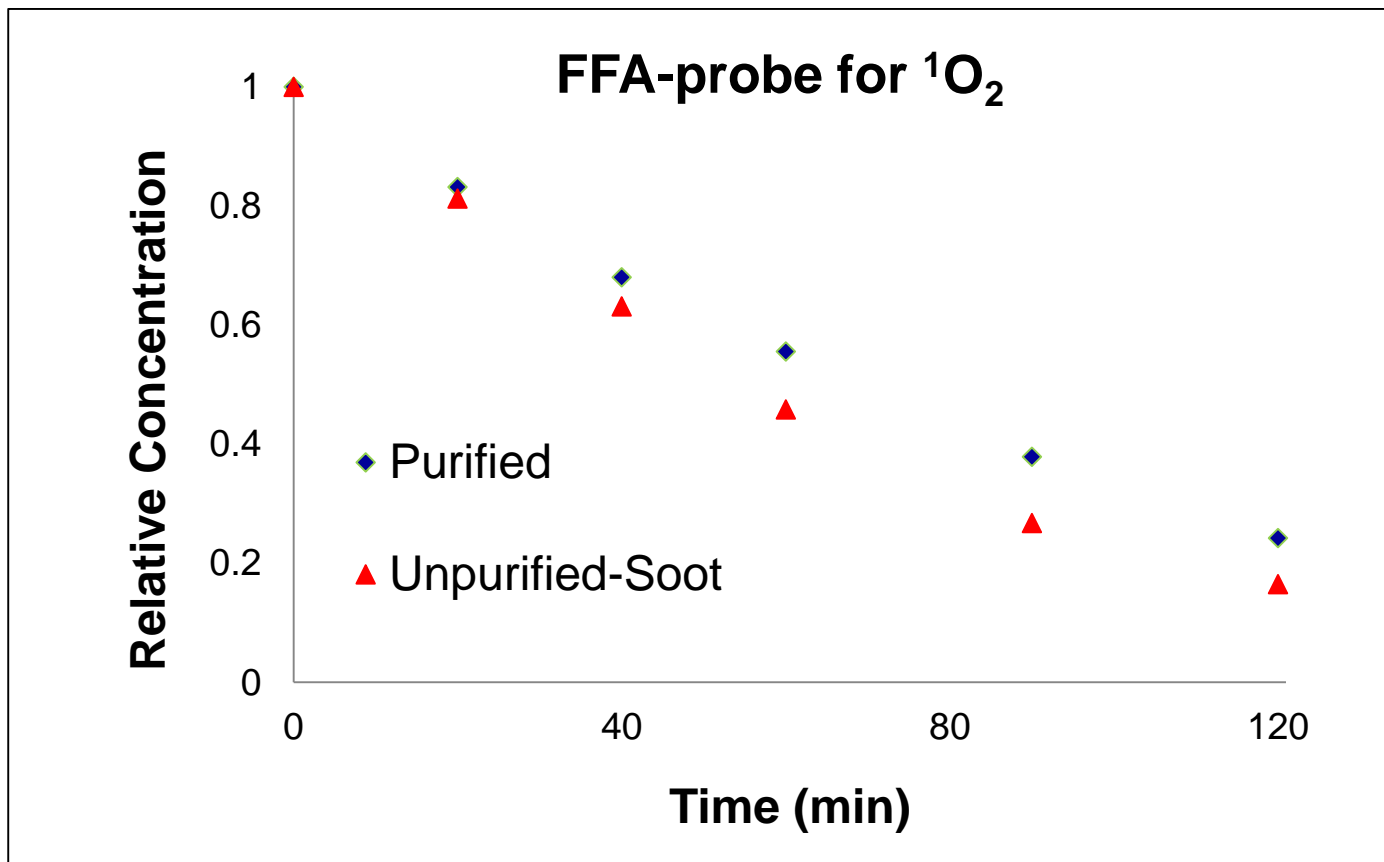


Most production is done for research (small quantities of highly purified material)

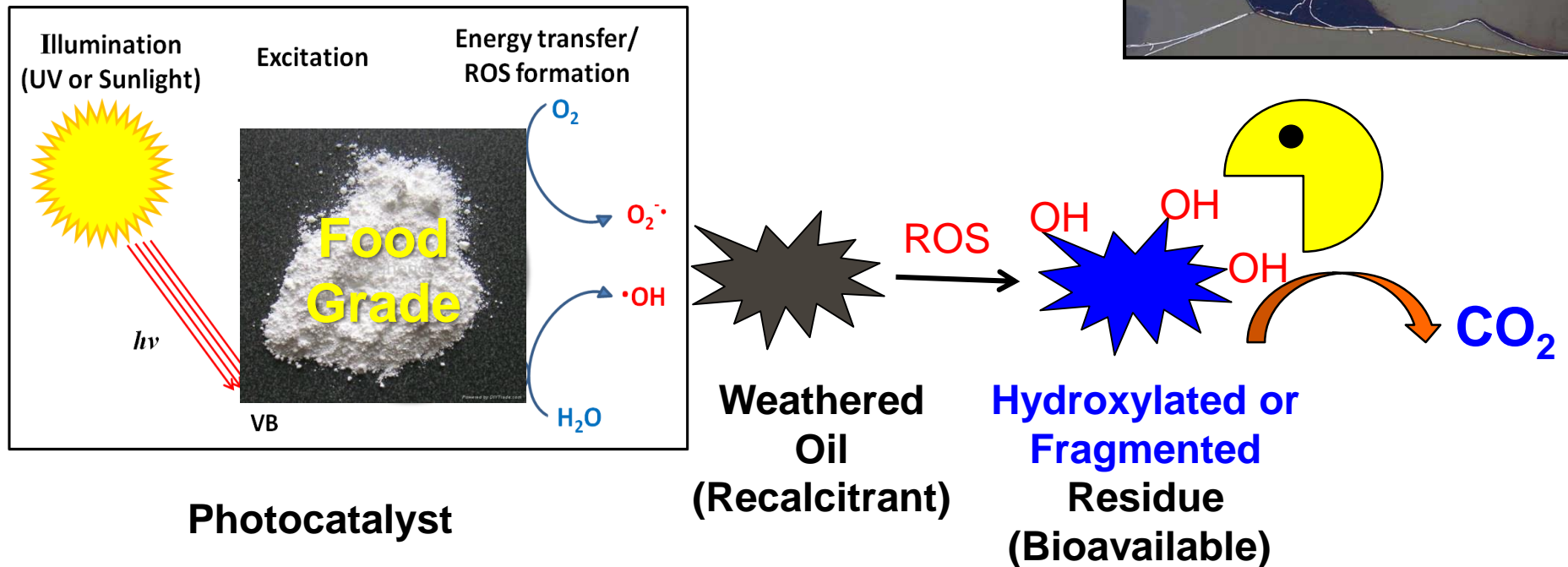
High purity requirements increase **separation cost** due to higher energy, solvent, & process time requirements

Avoid the diminishing returns of ultra high purity

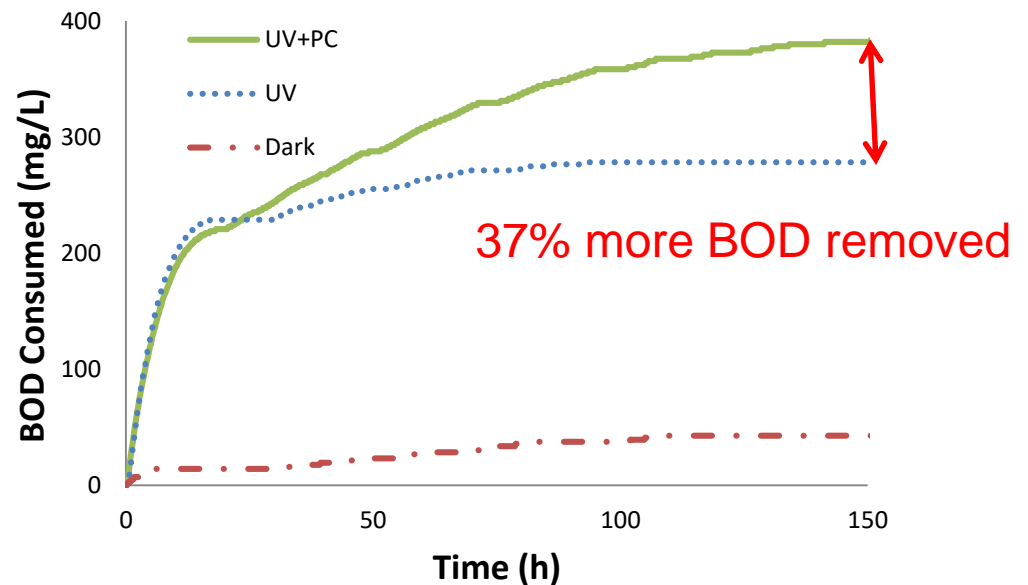
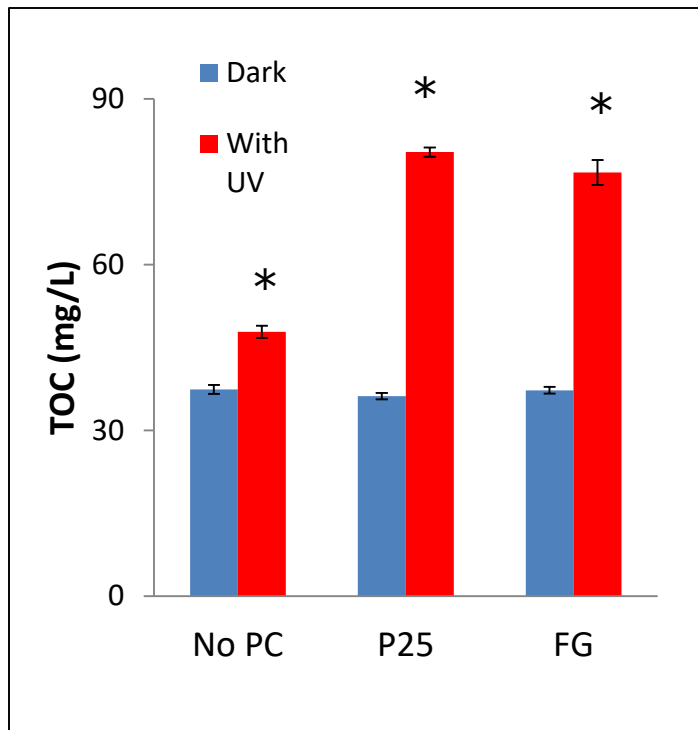
Less pure amino-C₆₀ cost less (20x) without significantly sacrificing reactivity



Photocatalytic Hydroxylation of Weathered Oil to Enhance Bioavailability and Bioremediation



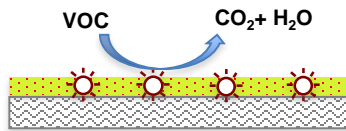
Photocatalysis Increased Solubilization and Biodegradation of Weathered Oil



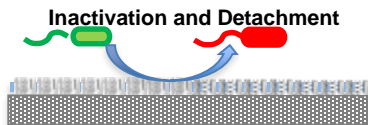
* statistically significant ($p < 0.05$) after 1-day exposure

Multifunctional coating

Photocatalytic degradation of VOC (1.3, 3.3)



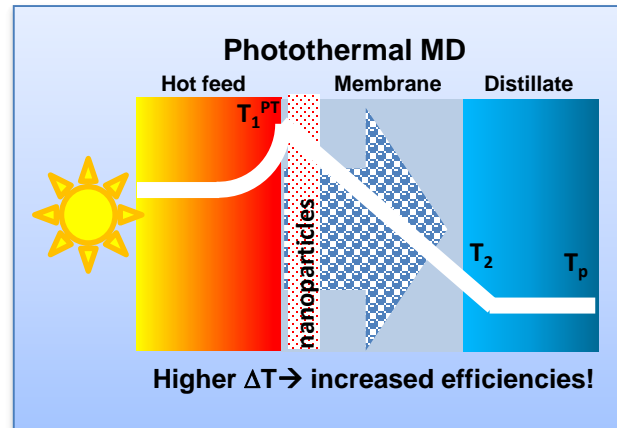
Anti-fouling/scaling (3.3)



Photothermal activity (2.2)

High performance base membrane

High porosity, super-hydrophobicity, low thermal conductivity (2.2)



Novel condensation surface

Novel biomimetic materials (e.g., desert beetles) (potential seed)

Membrane material development

Basic science

Reactor design

- NP/polymer interface (1.1, 2.3)

- Effect of Surface property on scaling and vapor condensation (2.2, 3.1)

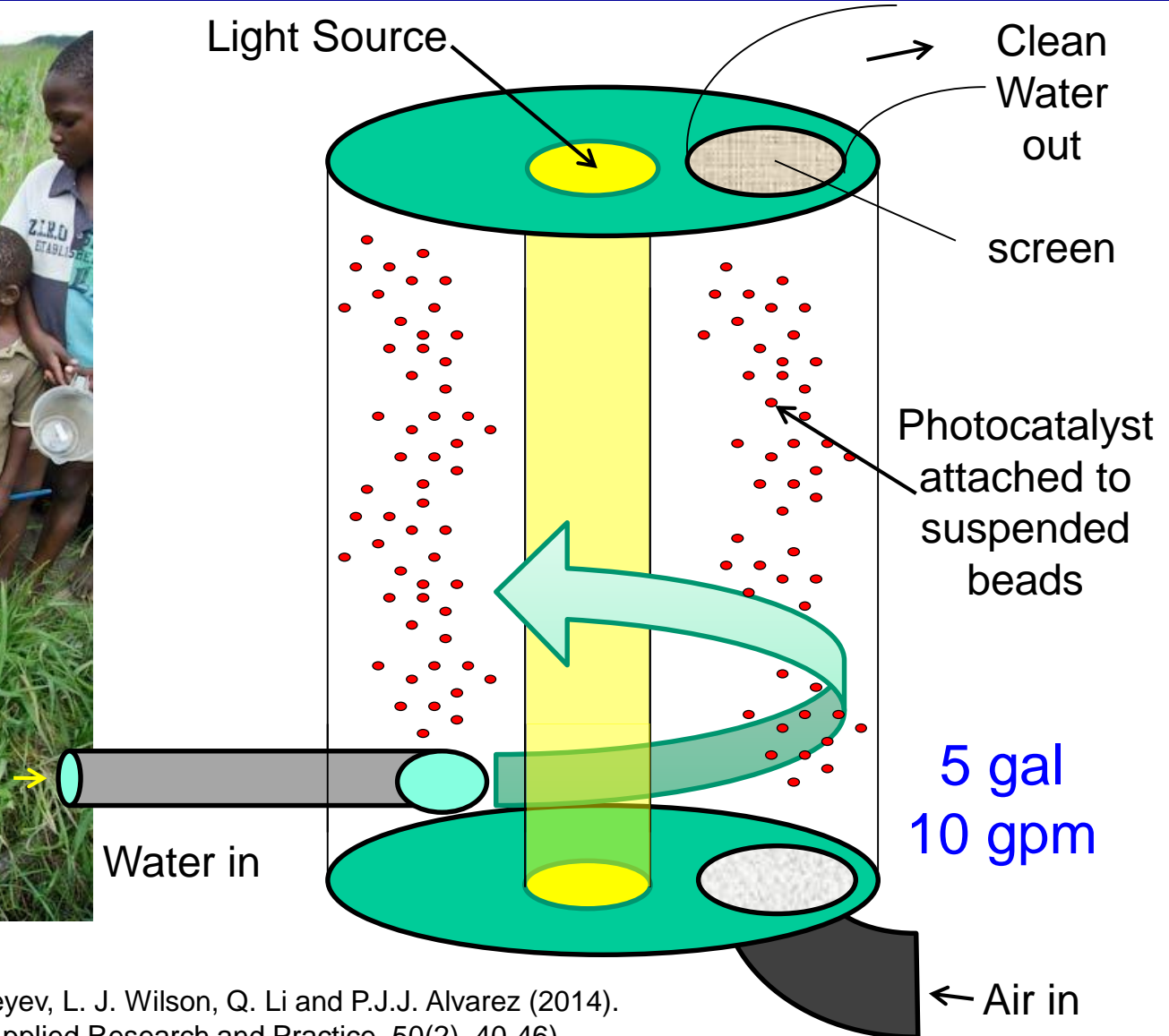
- NP-photon interaction (2.1)

- Light harvesting (2.4)

- Low cost, light weight membrane module (2.2)

- Heat recovery (NEWTskid)

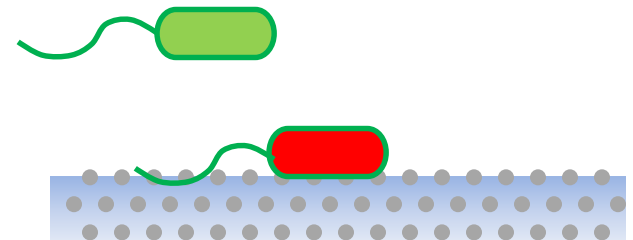
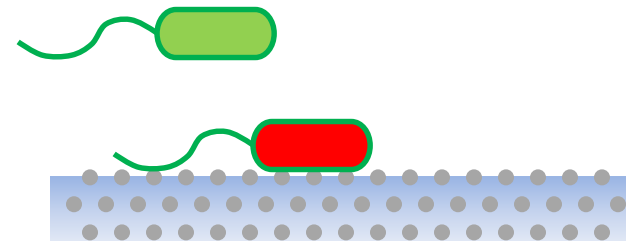
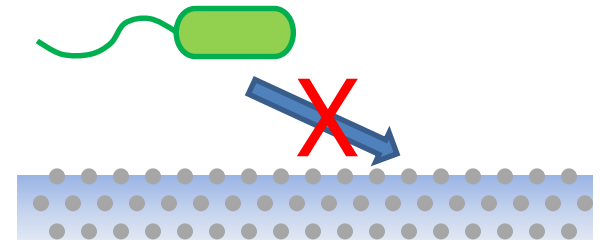
Fluidized Bed Photocatalytic Reactor for Point-of-Use Disinfection and Pesticide Removal





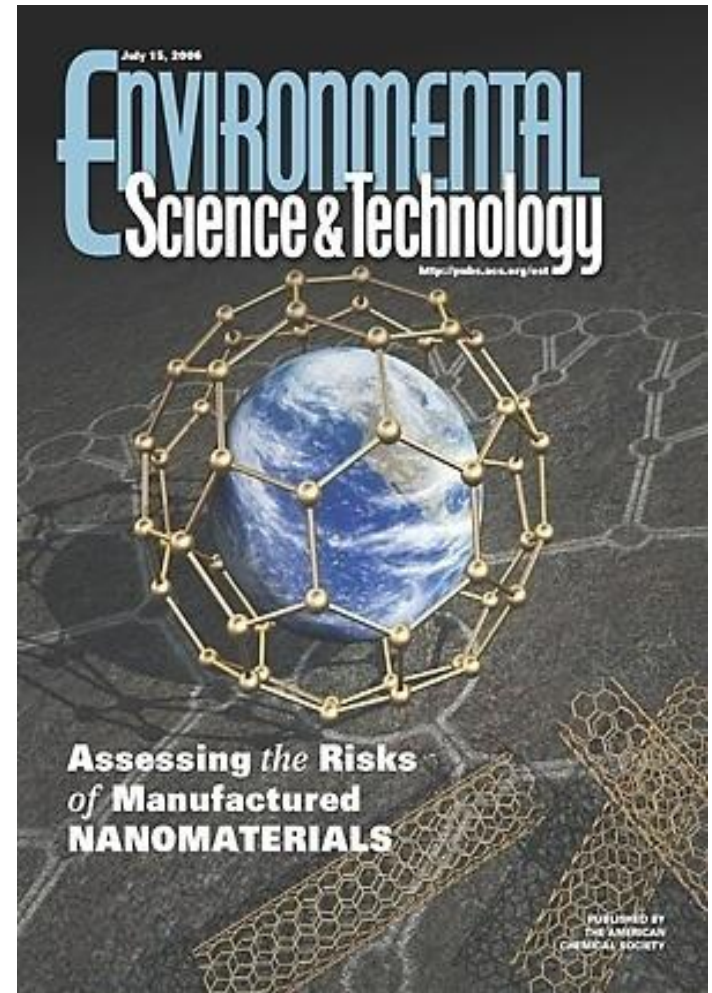
Biofouling Control

- * *Discourage adhesion*
 - * Nano-patterned topology
 - * Surface chemistry
 - * Interrupt quorum sensing
- * *Release novel antimicrobials from porous nanocarriers*
 - * Nanosilver or copper
 - * D-amino acids
- * *Photocatalytic ROS*
 - * Semiconductors, e.g., TiO_2
 - * Fullerene derivatives (self-cleaning surfaces)

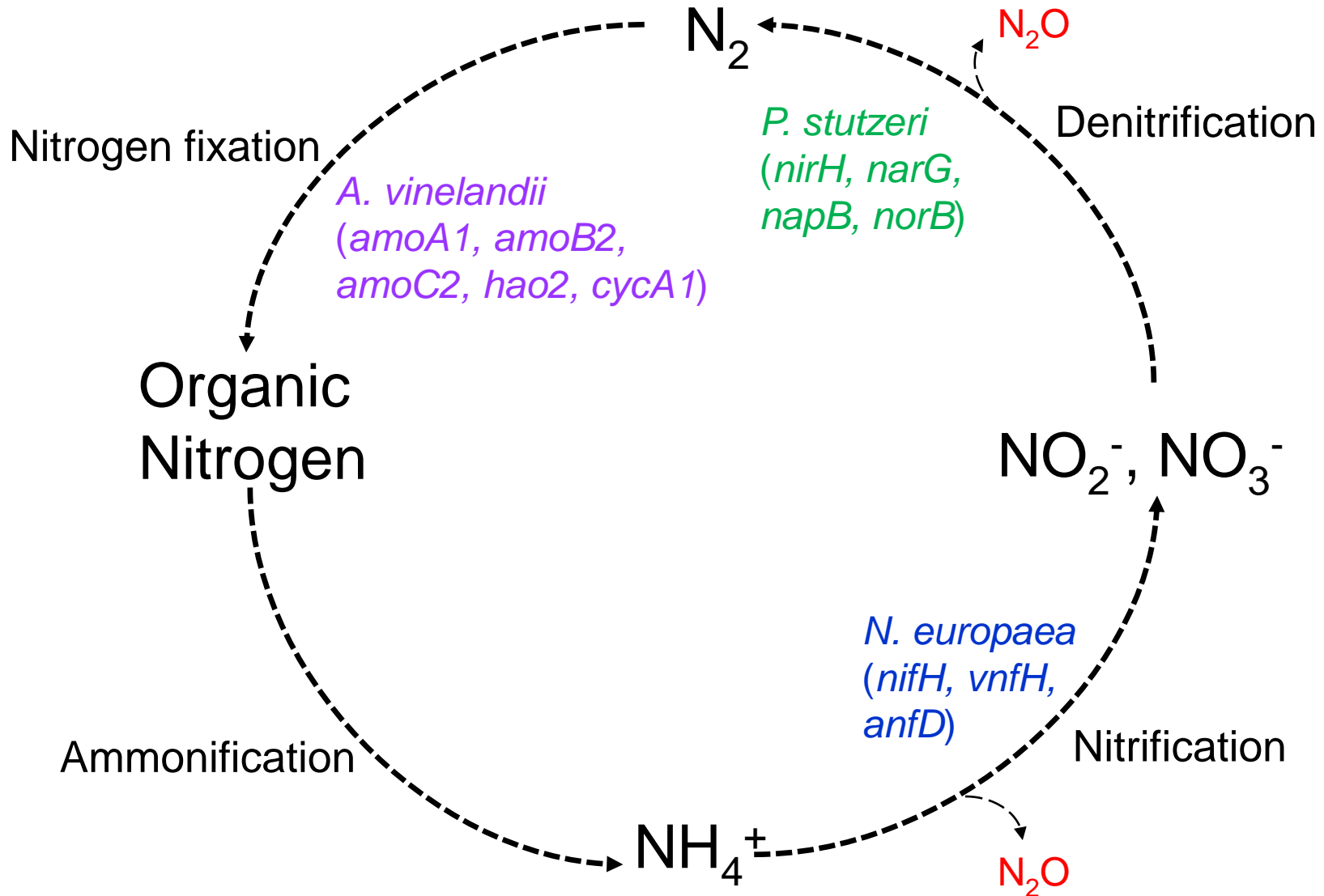


Conclusions

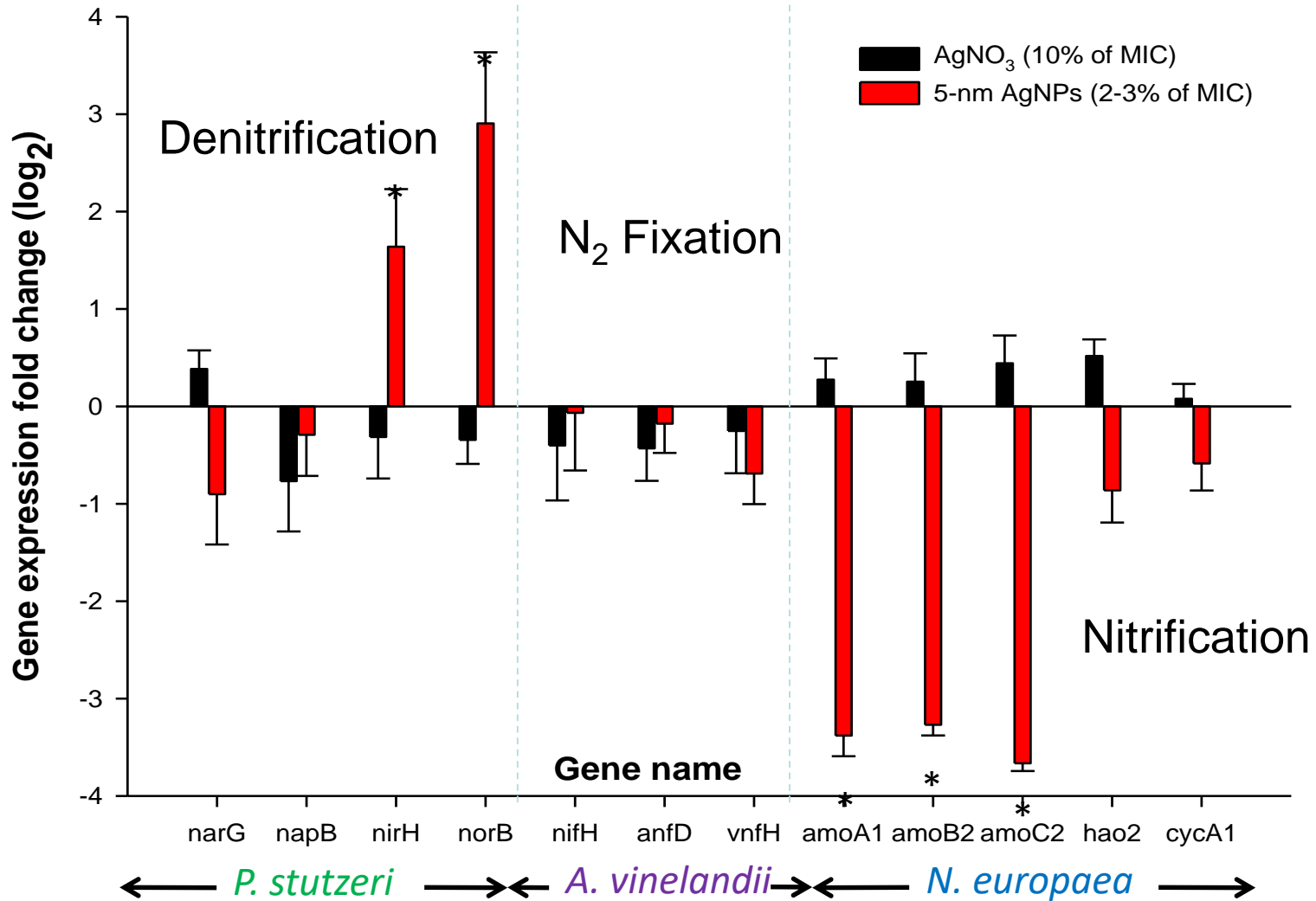
- Ecotoxicology
- Biodiversity and food webs?
- Biogeochemical cycling?
- *Mitigated by NOM, salts*



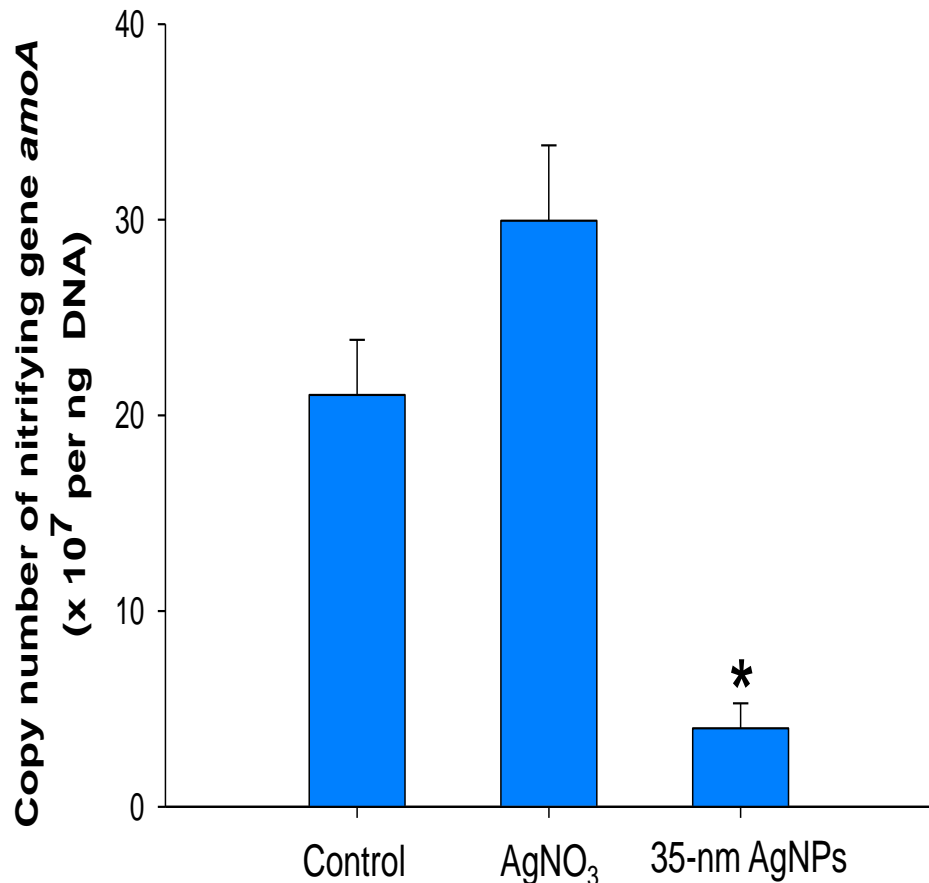
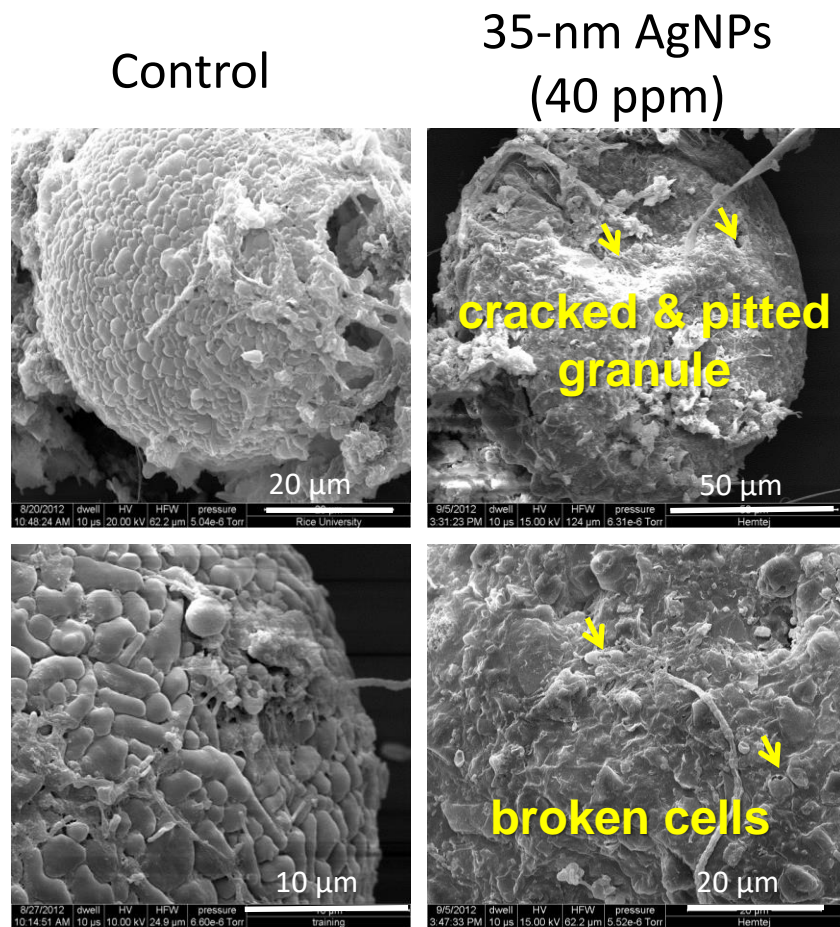
Potential Impacts to the N cycle:



Sub-lethal concentration of AgNPs induced denitrification but repressed nitrification genes



But AgNPs had higher impact than Ag⁺ on activated sludge



AgNPs damaged AS floc, which can affect clarification and recycling

AgNPs decreased abundance of nitrifiers, hinders N removal

Synthetic Nanoparticles in Natural Water

Example

$1.5 \cdot 10^3$ manufactured nanoparticles/ml

10^8 natural nanoparticles/ml (erosion, eruptions, combustion, etc)



Water for Energy – A Trillion-Dollar Challenge

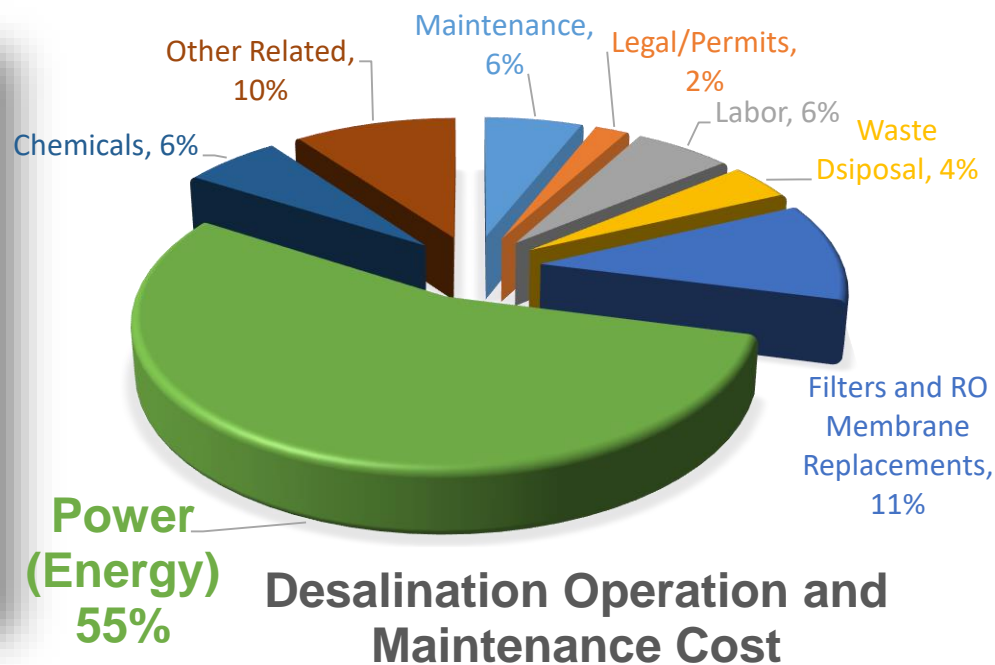
**Tailor-treat & reuse
produced waters for
EOR, agriculture,
desert greening, etc.**

Oil industry is a water industry
Water is a precious commodity
We can convert waste to value



Water/Oil Ratio = 10 (US), 14 (Can.) **\$1 trillion/yr challenge***

Energy for Water Treatment & Distribution



- 20% of electrical energy use in cities is for moving water¹
- Desalination and wastewater reuse is very energy-intensive²

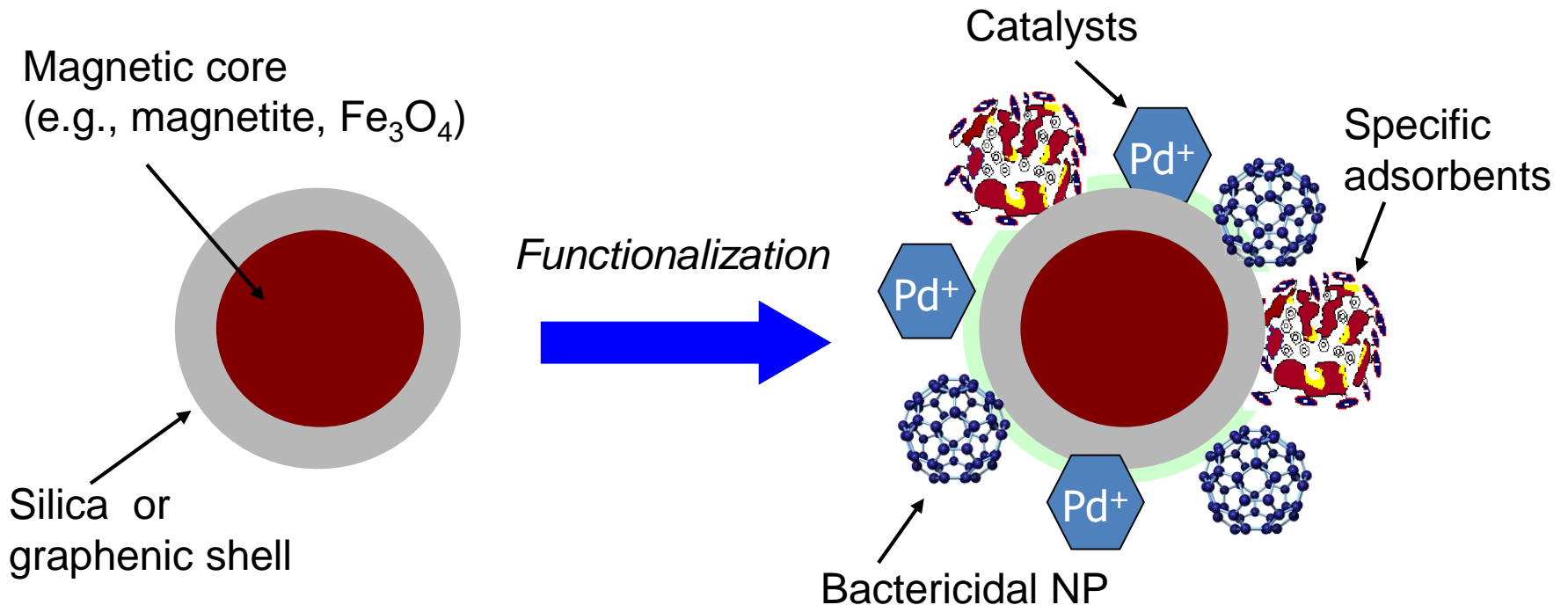
1. Electric Power Research Institute, Inc. Water & Sustainability (Volume 4): U.S. Electricity Consumption for Water Supply & Treatment –The Next Half Century. **2002**.

2. Water Reuse Association, Seawater desalination cost, January 2012



Multifunctional Nano-Sorbents

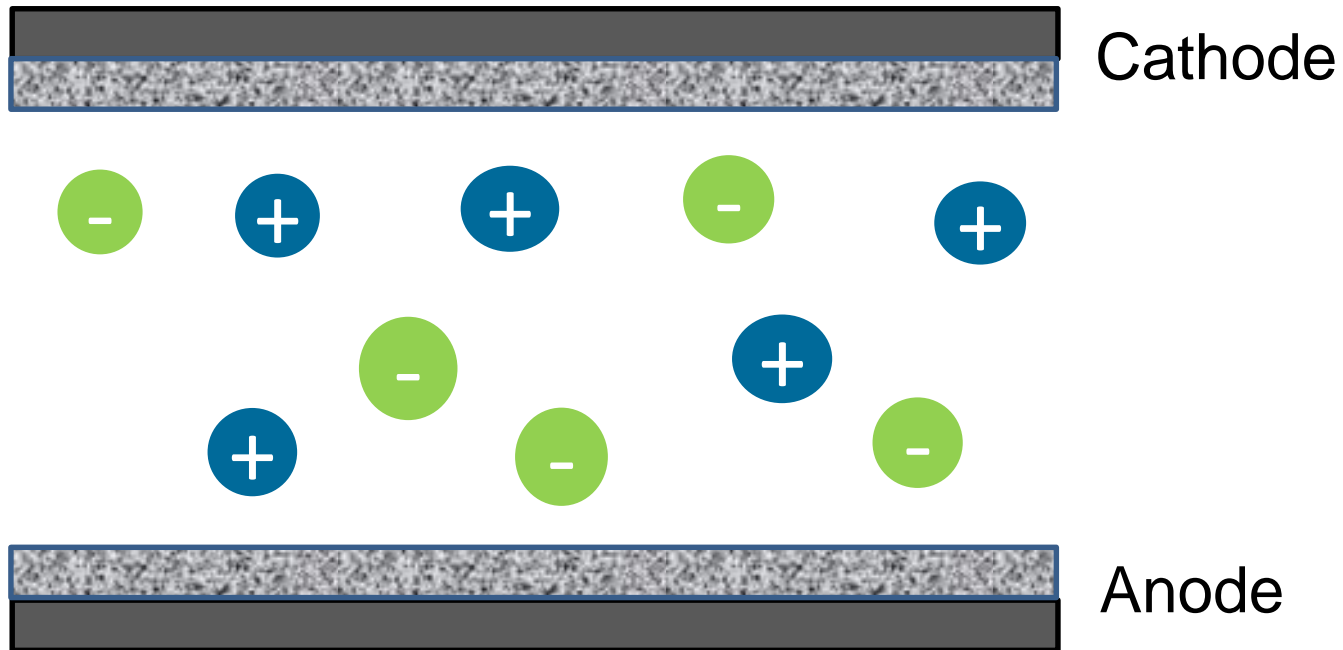
Selective removal of target contaminants by functionalized nanoparticles supported in macroscale structures or subject to (low-energy) magnetic separation for enhanced removal kinetics & reuse





Electrosorption for Scaling Control

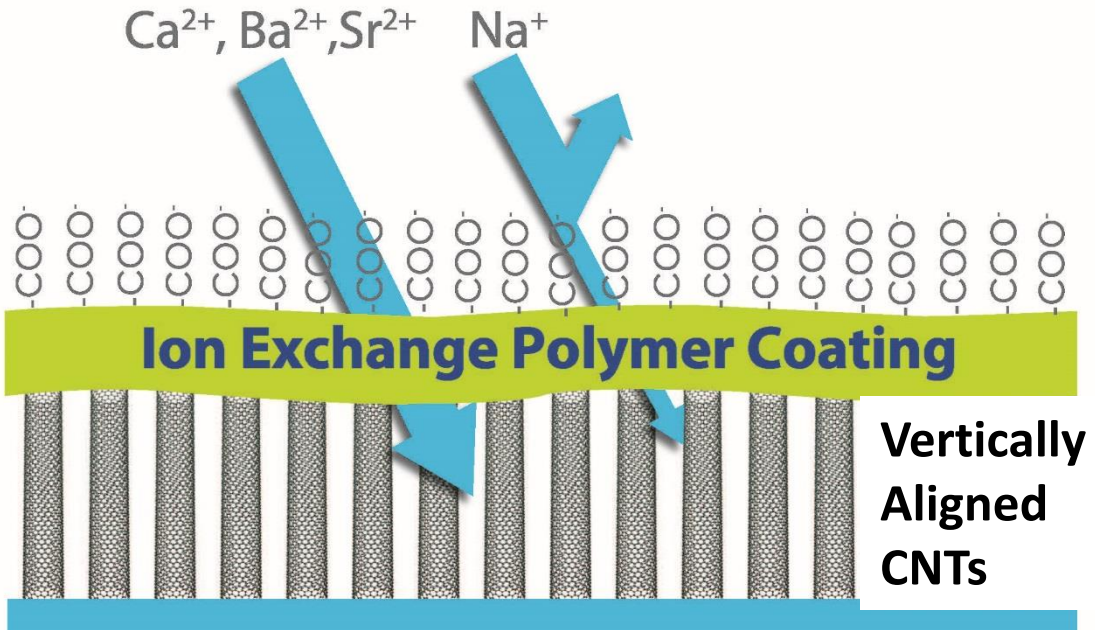
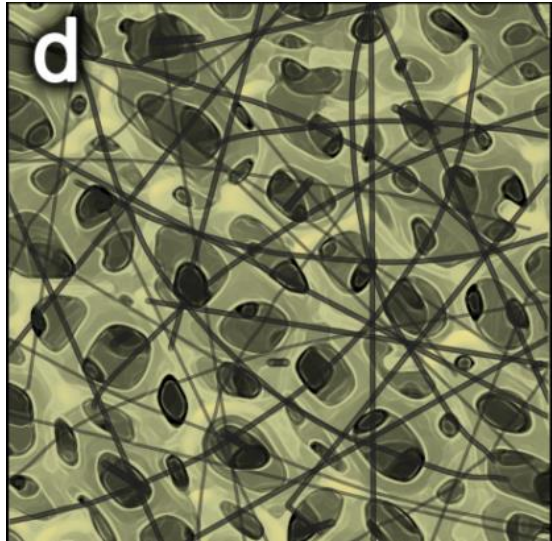
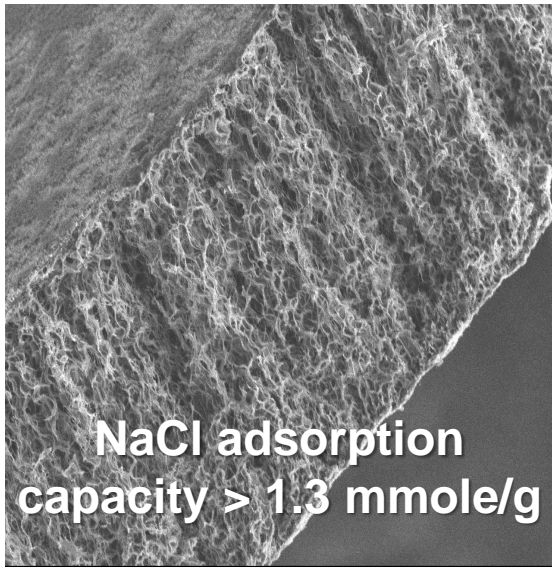
Nanocomposite electrodes to remove multivalent ions from brines, and generate smaller waste streams





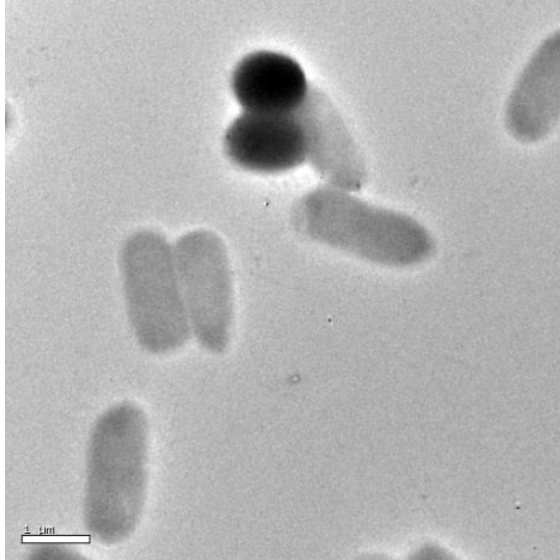
Nano-Enabled CDI

IX polymers enable preferential removal of divalent cations that cause scaling

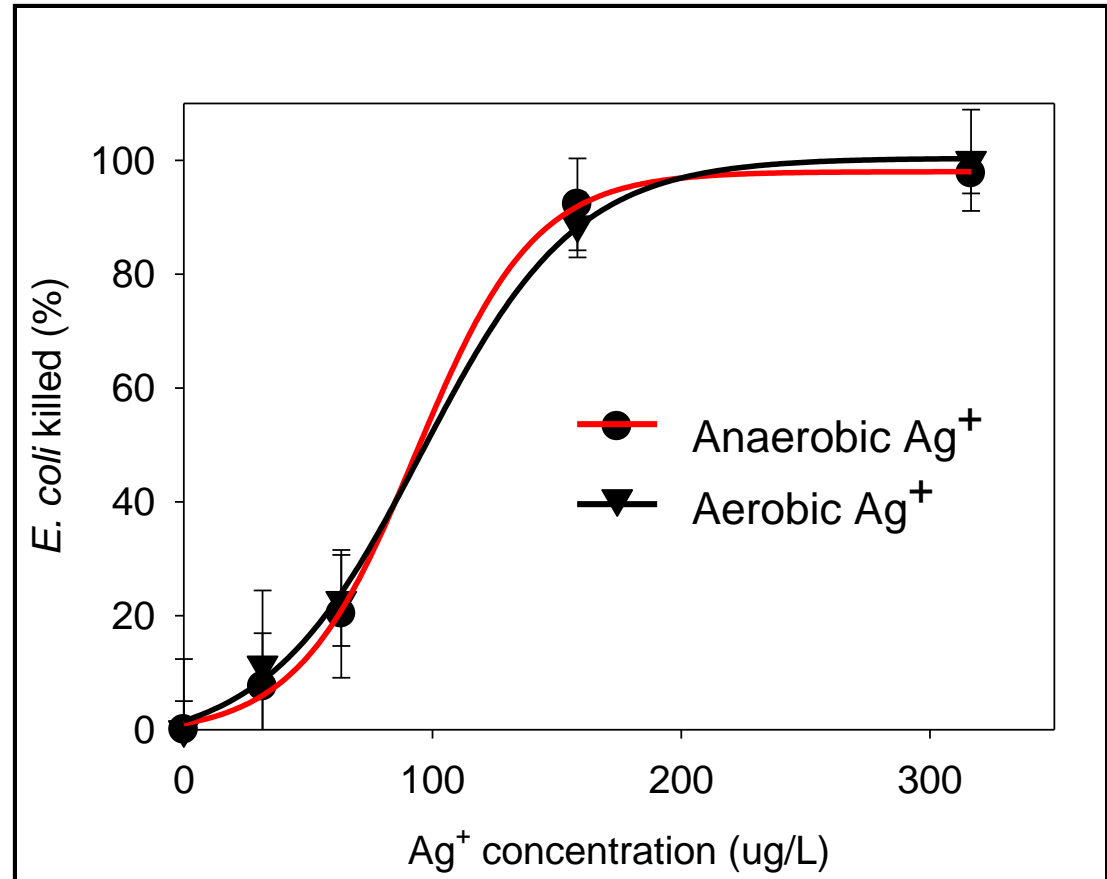


CNTs/graphene enhance sorption capacity, kinetics, mechanical strength and electrical conductivity

Similar Ag⁺ Toxicity under Aerobic & Anaerobic Conditions

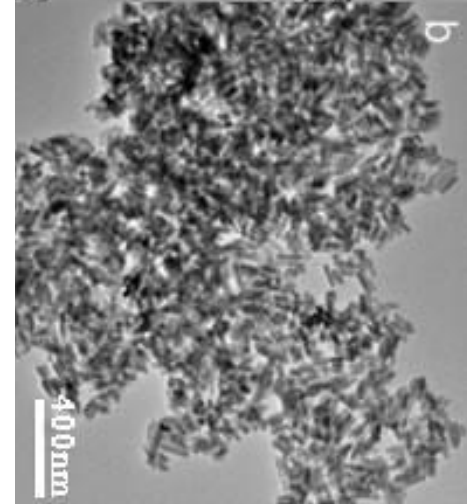
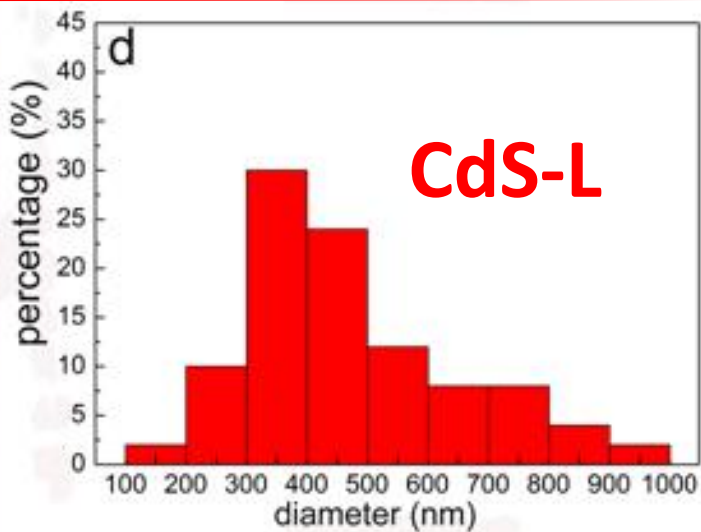
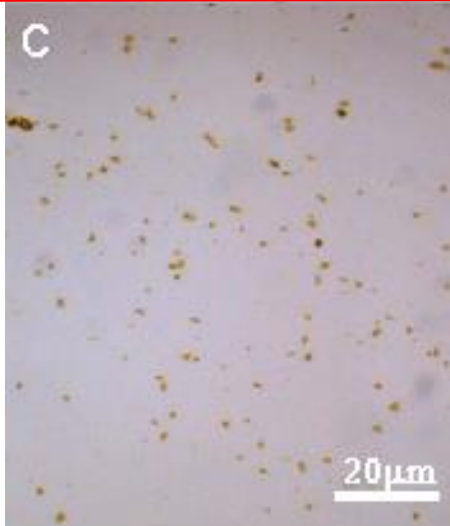
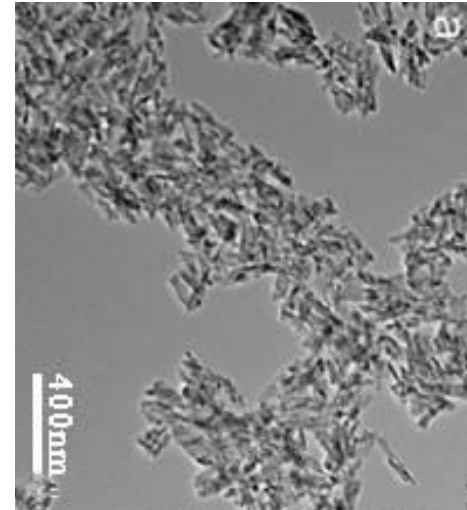
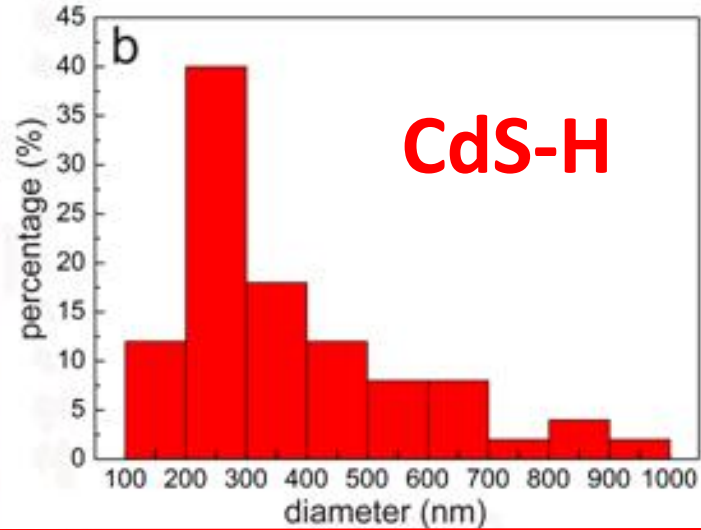
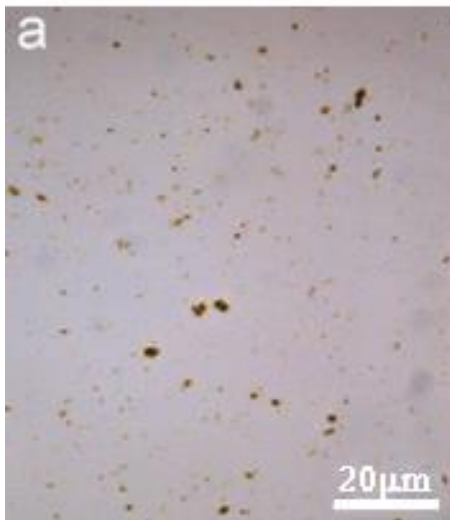


E. coli is facultative



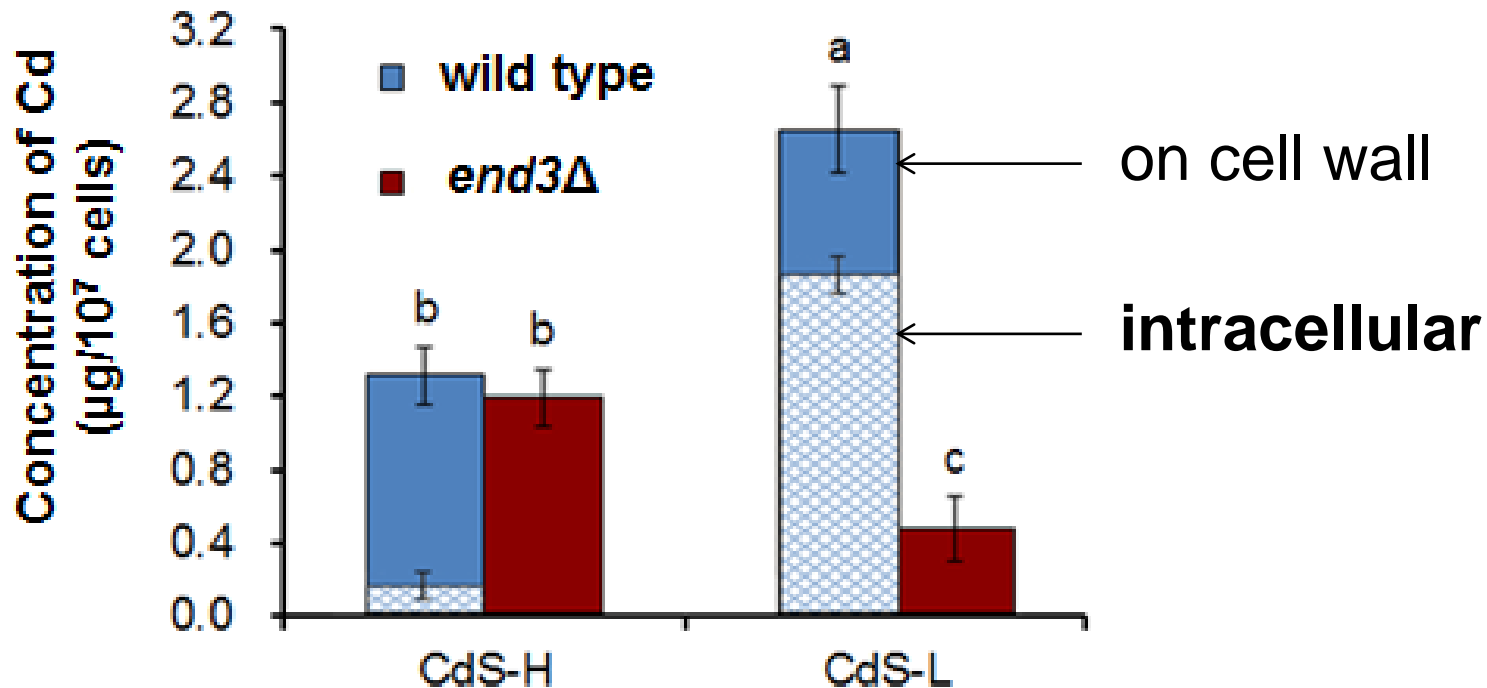
Statistically undistinguishable difference

Similar morphology and aggregate size



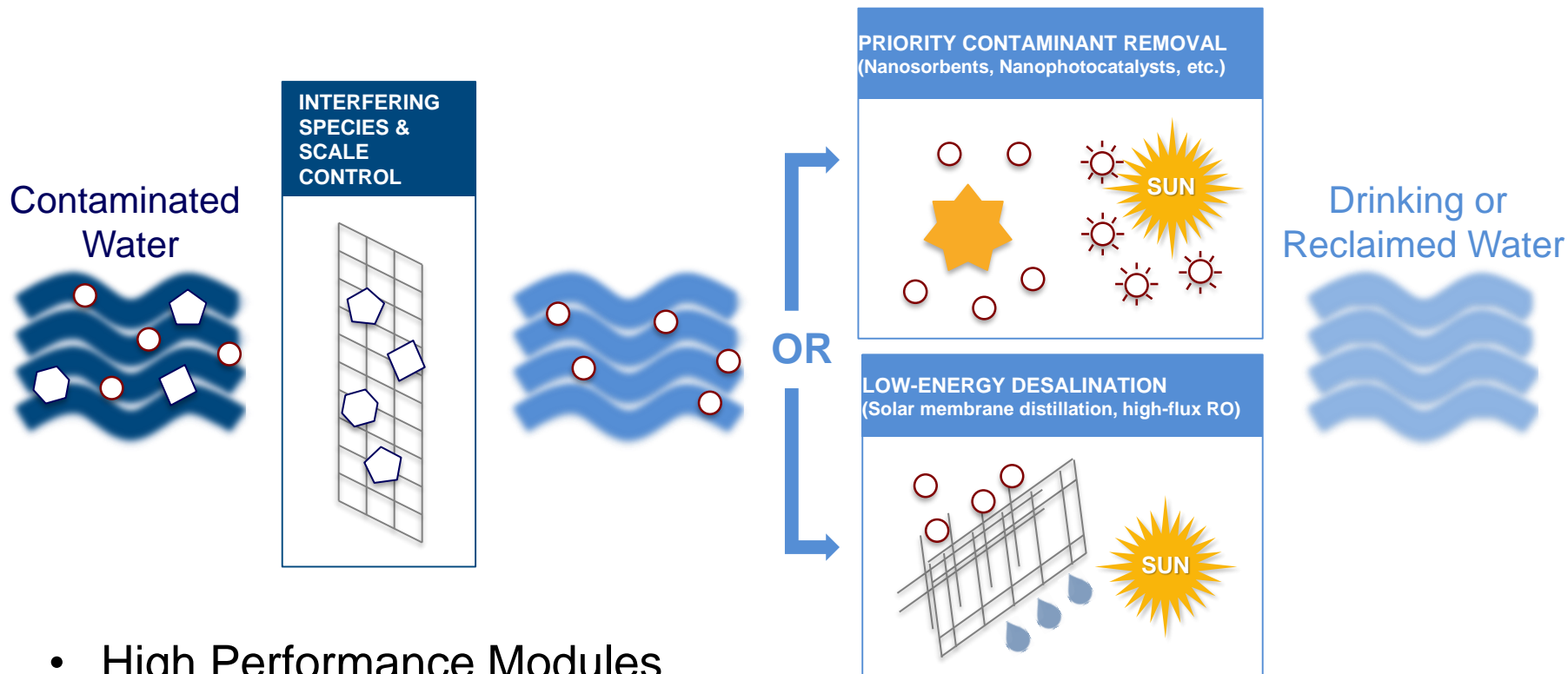
Total Cd accumulation in wild-type versus endocytosis-deficient (*end3Δ*) mutant yeast

- No difference for CdS-H (mostly trapped in wall)
- Significantly higher Cd accumulation for CdS-L in wild-type due to endocytosis



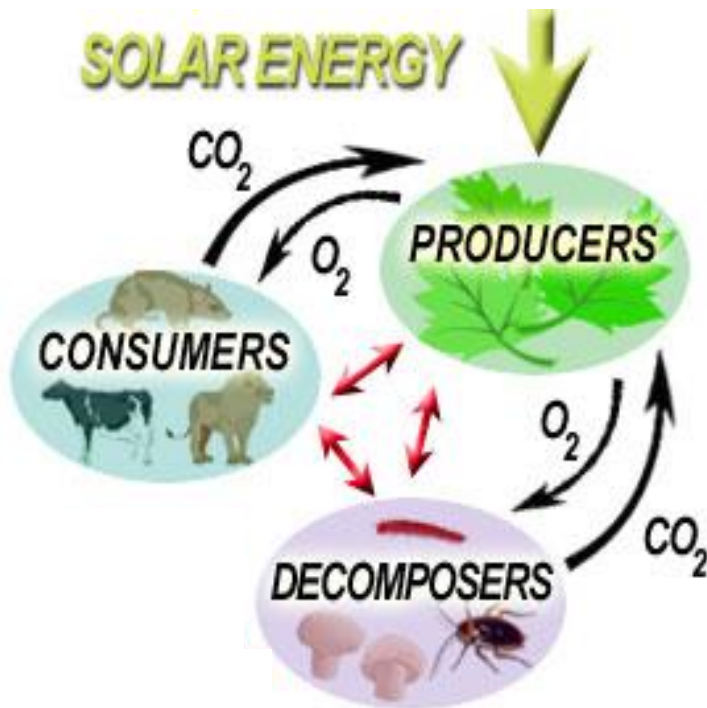
Modular Treatment Systems

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

Microbial-nanoparticle Interactions to Inform Risk Assessment

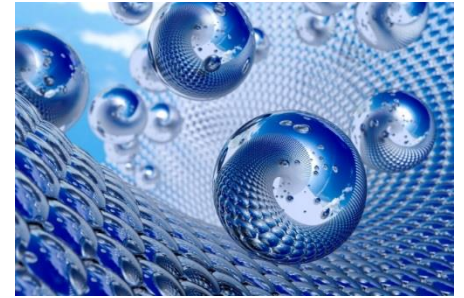


- Bacteria are at the foundation of all ecosystems, and carry out many ecosystem services
- Disposal/discharge can disrupt primary productivity, nutrient cycles, biodegradation, agriculture, etc.
- Antibacterial activity may be fast-screening indicator of toxicity to higher level organisms (*microbial sentinels?*)



NEWT Center

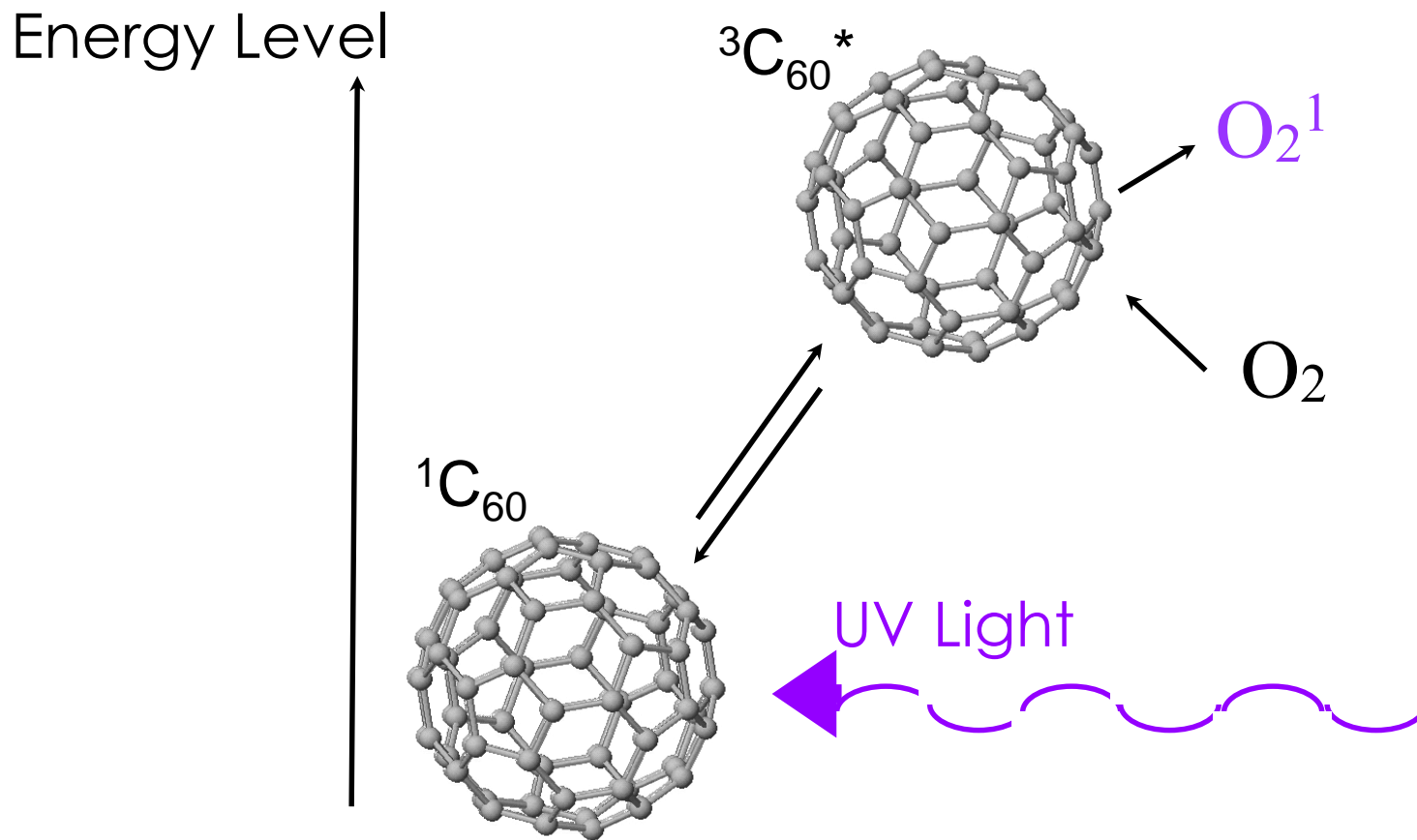
- The Nanotechnology-Enabled Water Treatment Center is the first national center to develop next-generation water treatment systems enabled by nanotechnology.
- ERC from NSF (\$37M for 10 yr)
- Innovation ecosystems with numerous industrial partners that help shape research.



Summary of nAg Release Implications

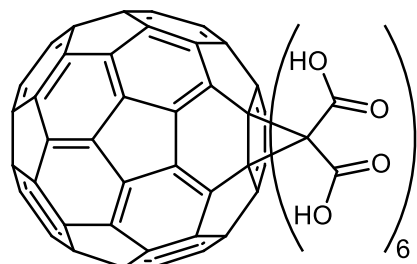
- Development of bacterial resistance & biofilm formation?
- Impacts to biological wastewater treatment processes?
- Impact nitrogen cycling?



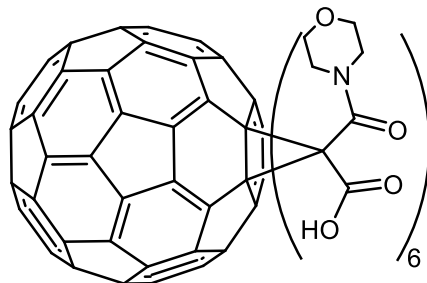


Light excites C₆₀ to triplet state. Energy transfer between ³C₆₀* and molecular oxygen gives rise to singlet oxygen (¹O₂)

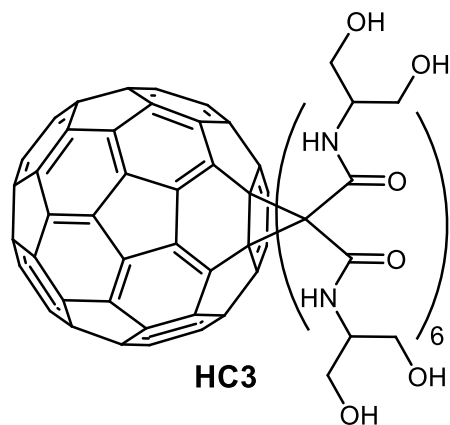
“Water Soluble” Derivatized Fullerenes



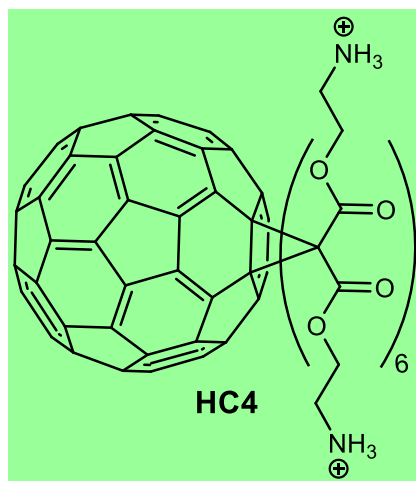
HC1



HC2

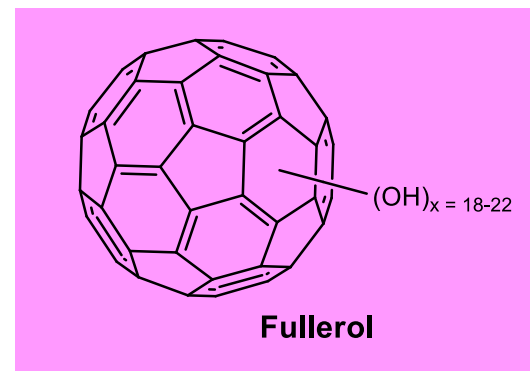


HC3



HC4

VS



Fullerol

* Commercially Available, MER Corp.

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

Superior $^1\text{O}_2$ Production confirmed by EPR & Laser Flash Photolysis