## Nanotechnology-Enabled Water Treatment: A Vision to Enable Decentralized Water Treatment and Reuse



Pedro J.J. Alvarez









## 

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-forperu/updates/



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



### Leap-frogging opportunities to:

•Develop high-performance multifunctional systems that are easy to deploy, can tap unconventional water sources, match treated water quality to intended use & reduce treatment cost.

•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?
- 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?
- What safety concerns must be addressed to commercialize nano-enabled water technologies? (Use bening ENMs & immobilize them)







- 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:** 

$$\mathcal{A} = \frac{T_1 - T_2}{T_f - T_p}$$

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, Urban, Ayala, Pimpinelli, **Nordlander & Halas**, NanoLett. **2014**, *14*, 4640-4645)



Enabling Technology Direct solar membrane distillation for low-energy desalination



## Higher $\Delta T \rightarrow$ increased efficiency!

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





## Electrosorption for Scaling Control

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



## **Nano-Enabled CDI for Scaling Control**



# (Photo)Disinfection & Advanced Oxidation

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



#### Advantages of Amino-C<sub>60</sub> as Photocatalytic Disinfectant



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



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

## 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



### **Need market-driven decrease ENM price**



Few commercial applications

- = low supply
- $\rightarrow$  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<sub>60</sub> cost less (20x) without significantly sacrificing reactivity



## **SUMMARY**

- 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





## 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.

## **Orivers 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.
- Reduce energy requirements

## 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





### Built by Rice Undergraduates



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





American's life expectancy at birth



- 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

## Nano = Dwarf (Greek) = 10<sup>-9</sup>

"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



**BASIC SCIENCE** 

AND DISCOVERY

TECHNOLOGICAL

INNOVATION

## **Operational Vision & Outcomes**

#### **APPLICATIONS AND OUTCOMES**





## 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



## **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

## **Responsible Nanotechnology**

"With Great Power, Comes Great Responsibility" Uncle Ben to Peter Parker in Spider Man

> Paul Hermann Muller Thomas Midgley



### **Quo Vadis, Nano?**



Maturity

"Nanohype" - Berube

### **Need market-driven decrease ENM price**



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## LAUDATO SI'



"We are the beneficiaries of two centuries of enormous waves of change...and, more recently, the digital revolution, robotics, biotechnologies and nanotechnologies. It is right to rejoice in these advances and to be excited by the immense possibilities which they continue to open up before us, for 'science and technology are wonderful products of a God-given human creativity."
### **Plate-and-Frame Configuration**

- Thin, patterned transparent poly(methyl methacrylate) sheet serves simultaneously as the top plate of the module, the optical window and the spacer that forms the feed flow channels.
- Mount it on a solar tracker to maximize sunlight collection.



## **Risk = Hazard × Exposure**



### **Example: Silver Nanoparticles**



Most Widely Used Nanomaterials In Commercial Products Source: Woodrow Wilson-The project on emerging nanotechnologies

### Is the antimicrobial activity of silver due to the nanoparticles themselves, or to the released Ag<sup>+</sup> ions, or both?

•And how do environmental conditions affect their relative influence?

### **Bioavailability and Toxicity of AgNPs**

Ag<sup>+</sup> is released only if Ag(0) is oxidized:  $4Ag^0 + O_2 + 4H^+ \leftrightarrow 4Ag^+ + 2H_2O$ (Solubility of  $Ag^0 \approx 0$ )



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



Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271–4275.

### No Toxicity Without Ag<sup>+</sup> Release



Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271–4275.

### AgNP Toxicity Can Be Explained by Dose-Response of Released [Ag<sup>+</sup>]



Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271–4275.

### "What does not kill you makes you stronger" Friedrich Nietzsche



Stimulatory effect after 6 h exposure to low Ag<sup>+</sup> concentration (Hormesis?)

Xiu Z., Q. Zhang, H.L. Puppala, V.L. Colvin, and P.J.J. Alvarez (2012). Nanoletters. 12, 4271–4275.

### Sub-Lethal Concentrations of AgNPs Could Also Stimulate Plants



### Increasing silver NP concentration

Wang J., Y. Koo, A. Alexander, Y. Yang, S. Westerhof, Q. Zhang, J. Schnoor, V. Colvin, J. Braam, and P.J. Alvarez (2013). Environ. Sci. Technol. 47 (10): 5442–5449.

# Sublethal Exposure to AgNPs (but not Ag<sup>+</sup>) stimulated biofilm development

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







Control 0.02 mg/L of Ag<sup>+</sup> 0.02 mg/L of AgNPs

Yang & Alvarez (2015). ES&T Letters. DOI: 10.1021/acs.estlett.5b00159

#### Sub-lethal Exposure of PAO1 to AgNPs also Upregulates Quorum Sensing, LPS, and Antibiotic Resistance Genes



### Why is nAg sometimes a stronger bactericide?



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

### More Effective Delivery of Ag<sup>+</sup> to Membrane and Cytoplasm



## CONCLUSIONS

- Implications: Ecotoxicology-Ecosystem services (primary productivity, food webs, nutrient cycling?) biodiversity? Toxicity to higher organisms? *Mitigated by NOM, salts*
- <u>Applications</u>: DBP-free disinfection, advanced (photo) oxidation processes, antifouling/corrosion coatings? functionalized membranes



## **Outlook for Developing Nations**

Despite current barriers (technical capacity, cost) the use of ENMs will increase in developing nations *(similar to cell phones)* for point-of-use water treatment and reuse, due to:

### Decreasing cost:

- Economy of scales
- Recyclability of immobilized NPs
- Avoid diminishing returns of ultra high purity
- Valuable properties imparted at low additive ratios

Savings on capital investment for new infrastructure in expanding mega-cities

## When Does NEWT Make Sense?

- Where current technologies do not meet current or upcoming DWT or WWT regulations;
- To treat recalcitrant compounds (e.g., pharmaceuticals) that escape WWTPs and hinder reuse (e.g., irrigation);
- Where there is insufficient infrastructure and one must rely on POU devices
- When NEWT enhances cost-effectiveness (e.g., faster, less energy, and less material)

### Feasibility Is within Reach (Photo-disinfection with TiO<sub>2</sub> is feasible for small villages if recycled)



Recycling makes photo-disinfection with TiO<sub>2</sub> competitive with traditional treatment processes *at small scales* 

(Assumes  $0.15/g TiO_2$ , 50 g/L used for treatment)

### Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment



# Join Us!

www.newtcenter.org





### 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

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

### Conceptual Improvements to Water Treatment Through Nanotechnology



Qu X., J. Brame, Q. Li and P.J.J. Alvarez (2012). Acc. Chem. Res. doi:10.1021/ar300029v

## **SUMMARY**

- Antimicrobial NPs can enable microbial control (e.g., DBP-free disinfection, fouling resistant surfaces and membranes, etc.)
- Sub-lethal concentrations of Ni<sup>2+</sup> and Cd<sup>2+</sup> hinder biofilm formation by inhibiting quorum sensing at the transcription level.
- Nanotechnology could offer opportunities for controlled released of bactericidal or QS-interrupting metals





Qu X., J. Brame, Q. Li and P.J.J. Alvarez (2012). Acc. Chem. Res. doi:10.1021/ar300029v

# Fracking in drought-prone regions represents both a water supply and pollution control challenge



### Use Brackish Groundwater for Fracking? (Geospatially consistent)



## 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



## 1) Need for Low-Energy Desalination

- High TDS represents a beneficial disposition challenge (discharge regulations)
- Multivalent cations (Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup>/Fe<sup>3+</sup>) interfere with performance of friction reducing polymers and also form scale (flow assurance)
- Naturally occurring radioactive materials
- Toxic inorganic contaminants (e.g., Zn<sup>2+</sup>)

## Desalination Technologies: Applicability and Water Recovery



### **Nano-Enabled Water Treatment @ Rice**

- Sand filter coated with nanomagnetite to remove As (pilot in Guanajuato, Mexico, reported by BBC, NY Times, Forbes and CBC).
- Fouling-resistant membranes that also inactivate virus (nAg, nano-TiO<sub>2</sub>)
- Pd/Au hypercatalysts to treat TCE (Pilot at Dupont site)
- Novel amino-fullerene photocatalysts to enhance UV and solar disinfection and advanced oxidation processes





### Proliferation of Multi-drug Resistant "Superbugs" (NDM-1 positive) from Sewage Treatment Plants



NDM-1 flow output (genes/day) was 4.6-fold greater than influent values

Yi L., F. Yang, J. Mathieu, D. Mao, W. Qing, and P.J.J Alvarez (2014). ES&T Letters. (1), 26-30

# 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*?)

## **Selected Antimicrobial Mechanisms**



### Vision: Nano-Enabled Water Treatment & Reuse

#### "Nano" particles:

- High surface areas
- Hyper-catalytic functions
- Tunable physical properties
- Multifunctional membranes
- Faster kinetics

Transformative Technologies to

clean water, enhance water infrastructure, & enable integrated water management & reuse



Enable high-performance water treatment and remediation systems with (1)Less infrastructure, (2)Less materials/reagents (selective targeting) (3)Lower costs & energy



Light excites  $C_{60}$  to triplet state. Energy transfer between  ${}^{3}C_{60}^{*}$  and molecular oxygen gives rise to singlet oxygen ( ${}^{1}O_{2}$ )

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

### "Water Soluble" Derivatized Fullerenes



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

#### Superior <sup>1</sup>O<sub>2</sub> Production confirmed by EPR & Laser Flash Photolysis
### **Example 2: Biofouling of Water Treatment Membranes**



# Fouling-Resistant UF Membrane Fabrication (Wet Phase Inversion)



room temperature

- Nanoparticle solubilisation in NMP. Ultrasonication (100 W, 4 min)
- Addition of PVP at 70 °C
- Slow addition of PSF while stirring at 120 °C

NMP = N-methylpyrrolidone ; PSf = Polysulfone ; PVP=Poly(vinylpyrrolidone)

### **Bacterial growth inhibition test**



Zodrow K., L. Brunet, S. Mahendra, Q. Li, and P.J.J. Alvarez (2009). Wat. Res doi:10.1016/j.watres.2008.11.014

#### **Nanoparticle Modifications in the Environment**



Alvarez P.J.J., V. Colvin, J. Lead and V. Stone (2009). Research Priorities to Advance Eco-Responsible Nanotechnology. ACS Nano 3(7): 1616-1619.

### Thanks! - Graduate Students and Postdocs NSF, EPA, CBEN, FAO, NERC, BP



- 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



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







- 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

# **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\***

# Energy for Water Treatment & Distribution



#### 20% of energy use in cities is for moving water<sup>1</sup> Desalination and wastewater reuse is very energy-intensive<sup>2</sup>

- 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



# 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.
- Reduce energy requirements

# **Research Needs and Opportunities**

- Network topology analysis to exploit the interconnectivity of complex water systems (e.g., integrated drinking water, wastewater & storm water networks to enhance water availability and reuse).
- Advanced materials and technologies to obtain drinking water from unconventional sources, and to enable reuse and resource recovery (e.g., drinking water, energy, nutrients) from challenging wastewaters.



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# **Top-Down Strategic Plan**



# 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 <sub>2</sub> & 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

# 7 Grand Challenges Related to Water



"Whiskey is for Drinking; Water is for Fighting Over"

### ~Mark Twain