Exploring the use of Raman Spectroscopy for defect characterization of Au-Pd catalysts for water purification systems.

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Overview

- Need for purification systems
- Current systems and issues
- Our system & current focus
- Raman Spectroscopy
- Preliminary Results
- Future Steps
- Secondary Project
- Thank you

Contaminants in Water

U.S. Environmental Protection Agency (EPA) issues a National Priorities List based on maximum contaminant level (MCL).

Example: TCE - < 5 ppb (0.005 mg/L) [1]

- TCE – Trichloroethene common degreasing agent [1,2]
  - Carcinogenic, neurological and reproductive toxin
- TNT – 2,4,6-trinitrotoluene – widely used as ammunition [3]
  - Causes liver necrosis and anemia [3]
- Triclosan – antibacterial commonly used in handwash/soaps [4,5]
  - Listed as a contaminant of emerging concern [4,5]
  - More data needs to be collected prior to establishing safe levels
  - Currently Minnesota Department of Heath has declared > 50 ppb as a level for Triclosan [5]

How can we make this safer?

Figure 1: Child drinking water. Source:Slate [1]

Current purification systems

- Palladium
  - Proven to be a useful catalyst in many applications including air pollution control[6]
  - Issues
    - Pd metal has certain active sites which react with sulfide and chloride ions (common in groundwater). These ions deactivate the palladium catalyst [1,2]
- Gold
  - Participates in catalytic reactions in the form of small nanoparticles.
  - Issues
    - By itself has a noble quality, is mostly unreactive.
- Combined Au-Pd
  - In the presence of Au, Pd is more resistant to deactivation by sulfide and chloride ions and there is an overall increased rate of reaction [1,2]
  - With Pd, Au is also a better catalyst which is otherwise slightly unreactive [1,2,7]

Current purification methods and issues

Shewanella Oneidensis[8]

- Lives in anaerobic conditions and respires metal.
- Tests show that Palladium nanoparticles can be made in the presence of a hydrogen donor. [8]
- Bacteria mediate the reduction process (dehalogentaion reaction), supports NPs on the cell wall and other structures

Issues

- Relatively slow – 24 hours
- Ineffective with certain contaminants such as Diclofenac, TCE.
- Long-term stability

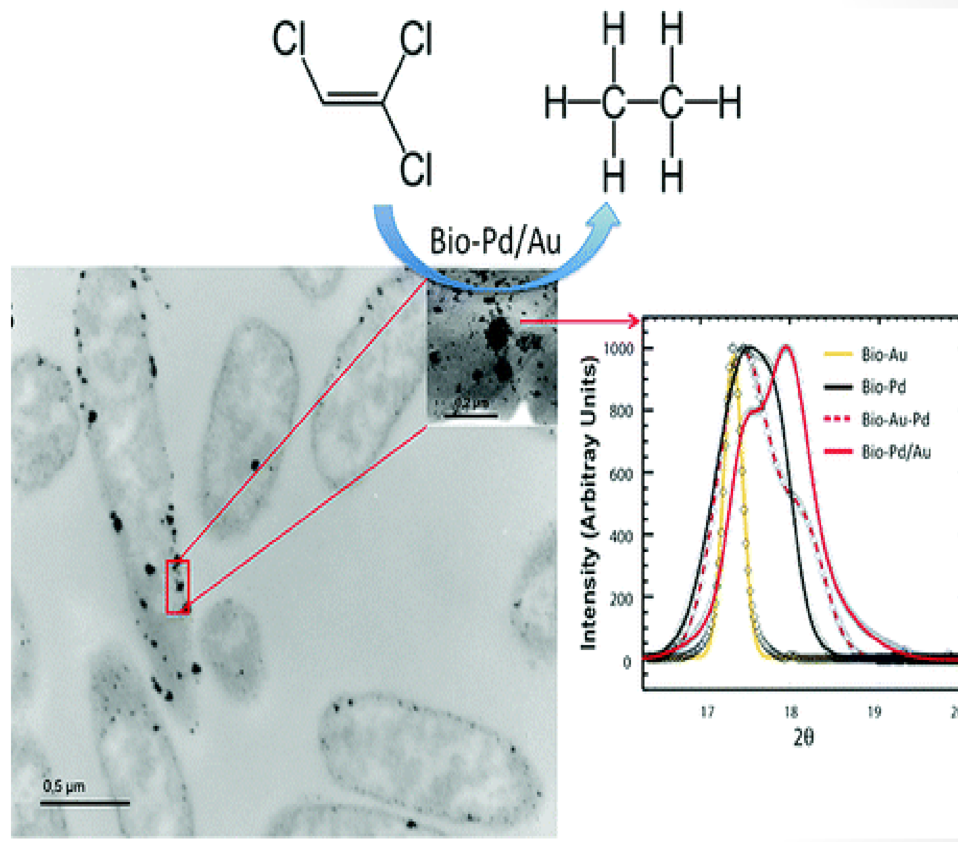

Figure 2: Shewanella Oneidensis [2]

Our solution?

- Au-Pd catalyst on various carbon substrates
  - Synthesis is patent pending
  - Relatively faster than current systems
  - Tested on Activated Carbon, Carbon Nanotubes, Nanographite, and Graphene
  - Successfully purified water contaminated with TCE, and Triclosan

Current focus

- Characterization of defects using Raman Spectroscopy
  - Explore defect characterization with Raman Spectroscopy for AuPd catalysts on carbon substrates.
  - Building a prototype to simulate actual purification conditions.

Raman Spectroscopy – A background

- Raman spec. measures the amount of light scattered by a molecule – inelastic scattering [9,10]
- Complementary to Infra Red spectroscopy method [9,10]
- Typically looks at vibrational modes of 10^4 cm^{-1} to 10^2 cm^{-1} (this is same as 10^{-4} to 10^{-2} λ)[9]
- Raman spec. looks at highly ordered covalent bonds with very little dipole moments.[10]
  - Particularly useful for Carbon bonds C-C bonds, sp^2 v.s. sp^3 [10,11]
  - Angle strain
  - Single and multiple layer sheets[12]

Useful for differentiating structural differences

- Differentiates between 3D graphite, 2D graphene, 1D carbon nanotubes and 0 D fullerenes (Buckminister C60) [11, 12]
- Differentiates between Graphene, Highly Oriented Pyrolytic Graphite (HOPG), Single Walled Nanotubes (SWNT), Damaged Graphene, Single Walled Nano Horns (SWNH) , and amorphous Carbon.

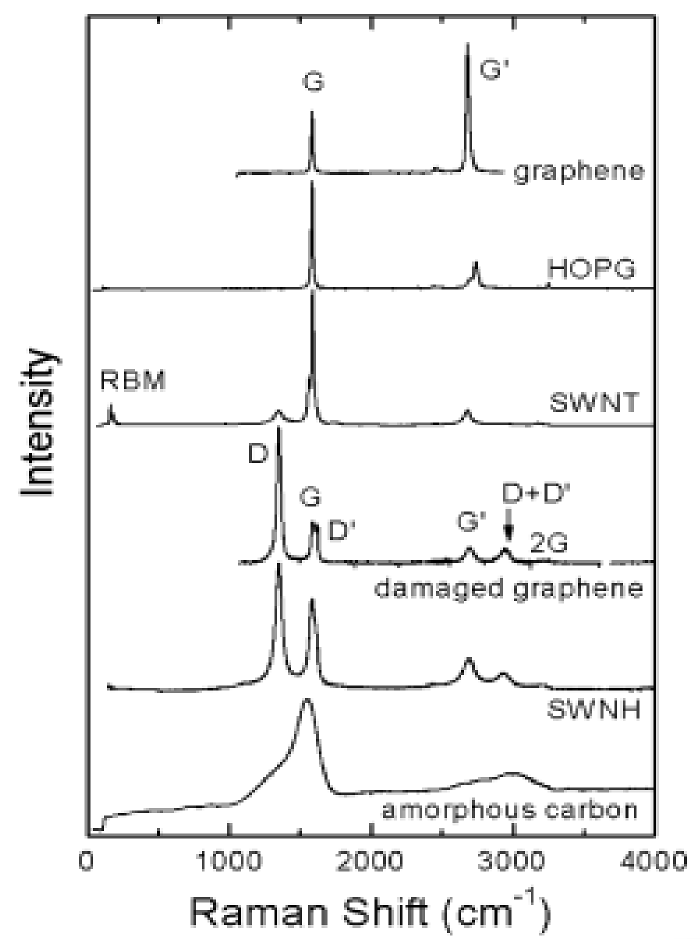

Figure 3: Raman scattering graphs of various sp2 nano carbons[3]

How are we using Raman Spectroscopy?

- Characterize the various peaks for each carbon substrate with and without the catalyst.
- 7 to 9 sites will be explored on each sample for each carbon substrate.
- Experimental Conditions
  - Horiba 800 UV Raman
  - 100 mW 532 nm laser
  - 200 nm aperture size
  - Neutral density filter was not used.
  - 250 cm $^{-1}$ to 3200 cm $^{-1}$ range

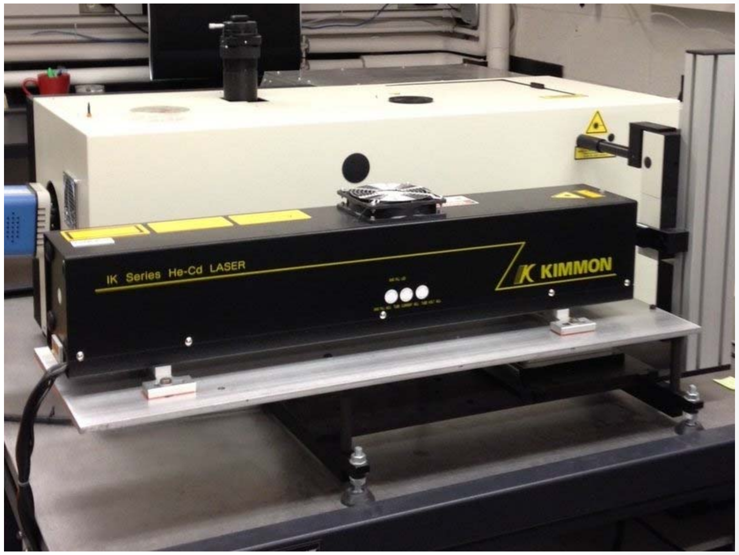

Figure 4: Raman Spectrometer [4]

Data analysis methods and preliminary results

- G peaks and D peaks were analyzed using Gaussian line fitting
- Defect ratio was calculated as AD/AG instead of ID/IG [13]
- Literature shows 1350 cm^{-1} and 1580 cm^{-1} for the G and D peak respectively[11, 12, 13,14,15]

Description	G peak (cm-1)	D peak (cm-1)
Activated Carbon as is	1345	1593
Activated Carbon with AuPd	1347	1594
Graphene as is	1350	1571
Graphene with AuPd	1351	1585

Table 1: Various peaks noted for the various carbon substrates

Preliminary Results

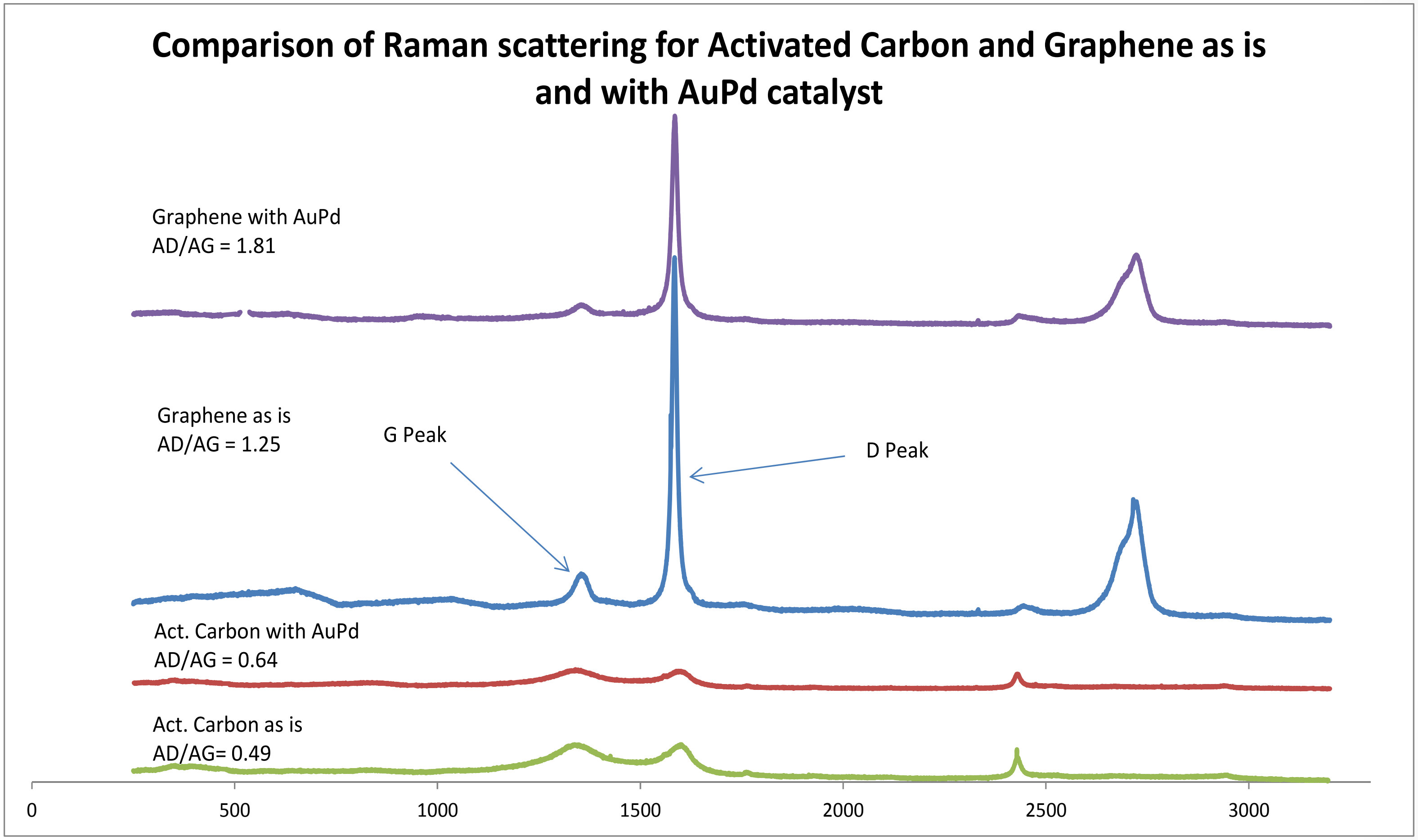

Figure 5: Comparison of G and D peaks for defect ratio

Need to complete more analysis before reaching a definitive conclusion

Prototype – in progress

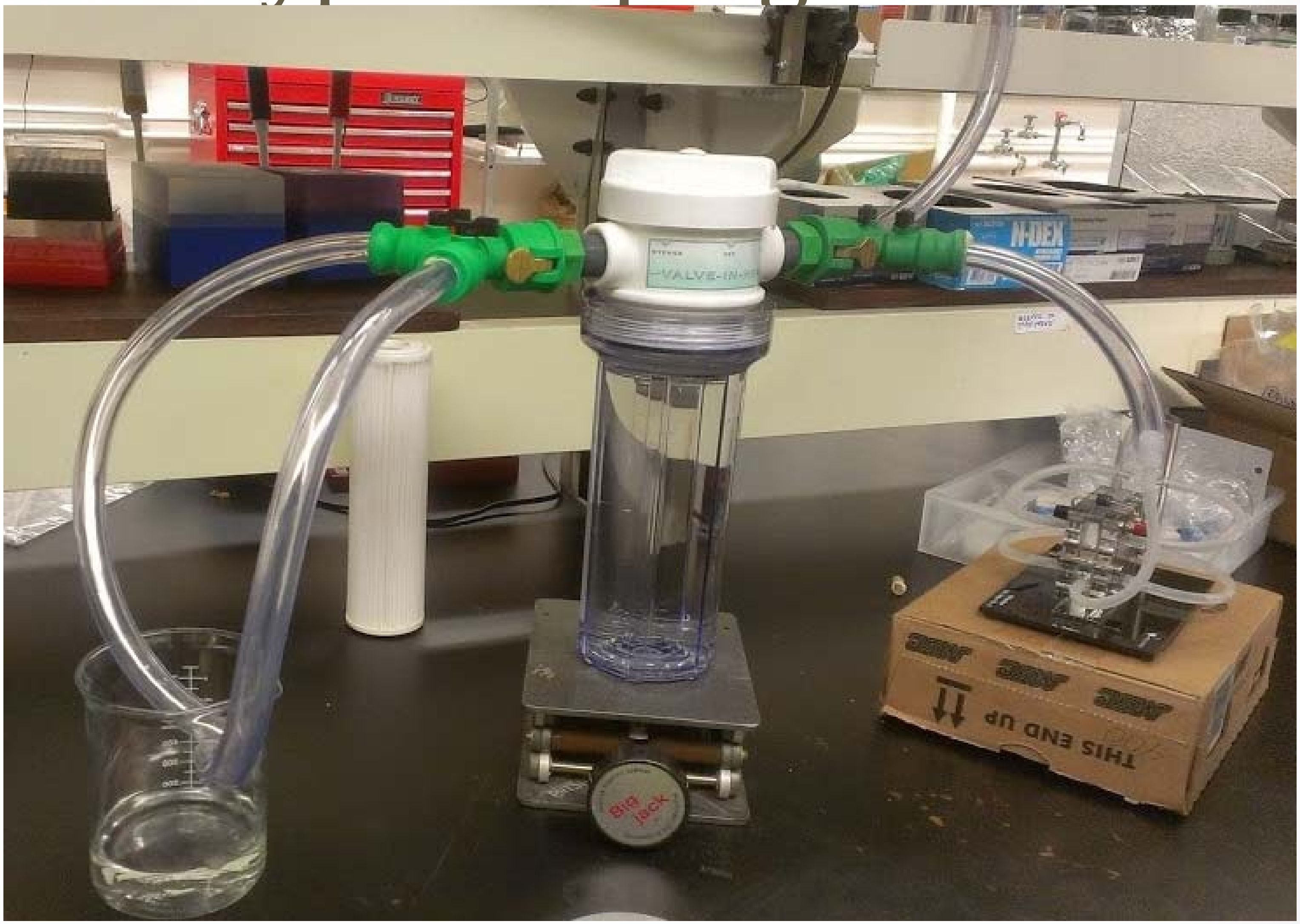

Figure 6 – Prototype

Future Steps

- Understand the impact of using a 532 nm laser versus a 514 nm laser.
- Analyze the relevant peaks for carbon nanotubes (2D peaks) using Lorentizan peak fitting[11,16]
  - Identify how many peaks are hidden under the overarching 2D peak.
- Complete the prototype.

Secondary Project – Chemical Safety Team

- Lead Chemical Safety Team
- Reorganized and categorized 343 chemicals according to flammability, reactivity and incompatibility.
- Cleaned several containers of unknown wastes and unlabeled samples
- Interfaced with Environmental Health and Safety Team (EHS) and the Chemistry Stock Room Manager at PSU
- Attained several secondary containers for storing incompatible chemicals together courtesy EHS
- Working on getting a fume hood for the bioengineering lab also courtesy of EHS.
- A total upgrade of approximately $10,000 (including a second-hand fume hood) done for $1000

Some pictures…

Figure 7: Second round of waste containers

Figure 8: Flammables Cabinet

What can you do to protect yourself?

- When starting in a new lab – note safety equipment
- Read MSDS/SDS information prior to using chemicals
- Find out PPE guidelines
  - PSU provide free lab coats.
  - Polyester v.s. flame retardant materials
- Read about your University's resources
  - Chemistry Stockrooms, Laser and Radiation teams, EHS departments.
- Use safe practices
  - While using gloves – don't touch every surface in the lab.
  - Do not throw used gloves in regular waste baskets.
  - Do not place wires where people can trip on them
  - Label your samples clearly
  - Use a fume hood

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