Degrading Organic Compounds in Simulated Produced Water by Creating Hydrogen Peroxide Catalytically

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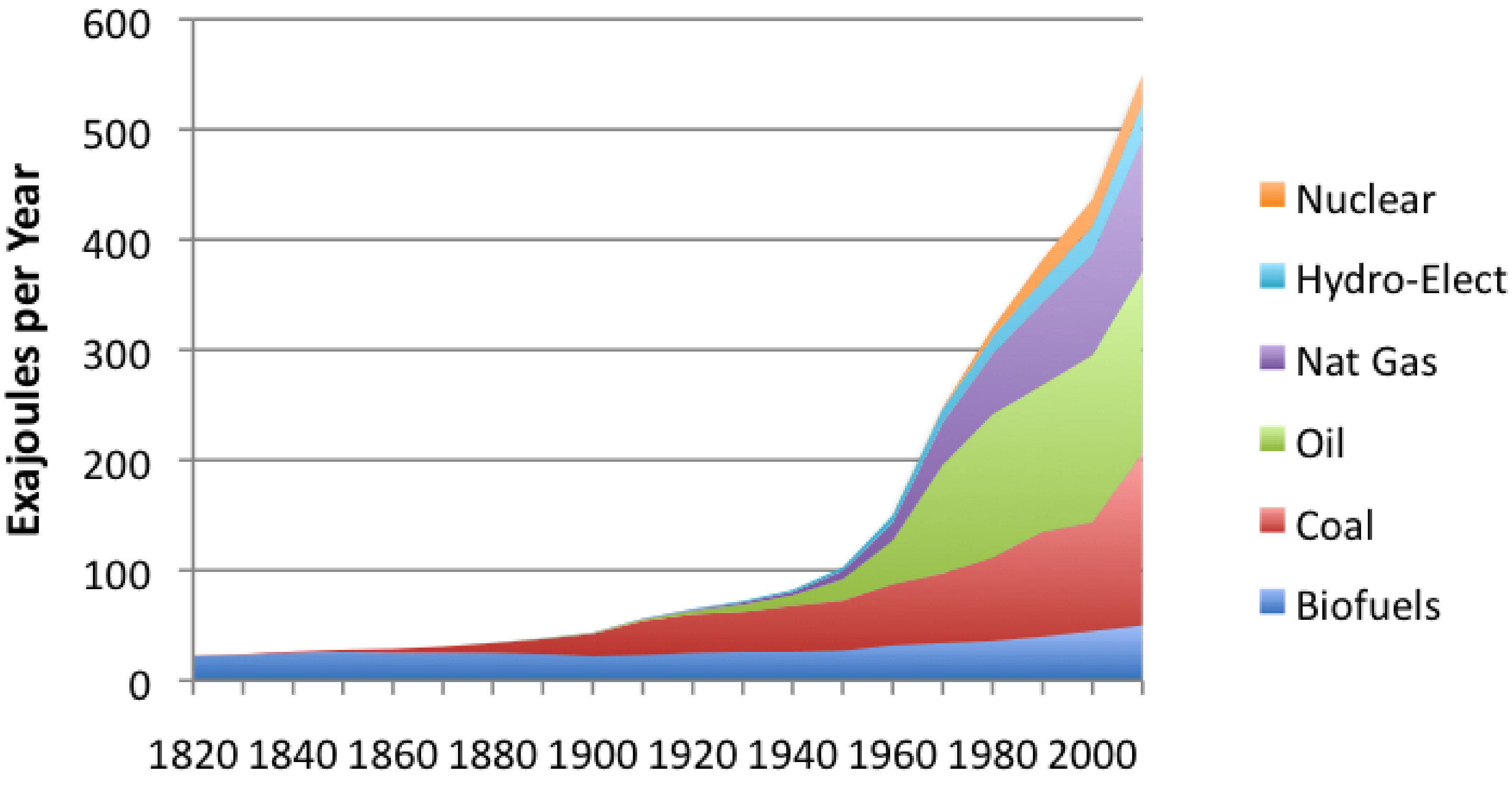
Presentation Outline

- Background of water research
- Nanotechnology-enabled water treatment (NEWT)
- The role of our group in NEWT
- How we can apply nanotechnology to use organic acids present in produced water to in-situ degrade the hazardous organics (e.g. BTEX)?

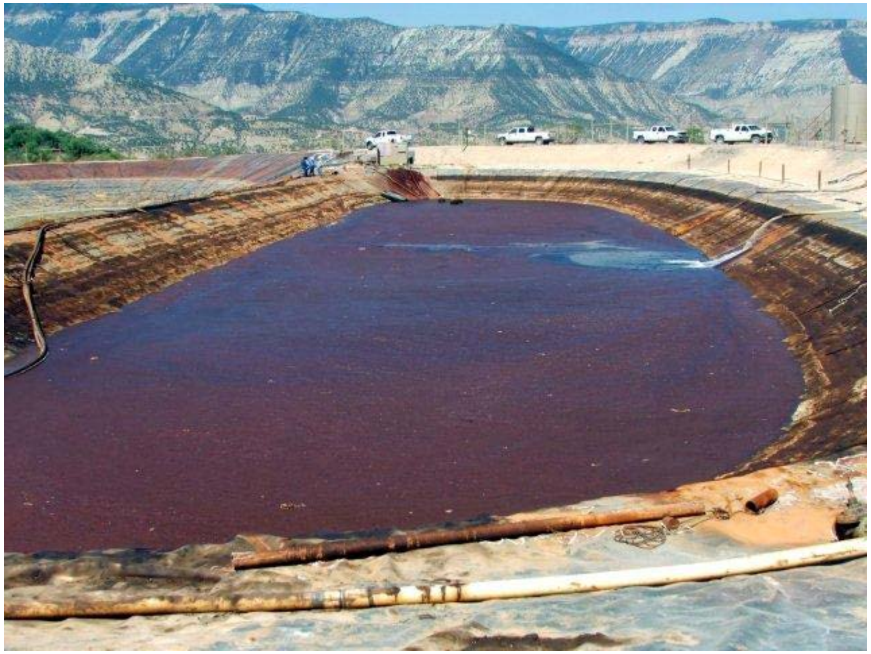
World Energy Consumption



(Note:1 exajoules is 10^{18} joules)

https://ourfiniteworld.com/2012/03/12/world-energy-consumption-since-1820-in-charts/

Importance of Water for Energy

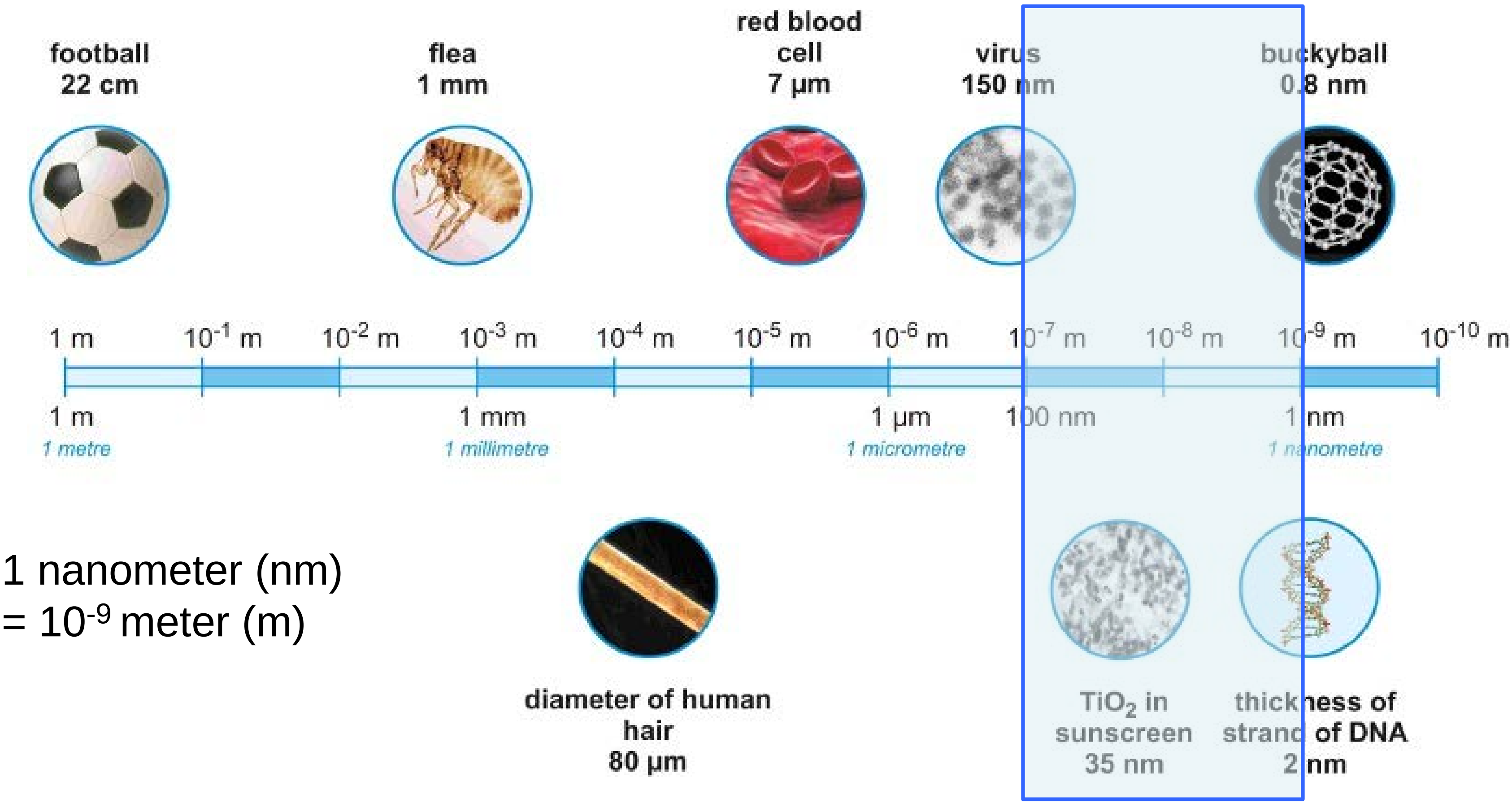


- Wastewater is the largest byproduct of the fossil fuel industry
- Water/Oil Ratio = 10 (US), 14 (Canada)
- Cost related to water including wastewater treatment, corrosion and biofouling…
- $1 trillion/year challenge!
- How to solve it?

Nanotechnology to Cleanup Water

"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 nanometer (nm)
= 10^{-9} meter (m)

Nanotechnology to Cleanup Water

Why Nano?

- Unique phenomena at nanosize enable novel applications
- Tap unconventional water sources, generate less waste and reduce the cost

Nanomaterial Properties	Examples of Enabled Technologies
Large surface area to volume ratio	Superior sorbents (e.g. nanomagnets 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 (antimicrobial, 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

Overview of the NSF-NEWT Center

NSF Nanosystems Engineering Research Center for
Nanotechnology-Enabled Water Treatment (NEWT)

Team RICE (Headquarter), UTEP, Arizona State University, Yale University

Mission of the NSF-NEWT Center

- Enhance the sustainable and efficient use (and reuse) of water resources in energy production
- Reduce the economic and environmental costs of the water footprint
- Alleviate water-related impairment (e.g., souring, corrosion, flooding)
- Increase energy efficiency, safety and reliability of urban water supply

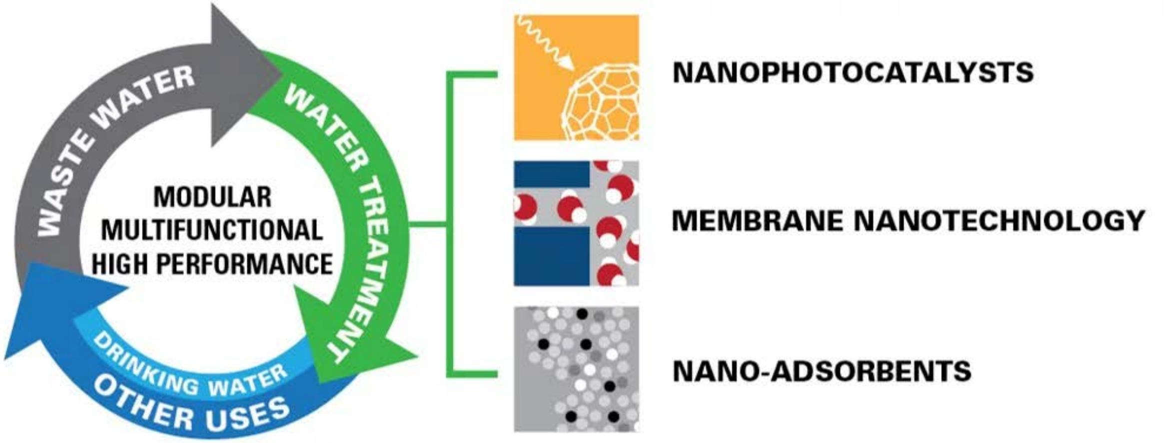
Overview of the NSF-NEWT Center

- **Treatment focus**

Drinking water treatment

Industrial wastewater reuse

- **Multidisciplinary approaches**



Primary Treatment Goals

- Reduce organic compounds

  (Why: Some organic compounds (e.g. BTEX) are hazardous to livings (if discharge), excessive organics may cause fouling in the formation (if reuse))

- Reduce bacterial

  (Why: Sulfate reduction bacterial (SRB) itself can cause plugging and the H_2S produced can cause corrosion and scaling (if reuse), health issues of the livings (if discharge))

- Reduce iron

  (Why: Fe(II) can form FeS and $FeCO_3$ scale. Fe(III) can precipitate as $Fe(OH)_3$)

Proposed Approaches

1. Fixed-bed heterogeneous catalysis for generating oxidants such as hydrogen peroxide (H_2O_2) from (i) air and water; and (ii) air with organic acids present in the water (contained in produced water) to degrade bacteria and sulfide.
2. Electrocatalytic oxidation and catalytic wet air oxidation of hydrocarbons in produced water using an electrochemical reactor to generate H_2O_2 or other oxidant in situ.
3. Magnetic nanoparticles and magnetic traps to remove ferrous and ferric iron from produced water.

Oxidant	Oxidation Potential, V
Hydroxyl Radicals	2.8
Ozone	2.3
Hydrogen Peroxide	1.8
Chlorine Dioxide	1.5
Chlorine	1.4

Produced Water Characteristics

Overview of some produced water characteristics from wells in the Marcellus region of Pennsylvania

Characteristic	Maximum	Average
TDS ($mg\,L^{-1}$)	345 000	106 390
TSS ($mg\,L^{-1}$)	7600	352
Oil and grease ($mg\,L^{-1}$)	802	74
COD ($mg\,L^{-1}$)	36 600	15 358
TOC ($mg\,L^{-1}$)	1530	160
pH	8.42	6.56
Alkalinity ($mg\,L^{-1}$ as $CaCO_3$)	577	165
SO_4($mg\,L^{-1}$)	763	71
Cl ($mg\,L^{-1}$)	196 000	57 447
Br ($mg\,L^{-1}$)	1990	511
Na ($mg\,L^{-1}$)	117 000	24 123
Ca ($mg\,L^{-1}$)	41 000	7220
Mg ($mg\,L^{-1}$)	2550	632
Ba ($mg\,L^{-1}$)	13 800	2224
Sr ($mg\,L^{-1}$)	8460	1695
Fe dissolved ($mg\,L^{-1}$)	222	40.8
Fe total ($mg\,L^{-1}$)	321	76

Toxic organic compounds (e.g. BETX)

Organic acids (e.g. formic acid, acetic acid)

H_2O_2 (OH·)

In-situ generation using nanomaterial

Gregory, K et al. *Current Perspective on Produced Water Management Challenges During Hydraulic Fracturing for Oil and Gas Recovery.* Envi. Chem. **2015.**

Proposed Model Organic Degradation

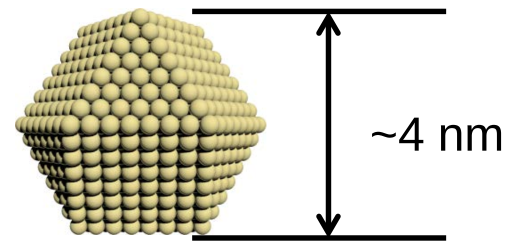
Formic acid + O_2

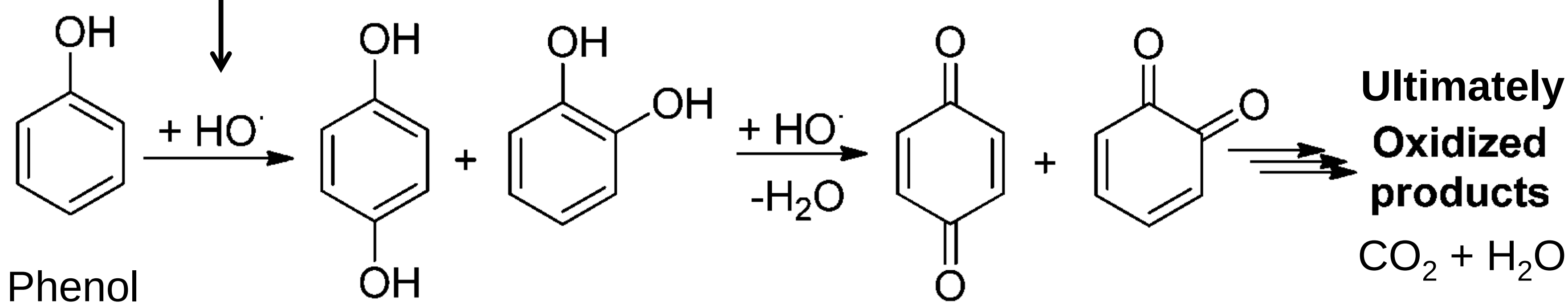
↓ Pd/Au

H_2O_2

↓ Pd/Au

Pd/Au Nanoparticle as a catalyst

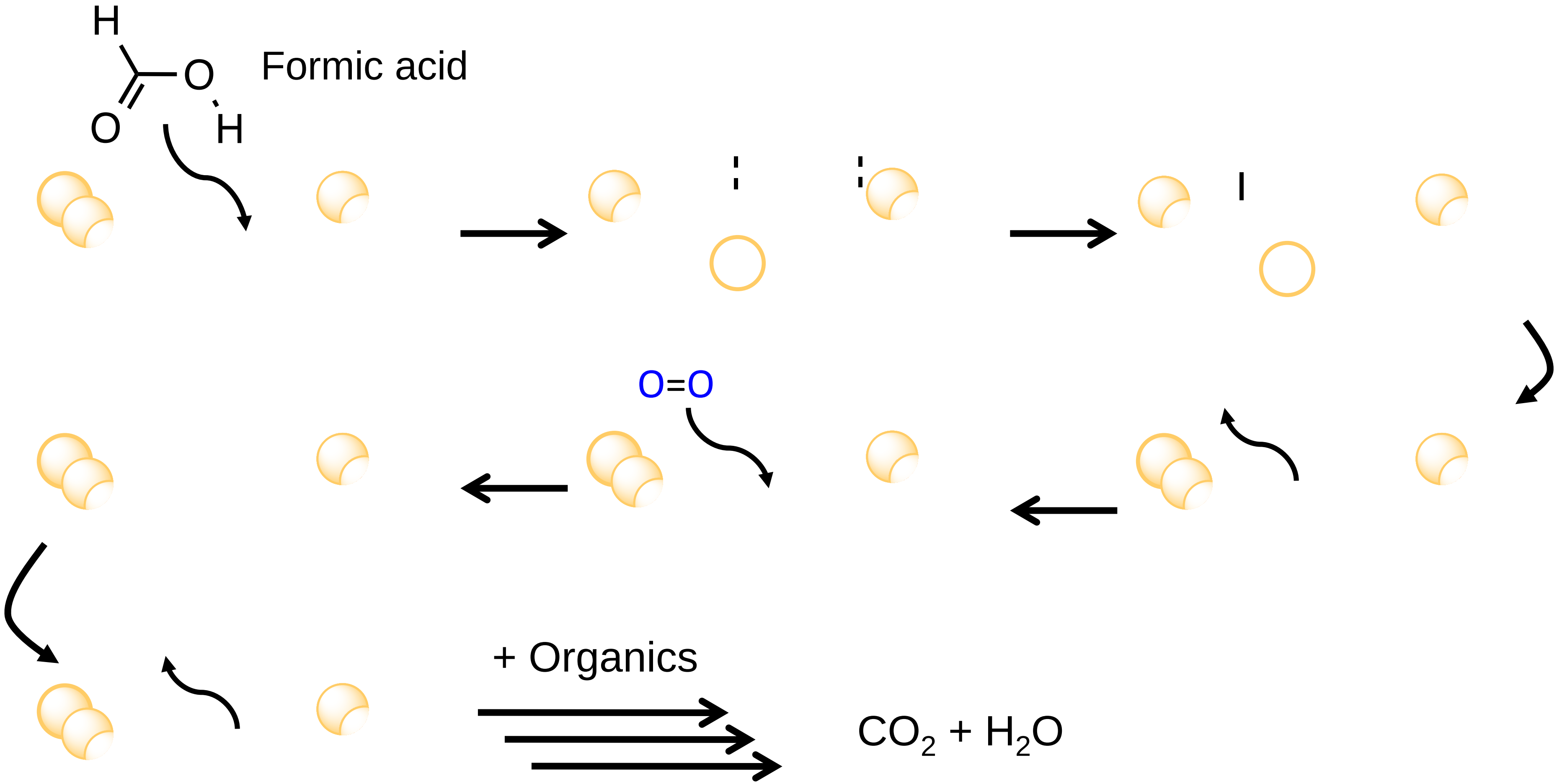




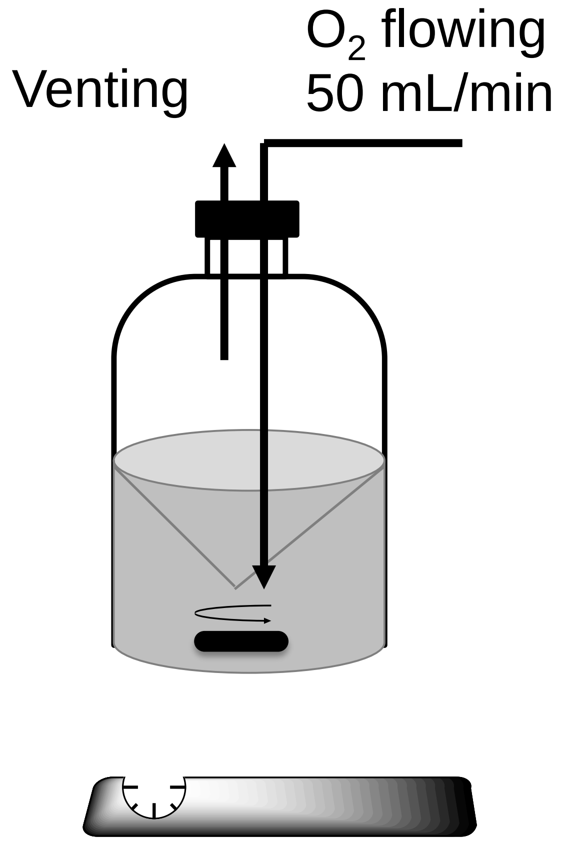
(Note: Formic acid was used as a model organic acid in produced water, and phenol was used as a model toxic organic compounds in produced water)

Mechanism of H_2O_2 Generation

General chemical equation: $HCOOH + O_2 \xrightarrow{Pd} H_2O_2 + CO_2$

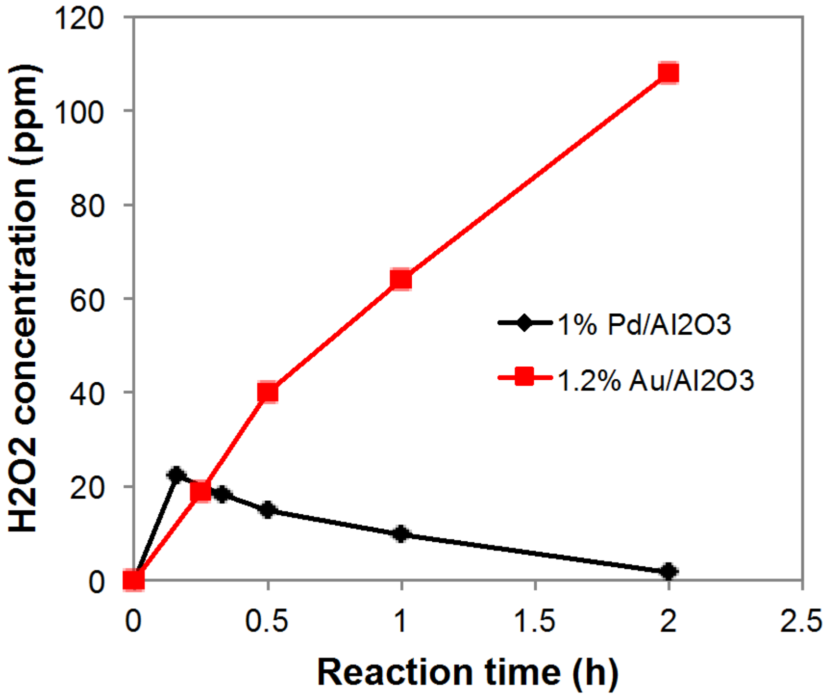


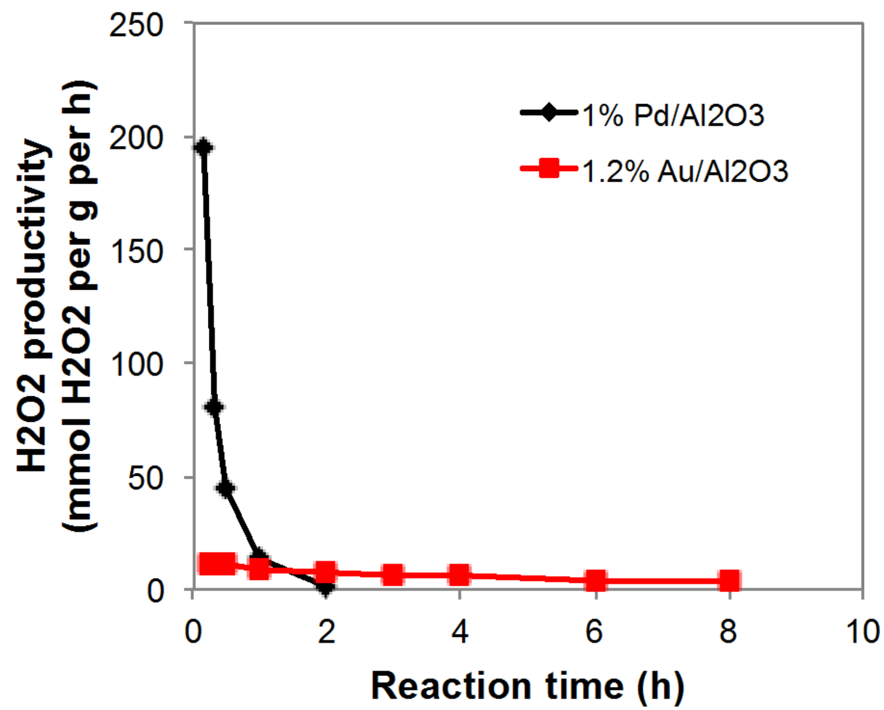
H_2O_2 Generation Setup



- 100 mL liquid volume
- 10,000 ppm Formic acid
- 20 mg 1% Pd/Al_2O_3
  (or 200 mg 1.2% Au/Al_2O_3)
- pH~3.5
- Room Temperature (~22 C)
- 1000 rpm stirring rate

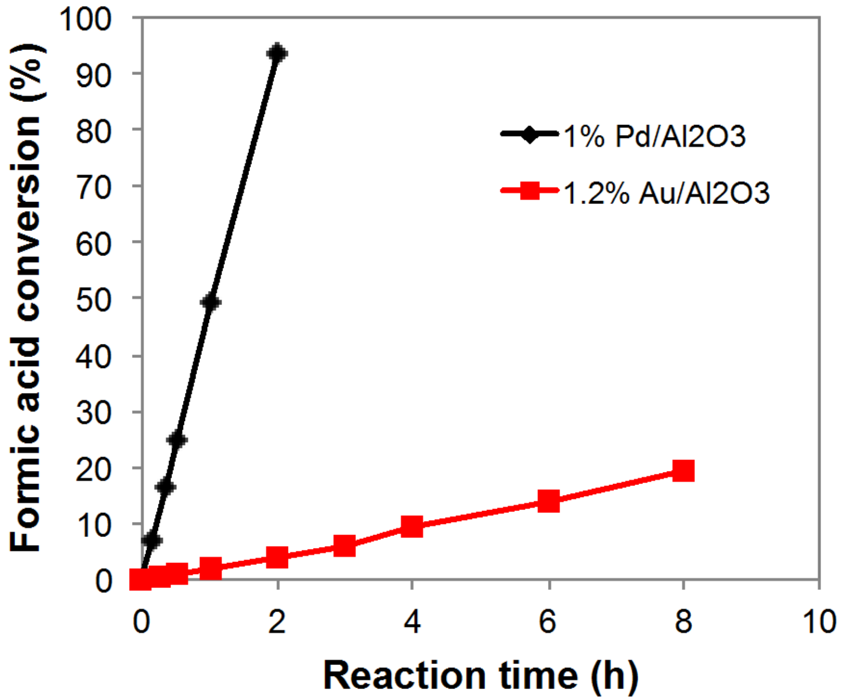
H_2O_2 Generation Profiles





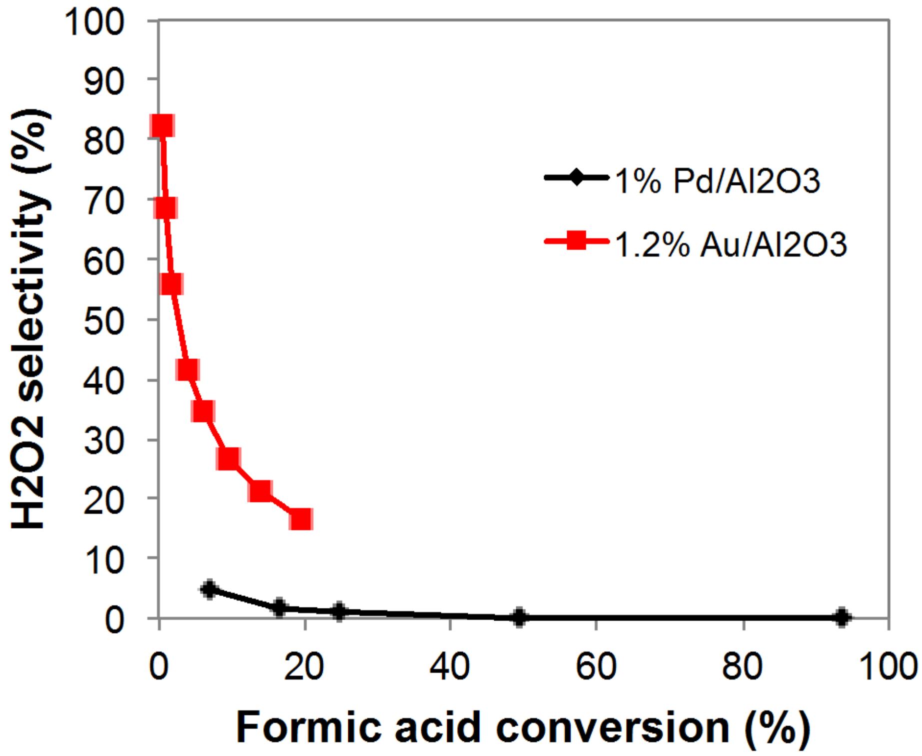
$$H_2O_2 \text{ productivity } (\text{mmol g}^{-1}\text{ h}^{-1}) = \frac{H_2O_2 \text{ concentration (mmol)}}{\text{catalyst amount (g)} \times \text{reaction time (h)}}$$

Formic Acid Conversion Profiles



	1% Pd/Al2O3	1.2% Au/Al2O3
k_{meas} (h^{-1})	0.644	0.018
k_{cat} (L per gcat per h)	3.22	0.009

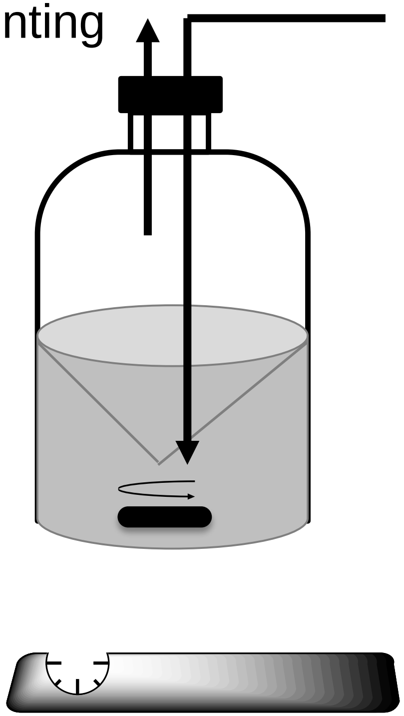
Formic Acid Conversion vs H_2O_2 Selectivity



H_2O_2 selectivity (%) =

moles of H_2O_2 formed / moles of formic acid consumed × 100

Phenol Degradation by the Generated H_2O_2



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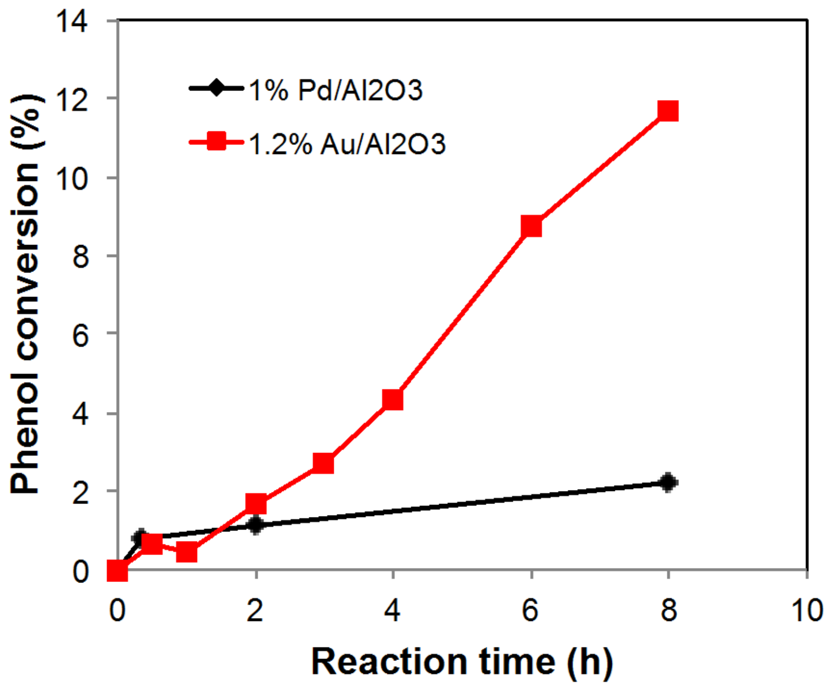
- 1000 rpm stirring rate

+

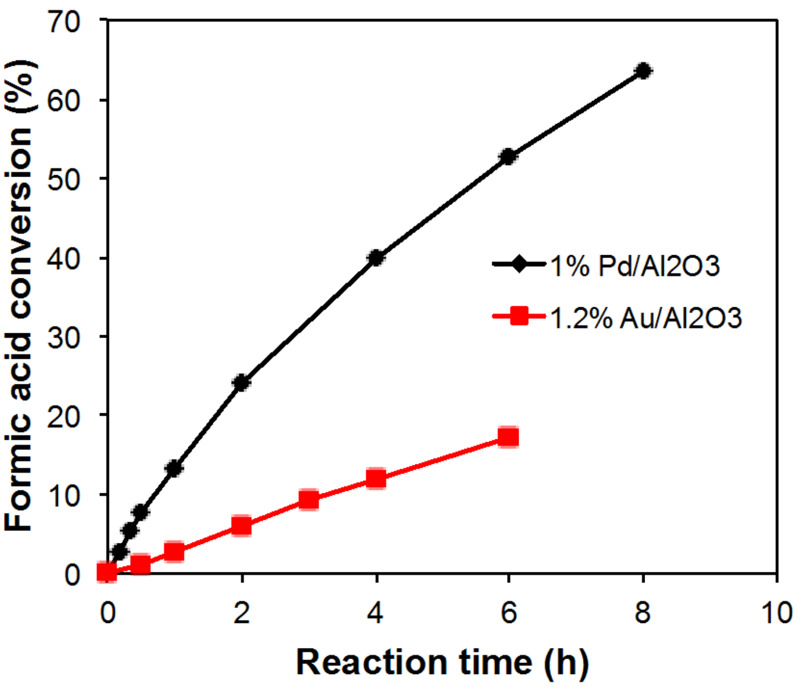
- 100 ppm phenol

Phenol Degradation Profile

Phenol degradation profiles



Formic acid conversion profiles



- Pd and Au are both active for the phenol degradation
- Formic acid usage efficiency for phenol degradation is higher on Au than Pd

Composition of Simulated Produced Water

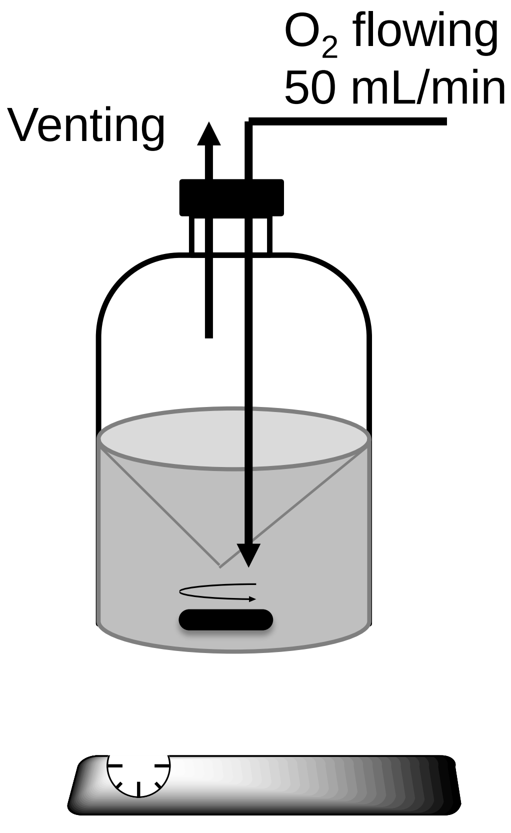
Oil & Gas Brine Water (OGBW) provided by NEWT center

General Parameters	*Specification*	
pH	7.0±0.25	
Constituents	*Concentration (mg/L)*	*Concentration (mM)*
Bicarbonate (HCO_3^-, initial)	50	0.82
Calcium (Ca^{2+})	6,940	173
Chloride (Cl^-)	99,719	2813
Magnesium (Mg^{2+})	520	21.4
Sodium (Na^+)	56,000	2436
Sulfate (SO_4^{2-})	550	5.7
Total Diss. Solids (TDS)	163,779	-
Ionic Strength	-	3,025

Note: Spiked with 5 mg/L iron(II) (Fe^{2+})

Model water receipt, NEWT, 2017

Phenol Degradation in Simulated PW



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  (or 200 mg 1.2% Au/Al_2O_3)
- pH~3.5
- Room Temperature (~22 C)
- 1000 rpm stirring rate

+

- 100 ppm phenol

+

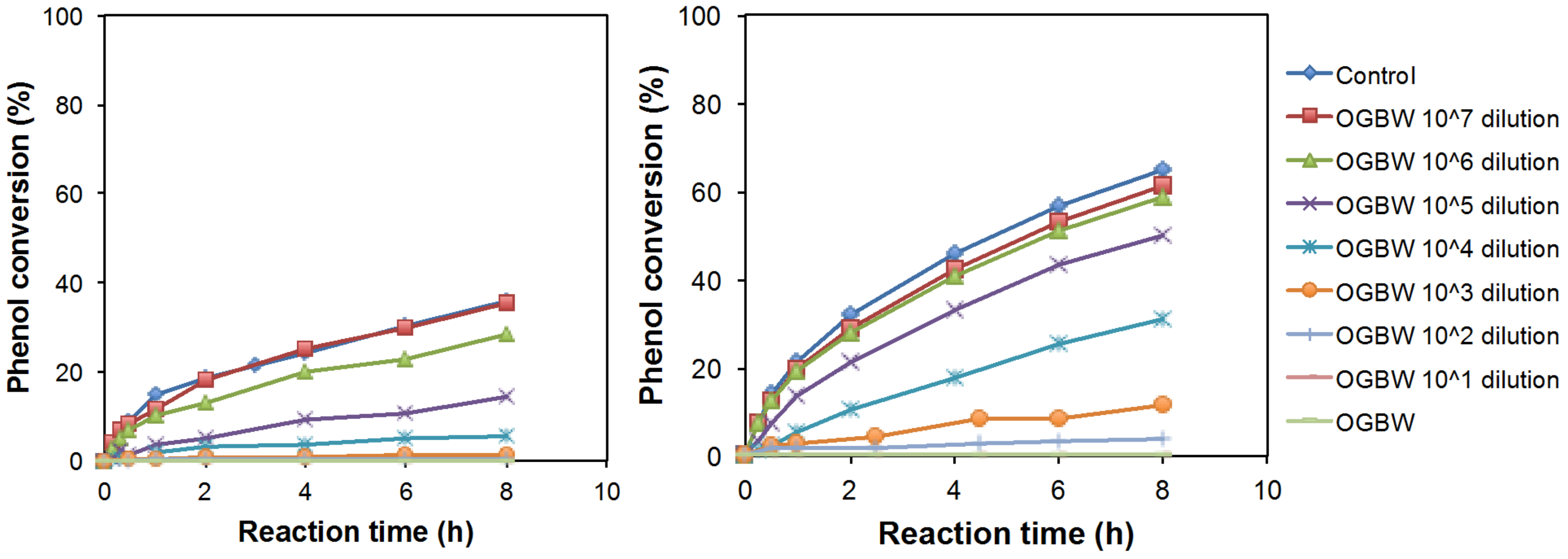
- 5 ppm Fe(II)
  (in the form of $FeSO_4$)

+

- Oil & Gas Brine Water (OGBW)

Phenol Degradation in Simulated PW

20mg 1% Pd/Al_2O_3 | 200 mg 1.2% Au/Al_2O_3



Summary and Future Work

- H_2O_2 can be formed in the conversion of model organic acid (formic acid) and O_2.
- Degradation (+90%) of model organic compound (phenol) can be achieved for both Pd and Au catalyst in diluted model produced water.
- This catalytic system will further be tested in real produced water

Acknowledgements

- NSF Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment (ERC-1449500) and Specialty Minerals
- Professor Michael S. Wong for his advice
- Dr. Ciceron Ayala for the assistance in TEM characterization
- Catalysis and Nanomaterial Group at Rice University

Group Photo April 2017

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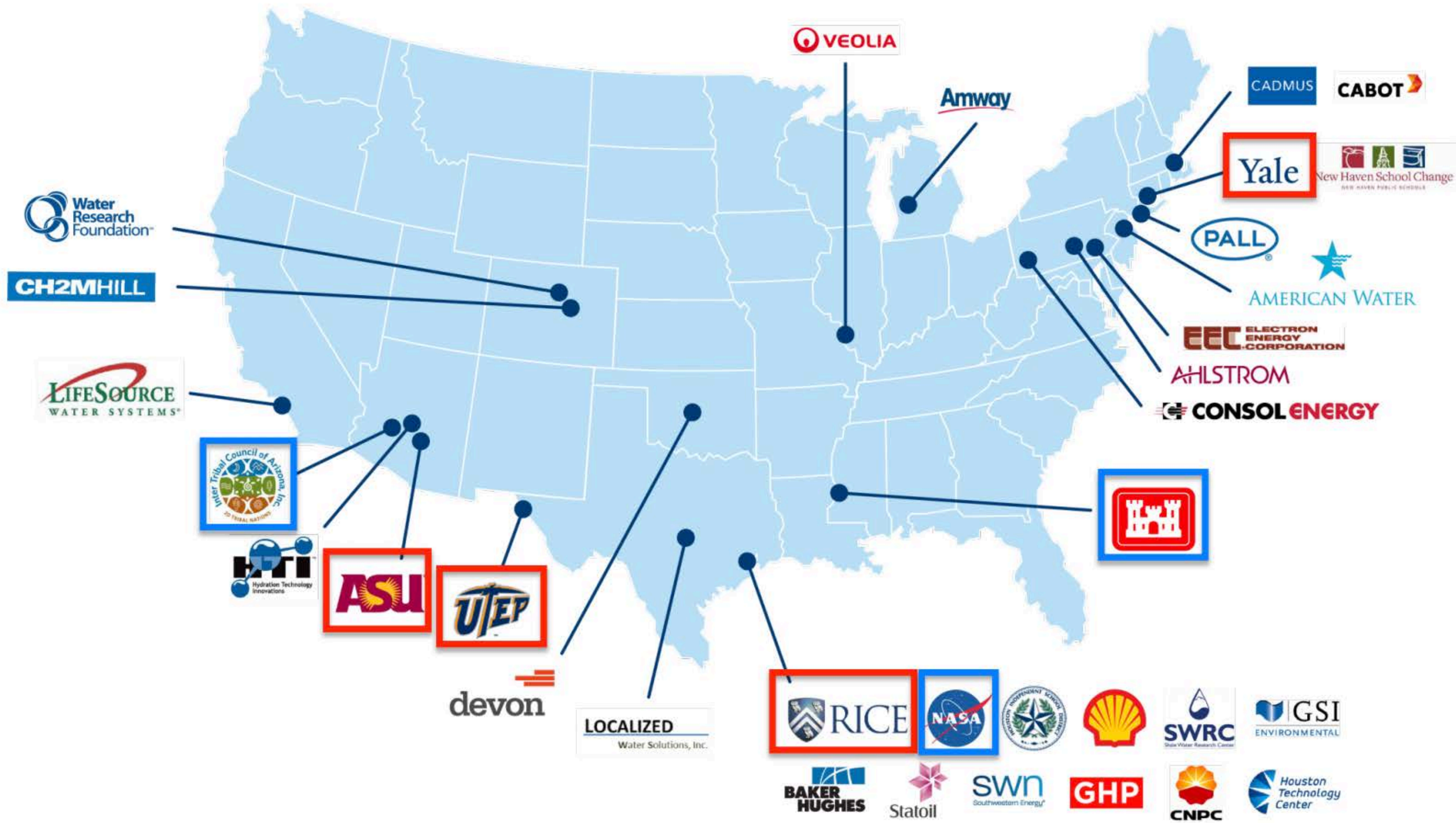
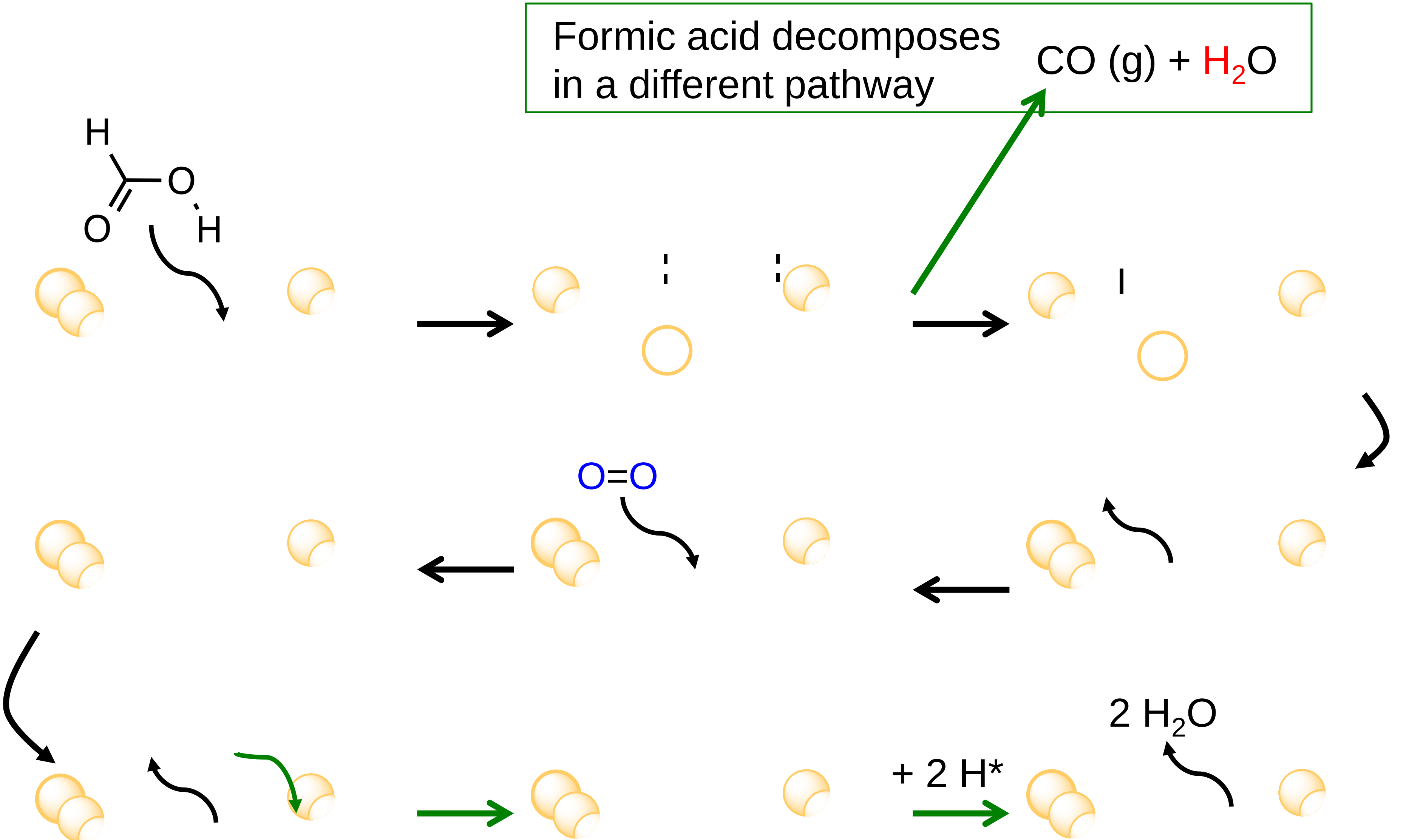


- Innovation across value chain (nanomaterial and equipment manufacturers, service providers, R&D and deployment partners, and users)

Thank You!
Any Questions?

Backup slides

Proposed mechanism of H_2O_2 generation with low selectivity



H2O2 re-adsorbs and decomposes