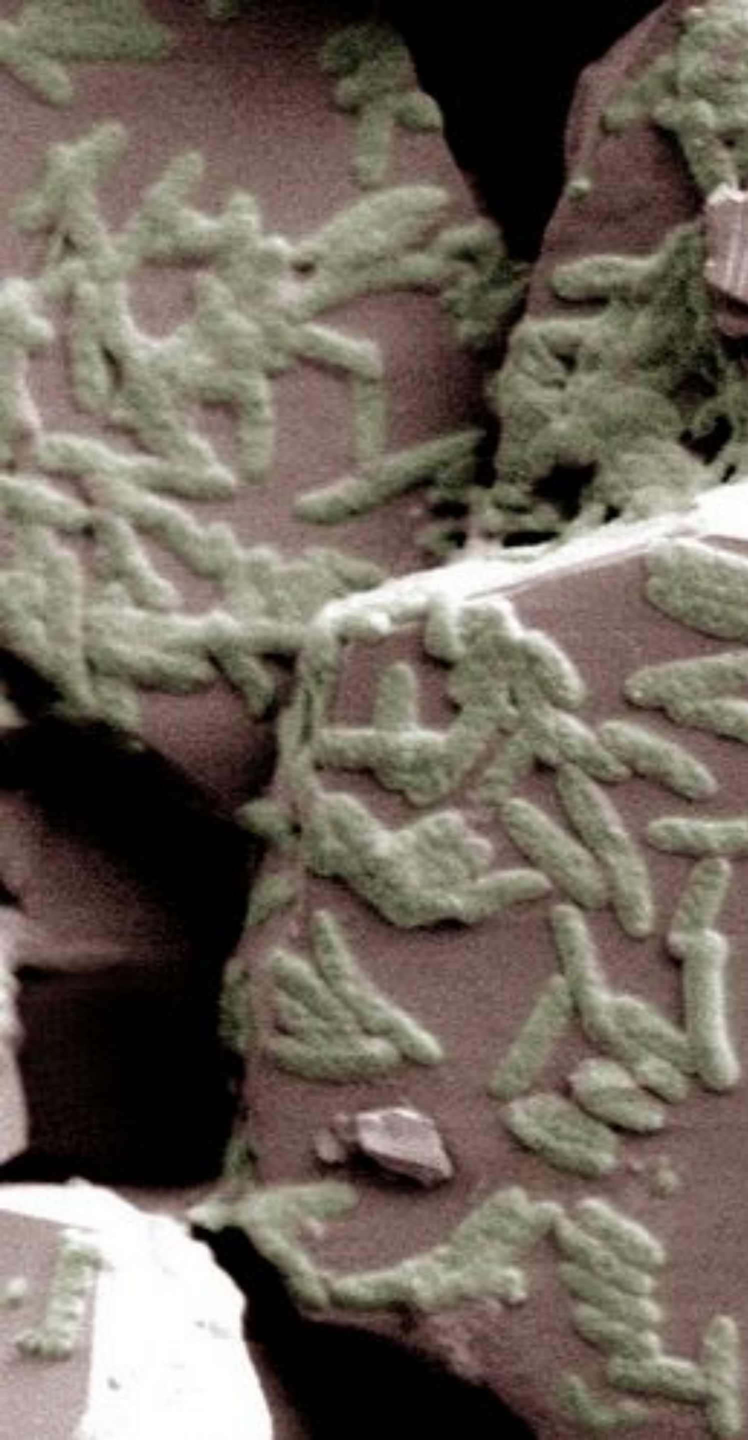

Biosynthesis of Molybdenum Disulfide Nanoparticles Using The Metal-Reducing Bacterium *Shewanella Oneidensis* MR-1

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Electrical, Computer and Systems
Engineering

61st Electronic Materials
Conference, University of Michigan,
Ann Arbor

June 27th, 2019

The Jefferson Project
at Lake George

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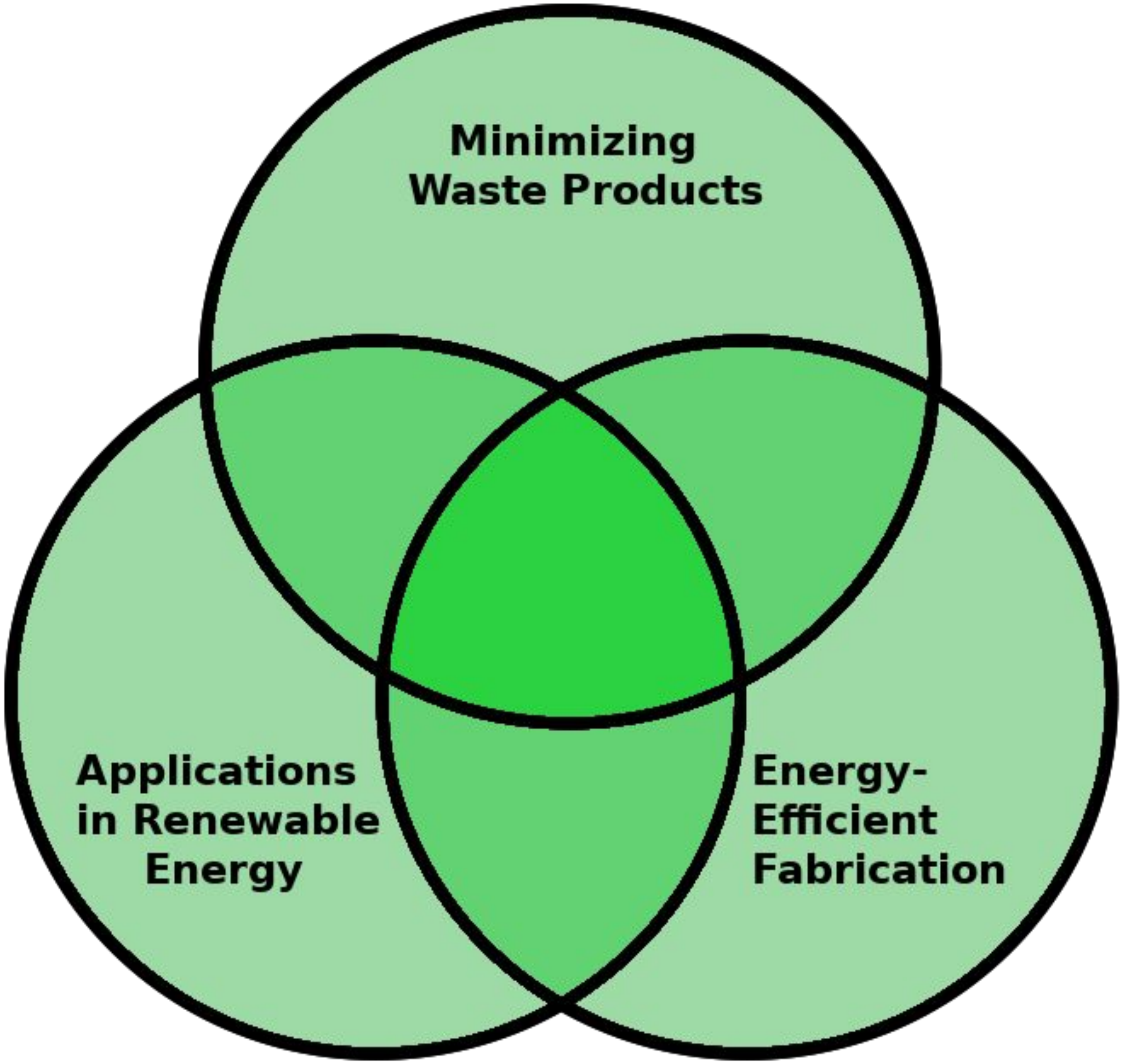
Introduction

What does it mean for electronics to be "green"?



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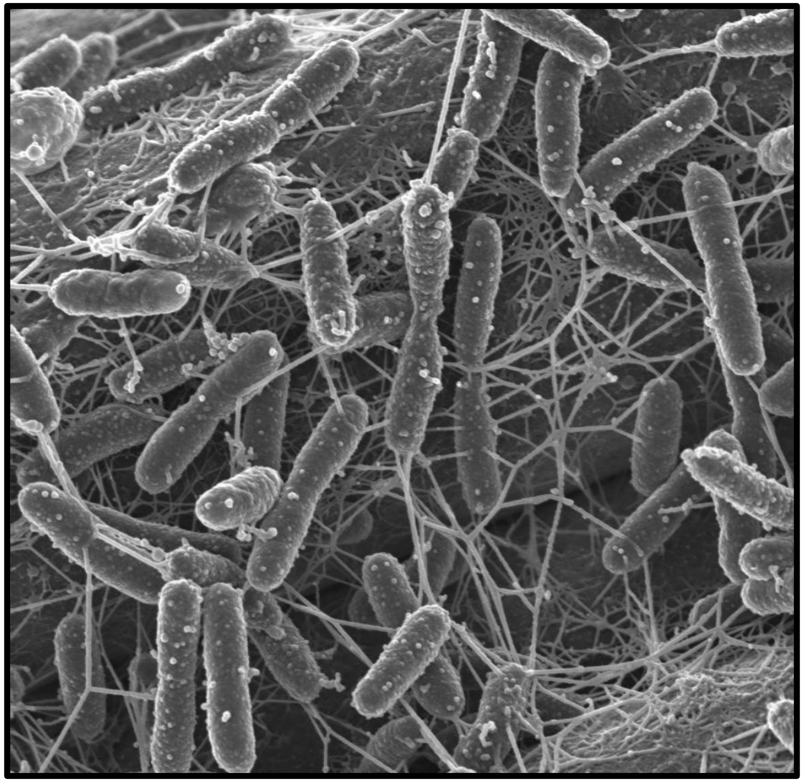
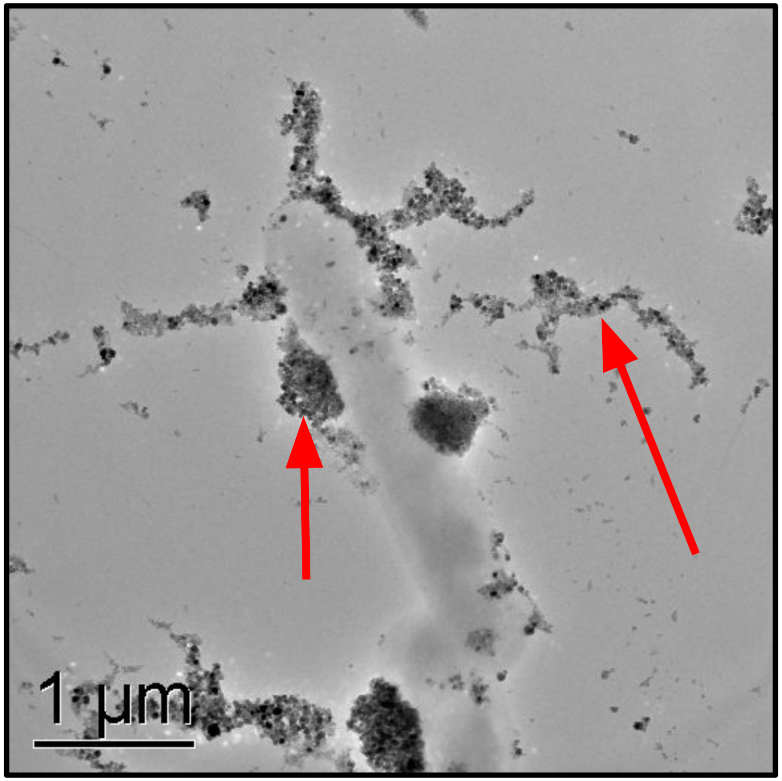
Shewanella Oneidensis MR-1: A Versatile "Nano-Engineer"

Dissimilatory Metal Reduction: "Breathing with Metal"



Bacterial nanowires [1]



Biomineralization [2]

- *Shewanella* is a facultative anaerobe (can exist in an aerobic or anaerobic state)
- Uses organic materials (lactate, pyruvate) as electron donors
- Can use a variety of metal and sulfur ions as electron acceptors
- Through its metabolic process (dissimilatory metal reduction), ***Shewanella*** **precipitates metal and metal sulfide nanoparticles**

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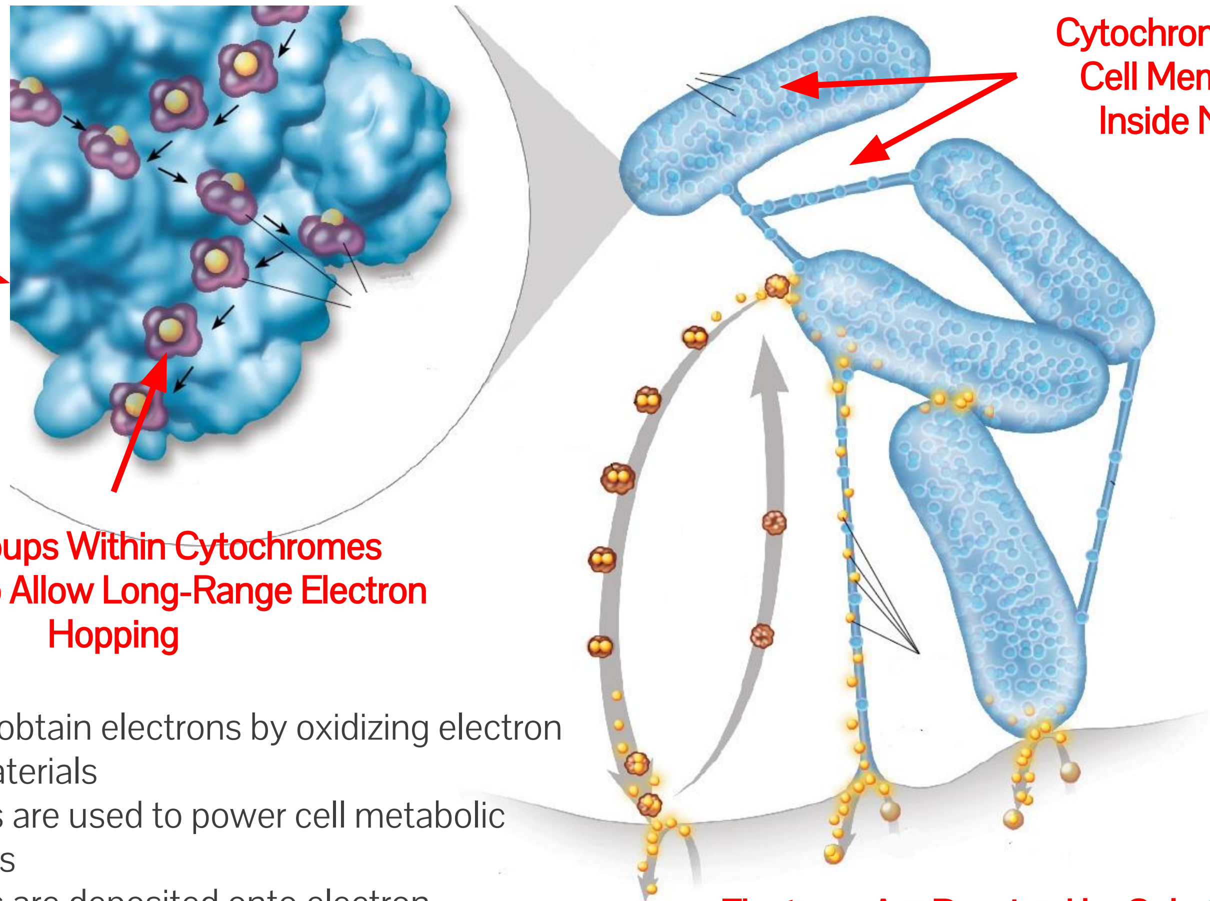
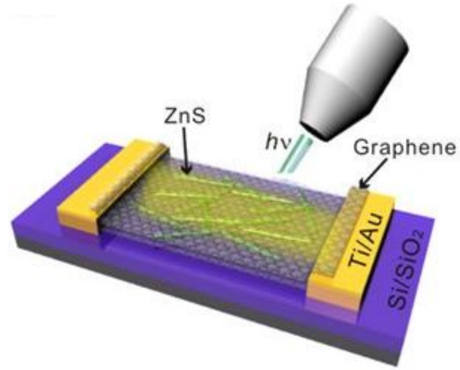
Introduction

Anatomy of a *Shewanella* Bacterial Nanowire



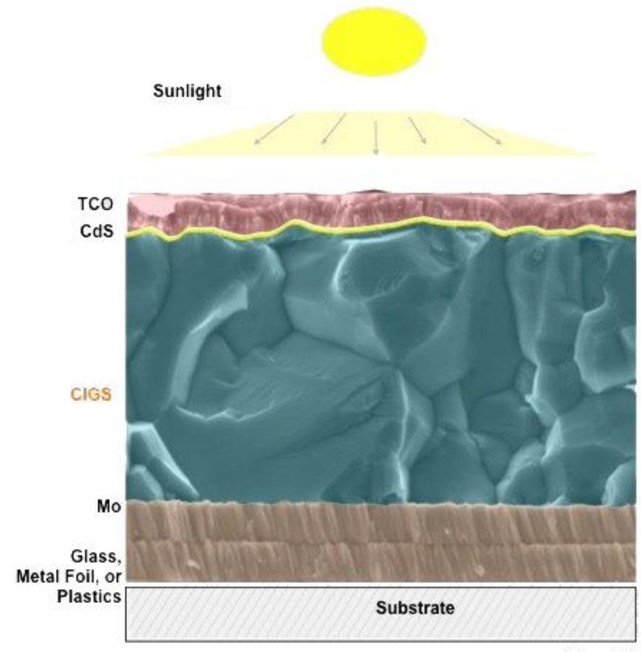
- Bacteria obtain electrons by oxidizing electron donor materials
- Electrons are used to power cell metabolic processes
- Electrons are deposited onto electron acceptors via several mechanisms [3]

Applications in Renewable Energy & Sensing



Lead Sulfide **Zinc Sulfide** **Cadmium Sulfide**

Metal sulfide nanoparticles have a wide range of applications in optoelectronic & photonic devices (solar panels, sensors, etc.)



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Energy-Efficient Fabrication

Conventional Nanomaterial Synthesis [4]

- High-Purity Reagents
- Chemical Surfactants and Stabilizers

→ Incubation (often at high temperatures) →

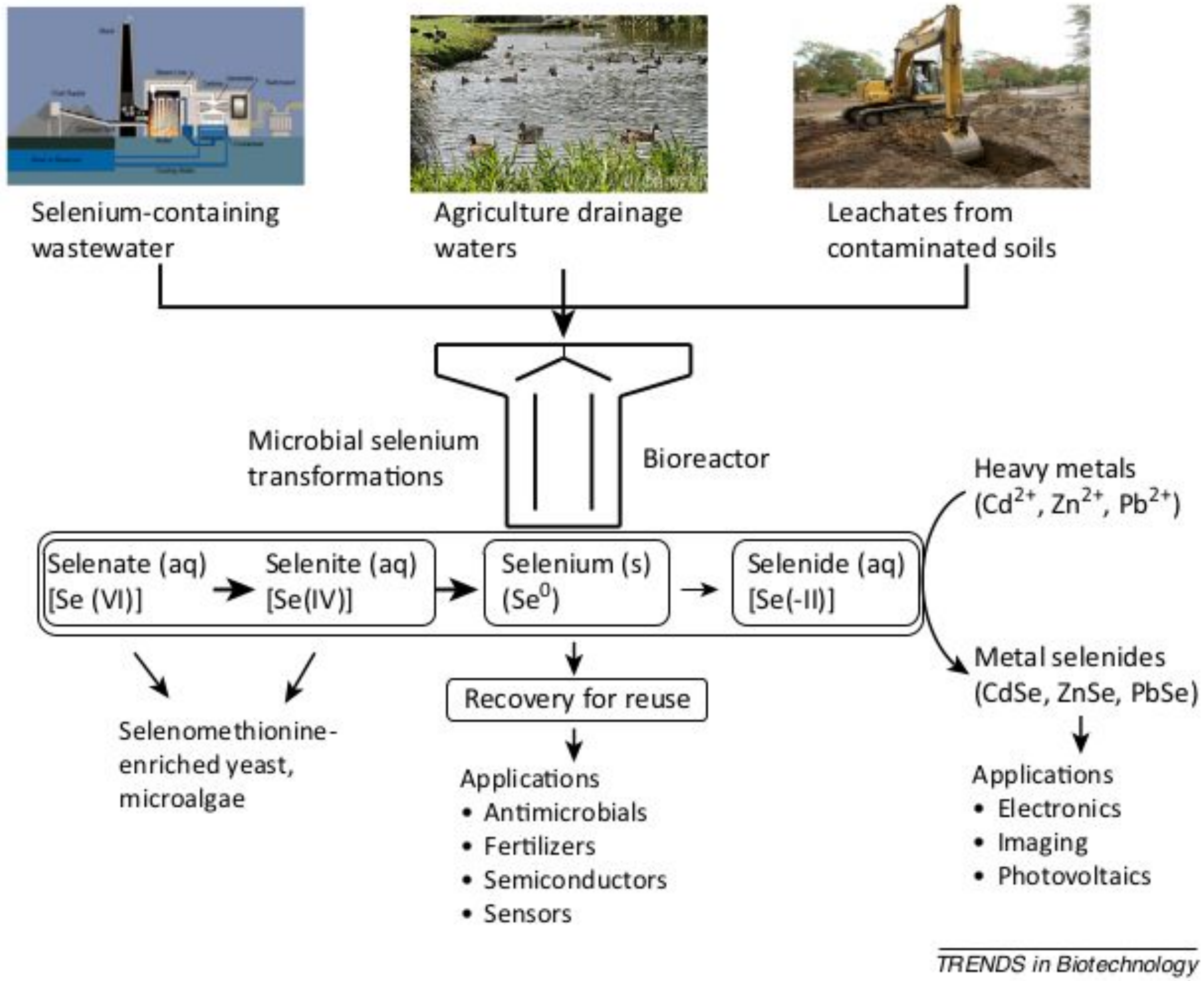
Nanomaterial Synthesis with Bacteria [5,6]

- Aqueous nutrient medium (can be industrial waste)
- Bacteria

→ Incubation at Room Temperature →

Bacteria are highly responsive to environmental variables during cultivation (pH [7], electron donor/acceptor cultivation [8], temperature [9], voltage [10] and even light [11]) - giving us options for cultivation control!

Minimizing Waste Products: Bioremediation & Re-Use



[12] Y. V. Nancharaiah and P. N. Lens, "Selenium biomineralization for biotechnological applications," Trends Biotechnol., vol. 33, no. 6, pp. 323–330, Jun. 2015.

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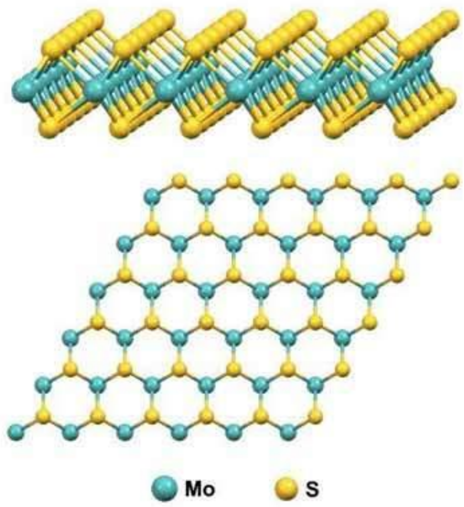
Molybdenum Disulfide Synthesis with *Shewanella*

- Bulk form has an indirect band gap similar to silicon [13]
- Monolayer form has direct band gap & photoresponsivity [13]
- Surface functionalizability [14]
- Commonly produced using H_2S at high temperatures [15]
- **Limited prior studies of potential MoS_2 biomineralization studies using bacteria**



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Molybdenum Disulfide Synthesis with *Shewanella*

Group A	10mM NaS_2O_3, Inoculated
Group B	20mM NaS_2O_3, Inoculated
Group C	10mM NaS_2O_3, Sterile
Group D	20mM NaS_2O_3, Sterile

- *Shewanella* was cultivated in a chemically-defined liquid growth medium containing lactate as an electron donor and thiosulfate as an electron acceptor
- Bottles consisted of four groups (left)
- Incubated at 30℃ for 2 days, then added 0.5mL of MoO_3 powder
- Harvested and characterized materials generated after 14 days

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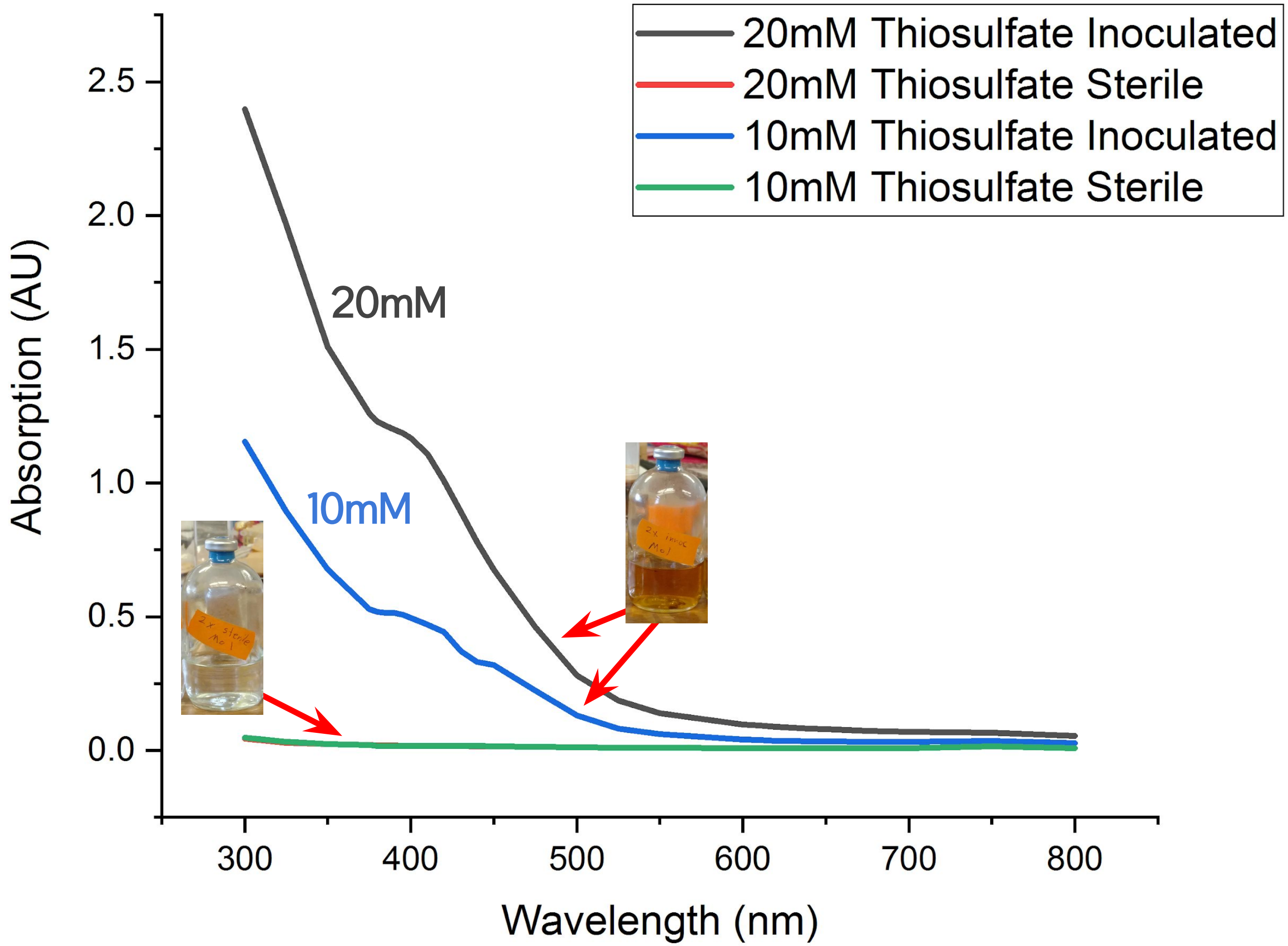
Results

Group A	10mM NaS_2O_3, Inoculated
Group B	20mM NaS_2O_3, Inoculated
Group C	10mM NaS_2O_3, Sterile
Group D	20mM NaS_2O_3, Sterile

- **After two weeks, the inoculated bottles had turned orange-brown and contained black biofilms.**
- The final pH of the bottles was measured at 6.8 (within tolerable range for *Shewanella*)



- Liquid was placed in cuvettes and analyzed using a UV-Vis spectrophotometer
- **Absorption curve agrees with prior published results for MoS_2 nanoflakes [16]**
- **Absorption was stronger in bottles with higher thiosulfate concentration, pointing to thiosulfate reduction as a key component of precipitation**

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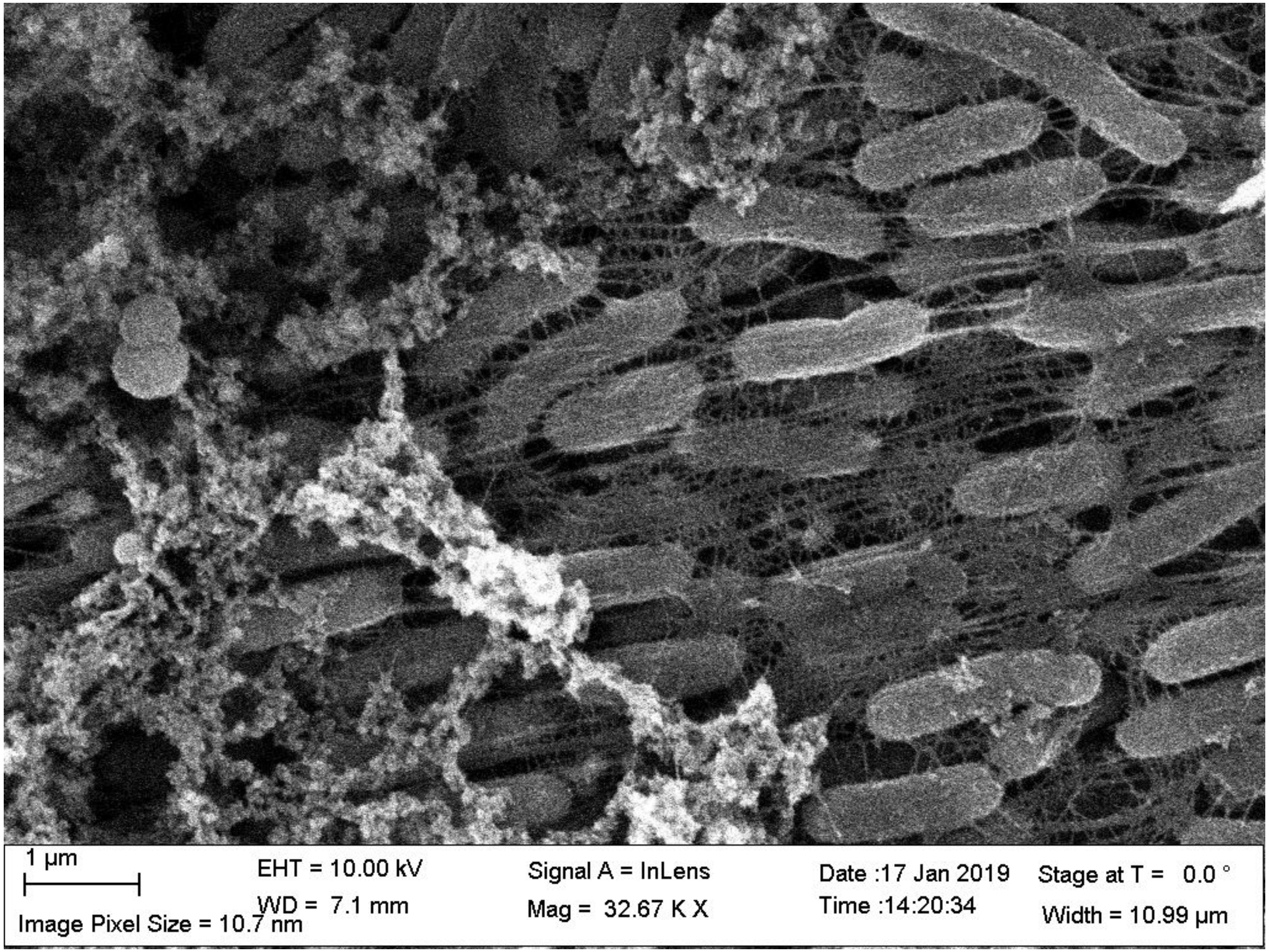
Results



- SEM revealed that the inoculated sample contained biofilms **rich in bacterial nanowires**
- EDS revealed that biofilms contained **3-5% Mo/S** (the peaks of Mo and S overlap). The Mo and S signature in the sterile batch was minimal.

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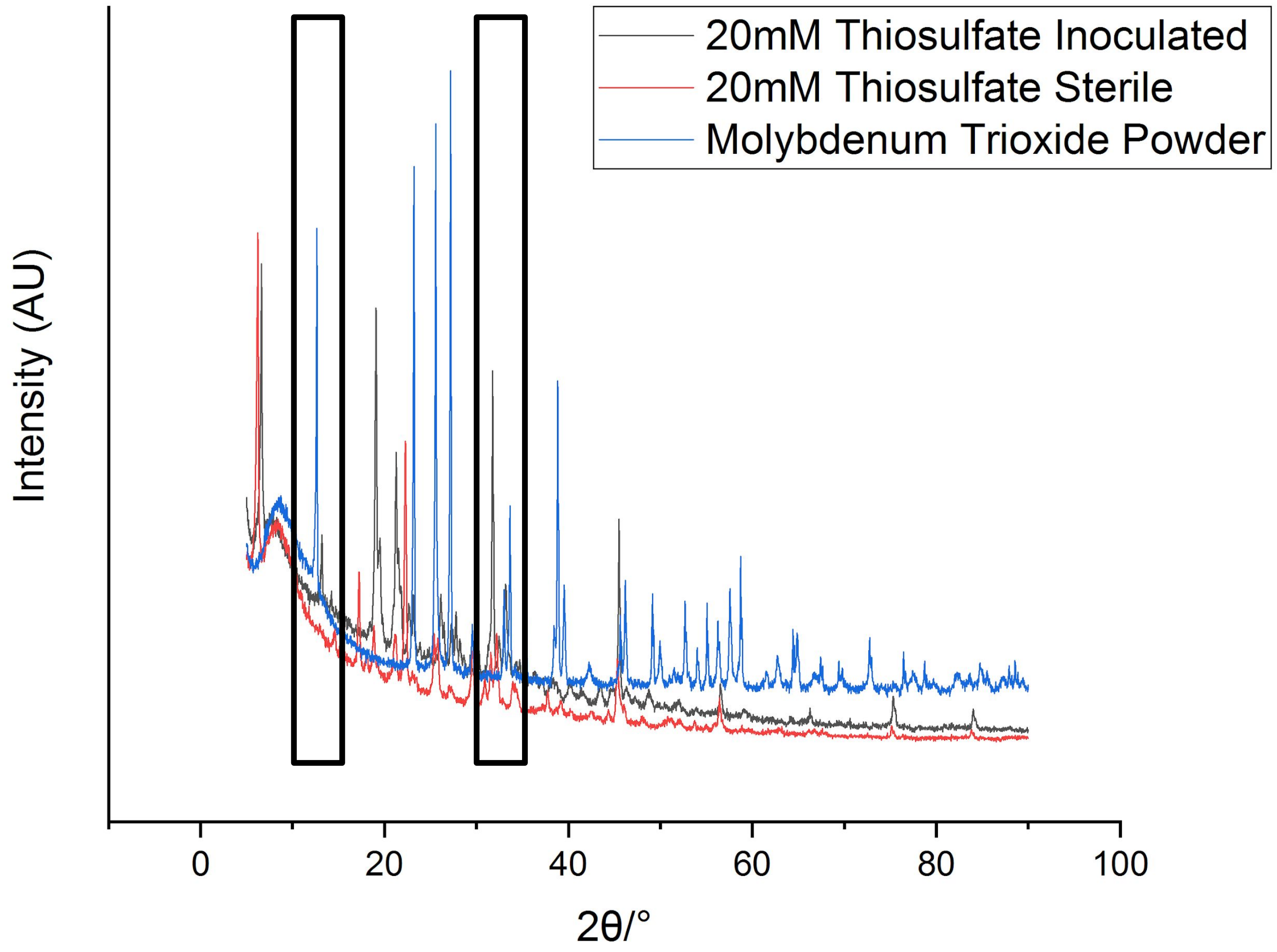

Results

- Liquid from both inoculated and sterile bottles was dried in a 100°C furnace and analyzed using XRD
- Solution did not visibly separate with separation, so salts remained in dry powder, creating a more peak-dense diffractogram

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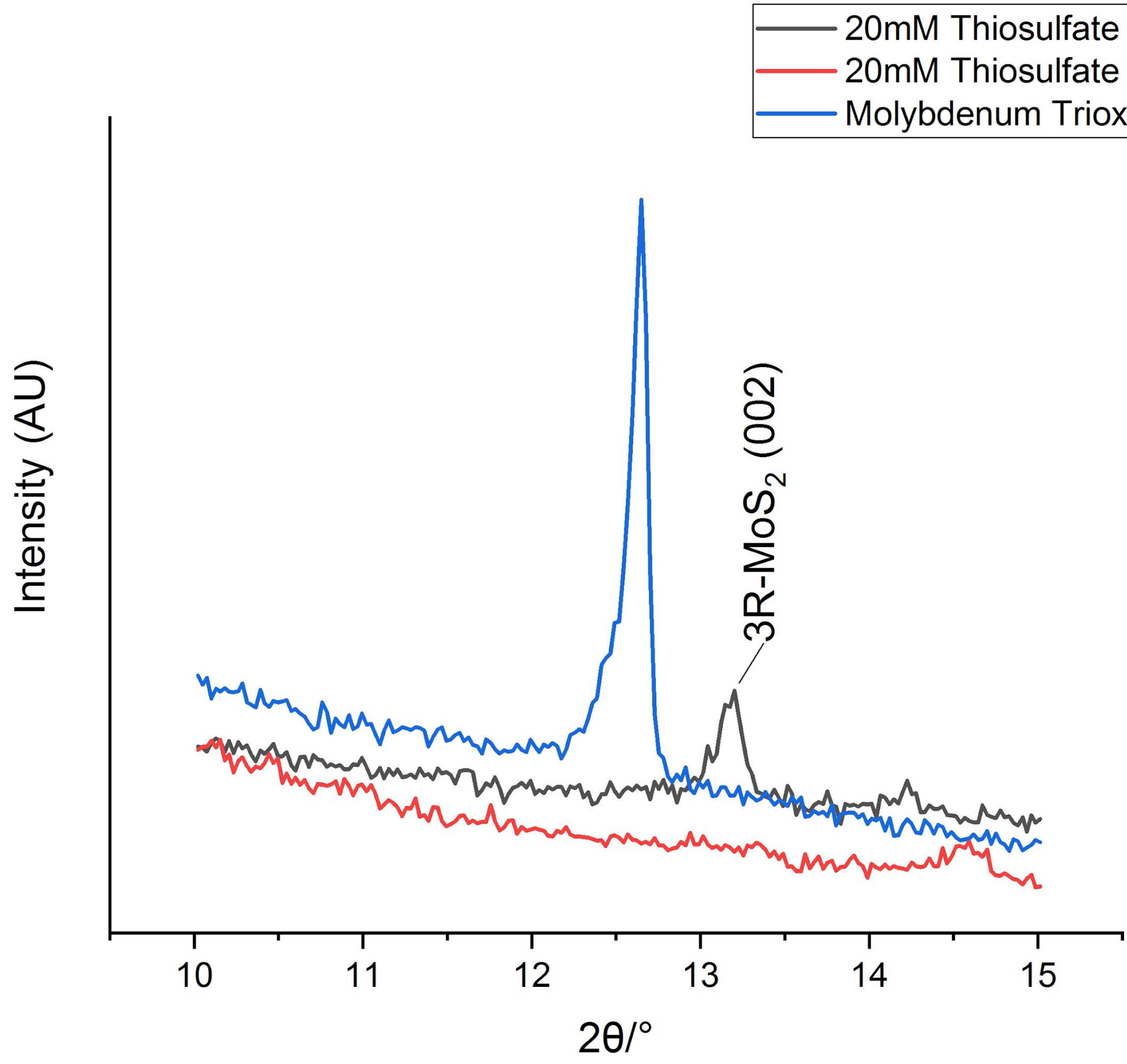

- Spectrum of inoculated bottle (blue) exhibited a peak at 13.2 degrees that was not visible in the sterile batch (red) or molybdenum trioxide powder (yellow)
- **This peak is consistent with the (002) peak for rhombohedral molybdenum disulfide [16]**

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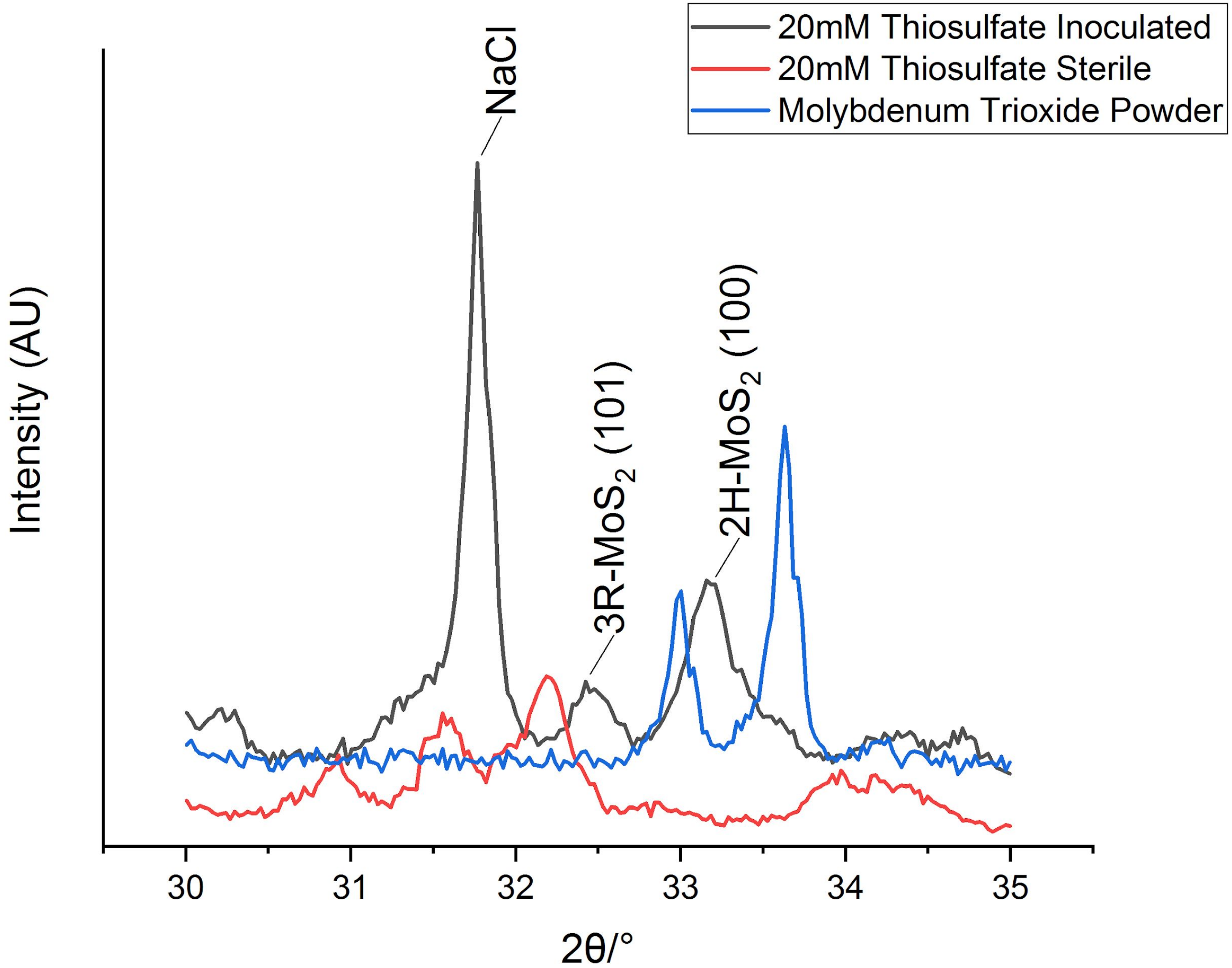

- ➢ Spectrum of inoculated bottle (blue) exhibited a peaks at 32.5 and 33.2 degrees consistent with the MoS2 rhombohedral (101) peak and hexagonal (100) peak, respectively [16][17]
- ➢ The sterile batch and MoO3 reference sample did not exhibit the same peaks
- ➢ The peak located between 31 and 32 degrees matched to NaCl reference peaks

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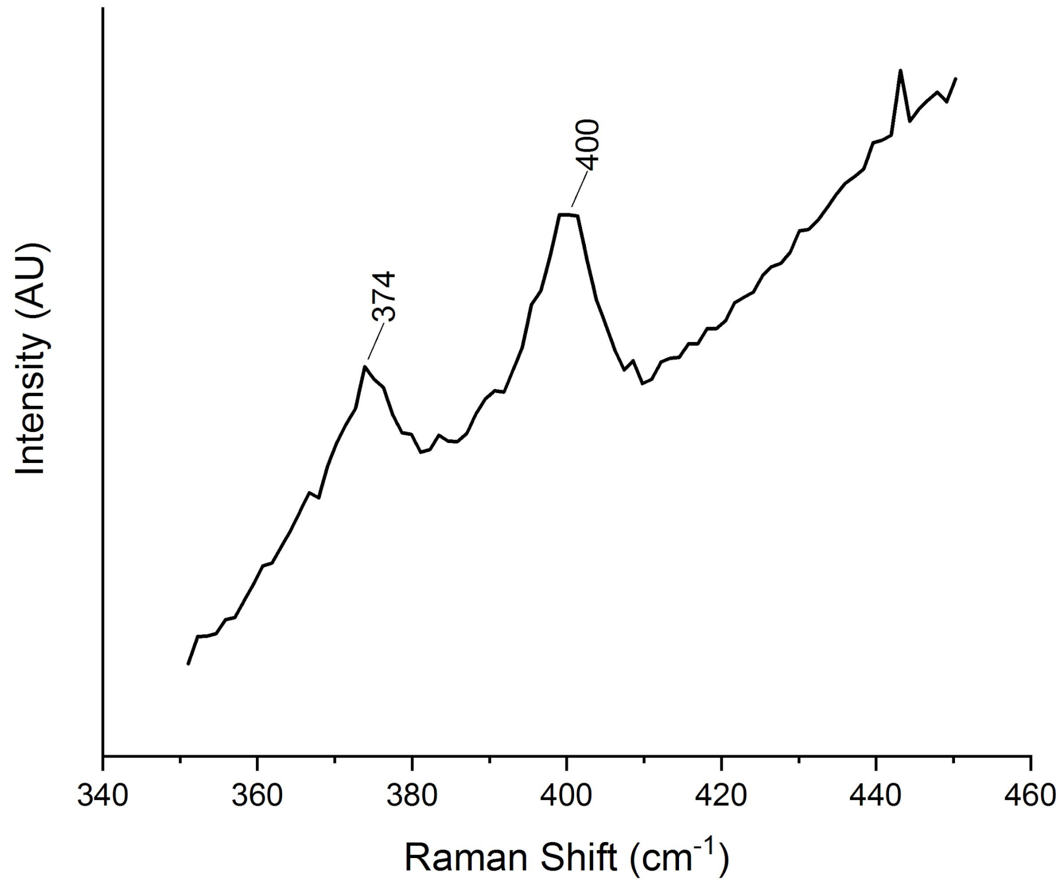
Results



- ➢ Black biofilm from inoculated Mo bottle was harvested and air-dried on a microscope slide
- ➢ Sample was then analyzed using a Raman spectrometer and a 514nm laser
- ➢ Series of 10 laser pulses was used with an 100s exposure time on each pulse
- ➢ **Raman peaks at 374 cm^{-1} and 400 cm^{-1} agree with MoS_2 reference peaks [18]**
- ➢ **Raman spectrum of liquid medium from same bottle contained no visible peaks**

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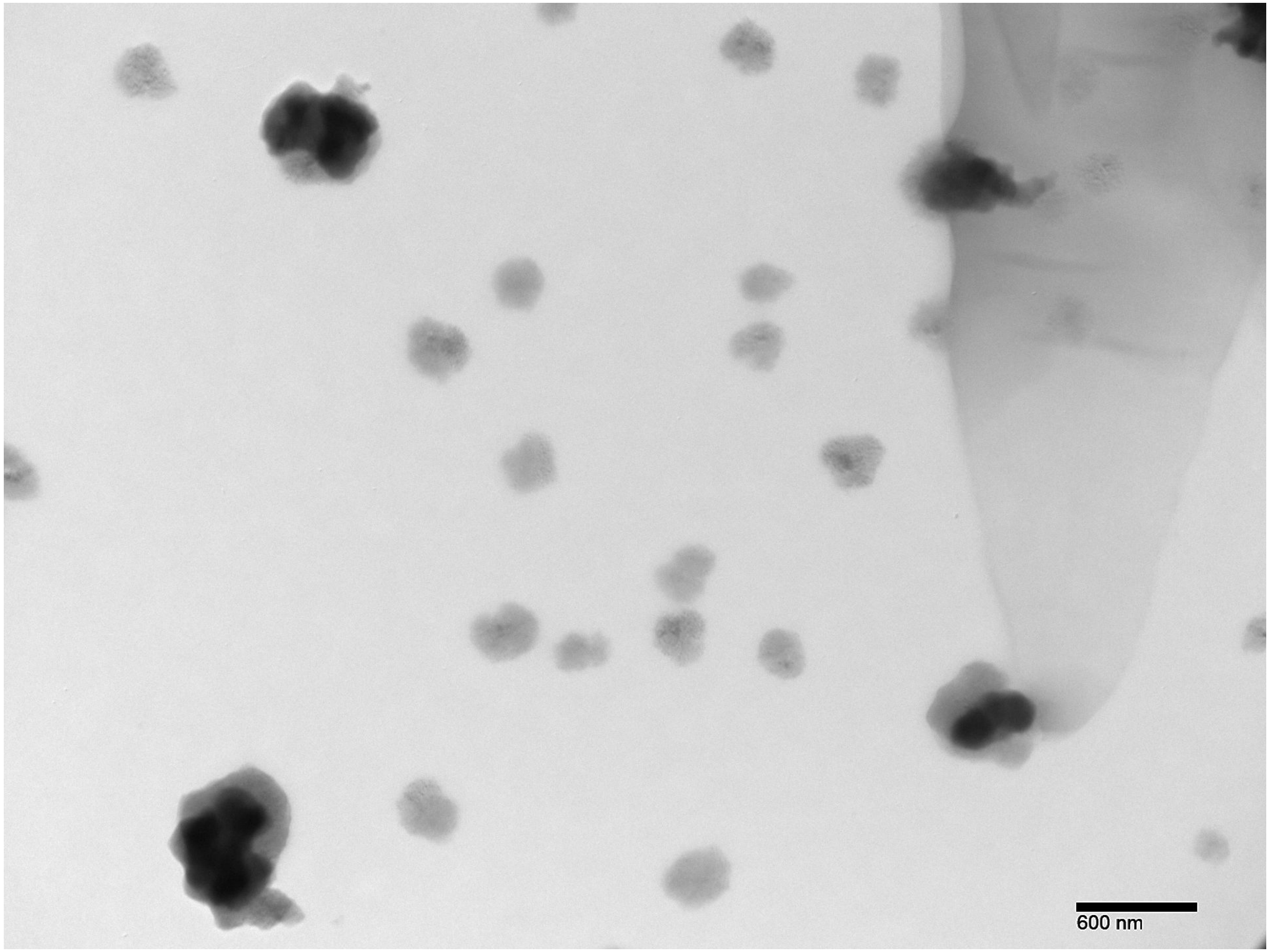

TEM analysis of the inoculated Mo batches revealed nanoparticles (both individual crystals and aggregates) with a size of approximately 50-200nm

Results

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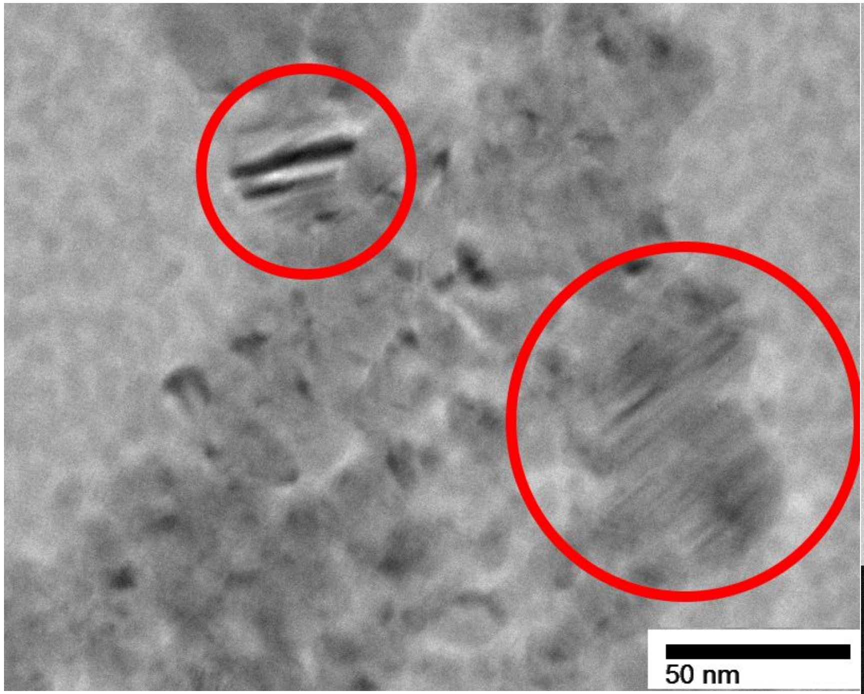
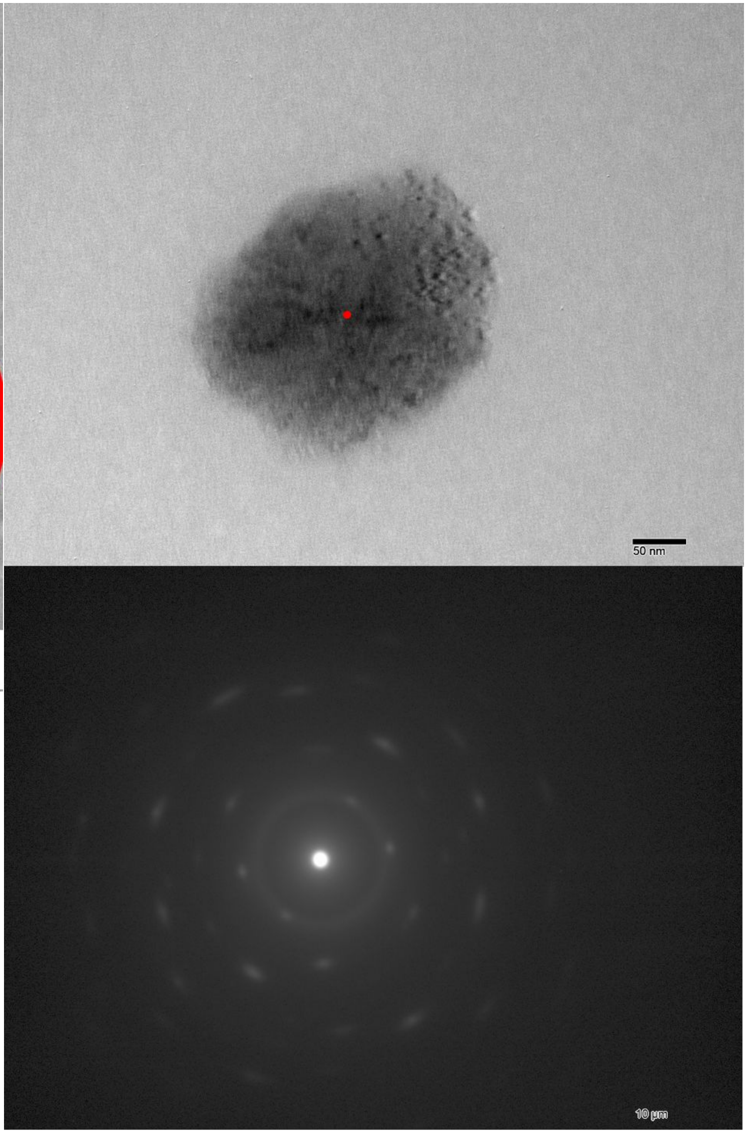
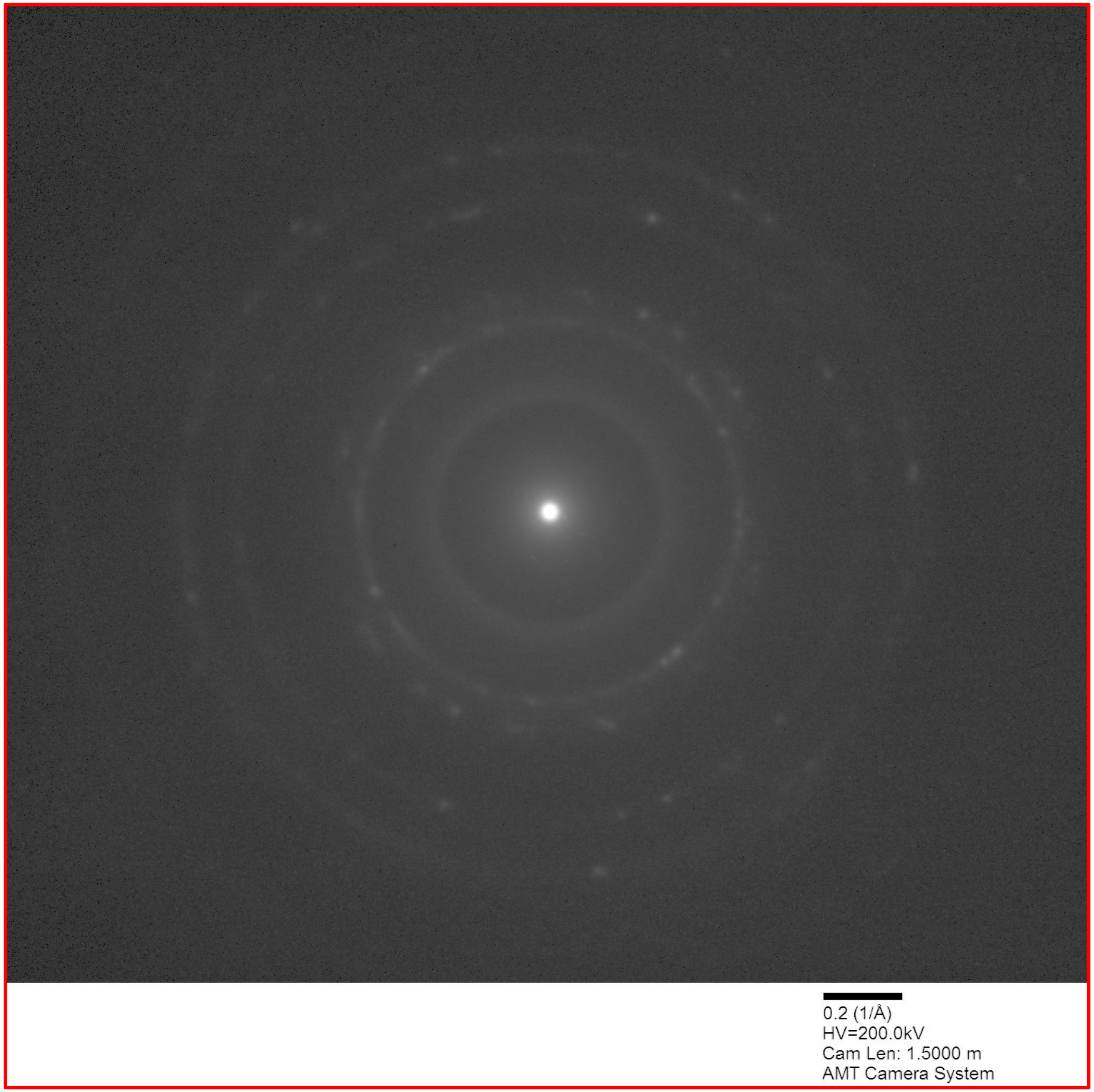




Imagined & diffraction analysis of the individual particles & aggregated revealed crystallinity



D-spacing analysis performed using an aluminum standard found that spacings were consistent with hexagonal molybdenum disulfide [19]

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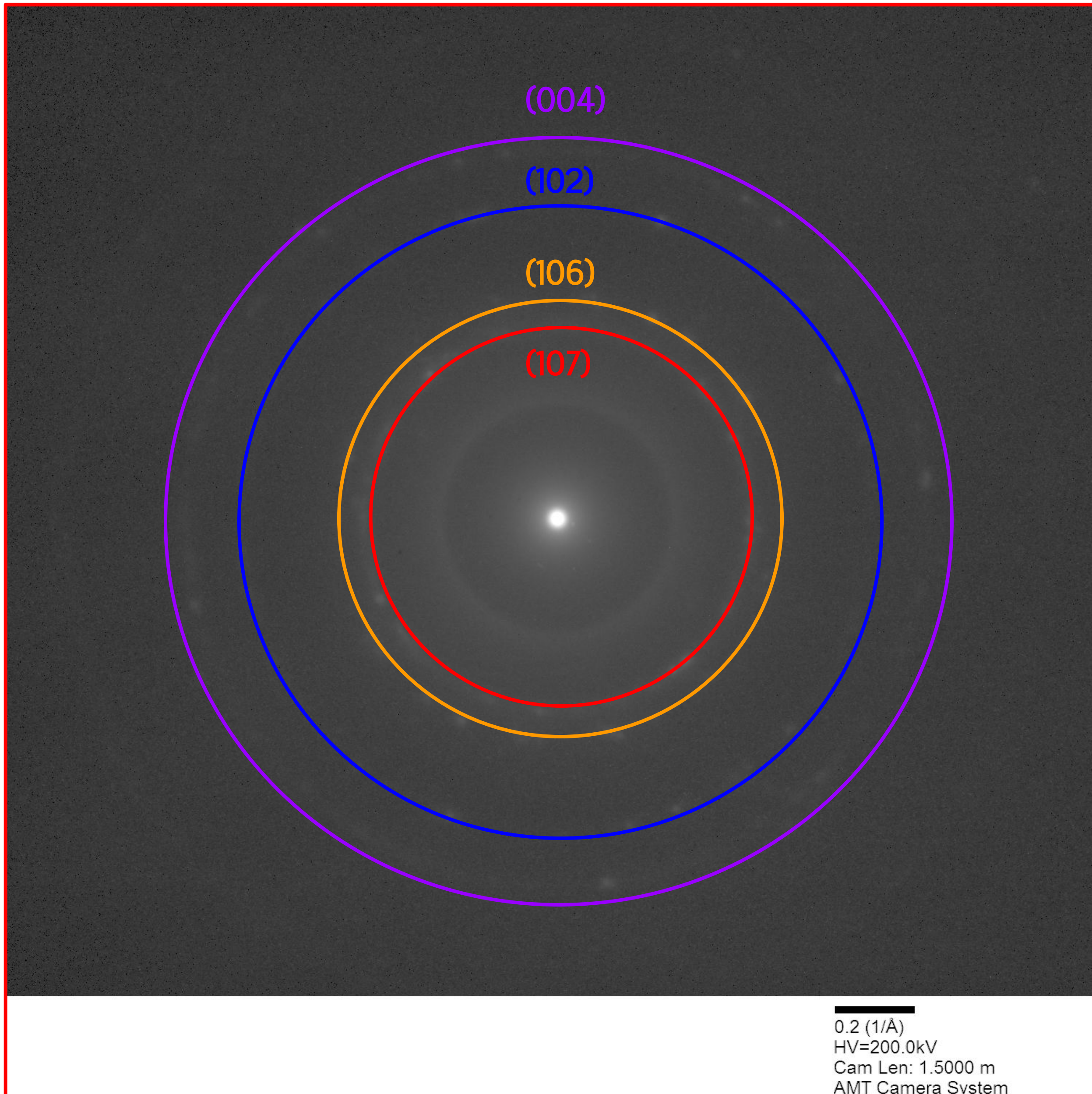

D-spacing analysis performed using an aluminum standard found that spacings were consistent with hexagonal molybdenum disulfide [19]

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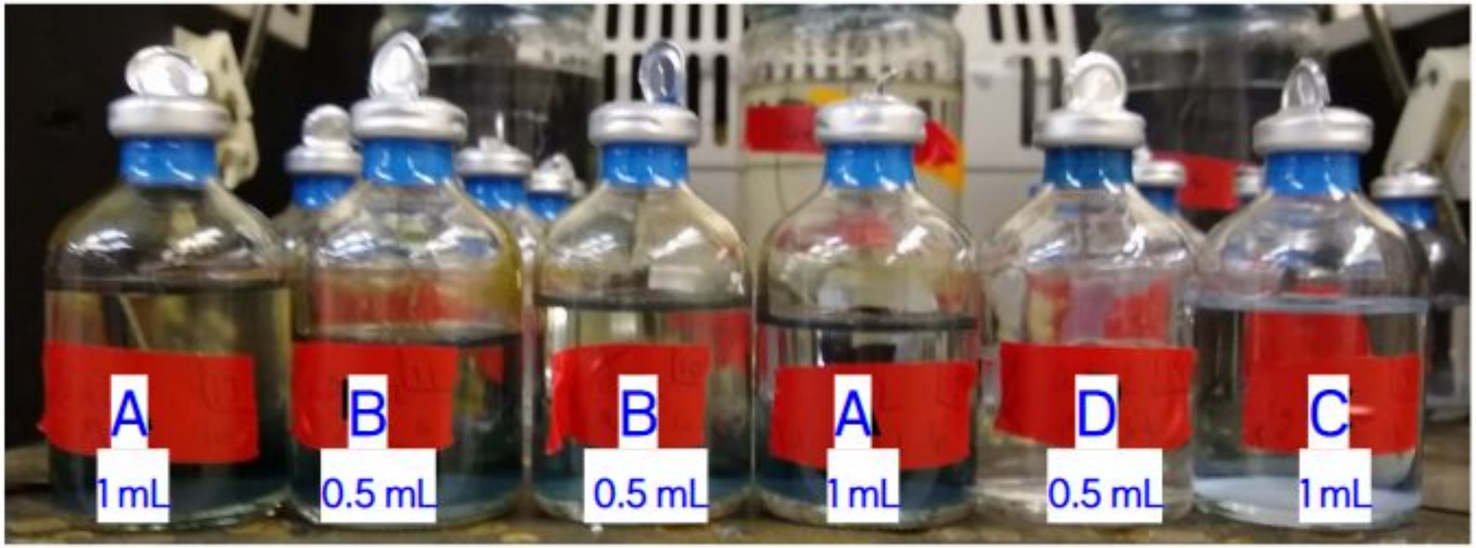
Conclusions & Future Work

Conclusions

- We have successfully synthesized MoS_2 nanoparticles at room temperature using *Shewanella* **(this is the first known instance of doing so)**
- **The proposed mechanism is a combination of H_2S formation and dissimilatory reduction of Mo(VI) to Mo(IV) at the surface of the *Shewanella* biofilms**
- MoS_2 nanoparticles tend to be a few hundred nanometers in size, can be single crystals or polycrystalline, and may contain several different crystal structures

Future Work

- Improving control over nanomaterial growth and composition via control of cultivation conditions *(see below)*
- Continuous (bioreactor) cultivation due to variability of batch culture
- Further isolation & purification of bio-nanomaterials
- Deposition of nanomaterials onto conductive substrates & characterization of photocurrent behavior
- Investigation of new potential materials amenable to biosynthesis



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Conclusions & Future Work

Thank You!

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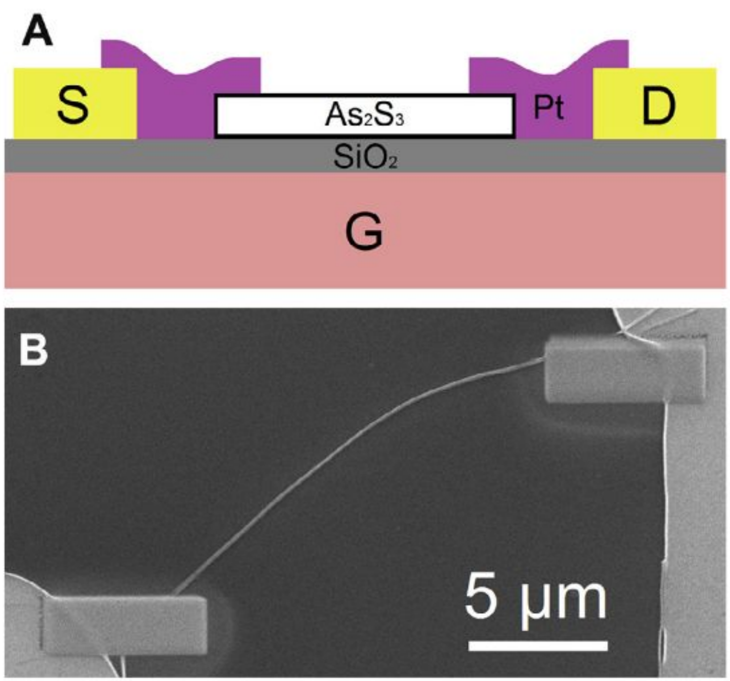
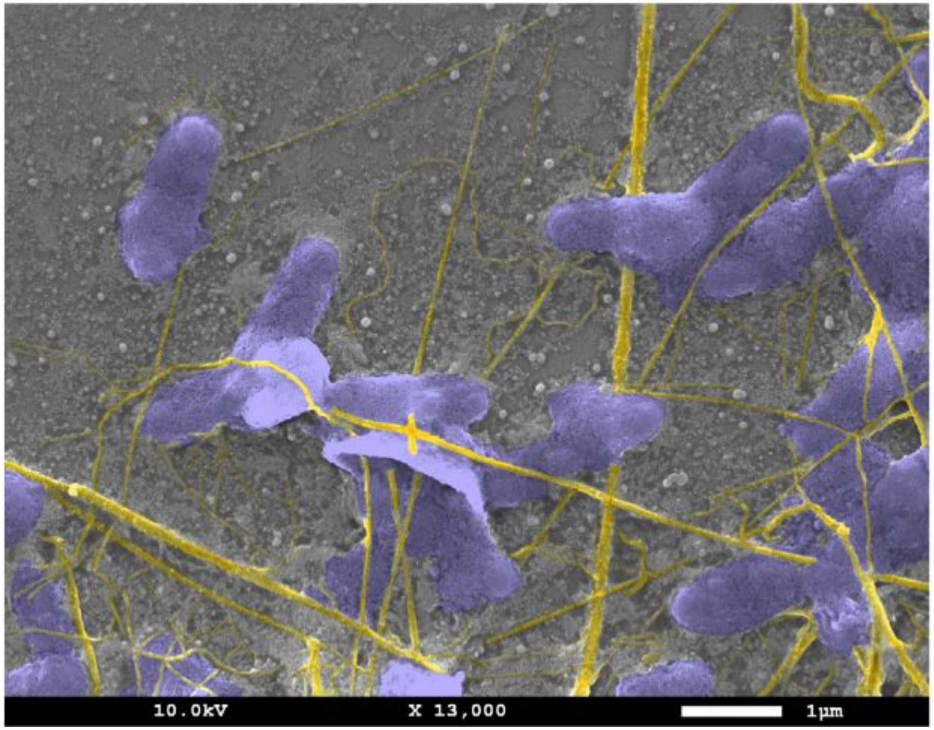
References

Extra Slides

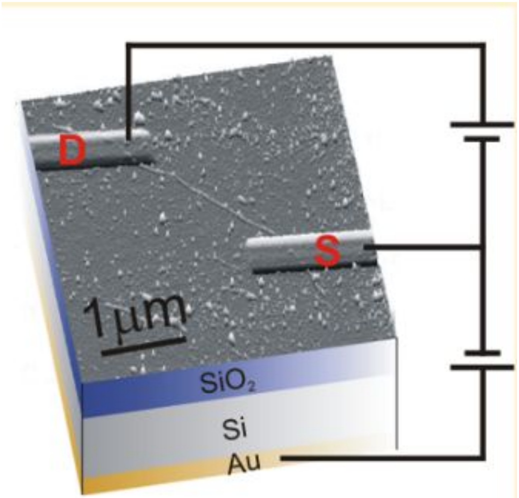
Prior Results: Biosynthesized Nanofibers

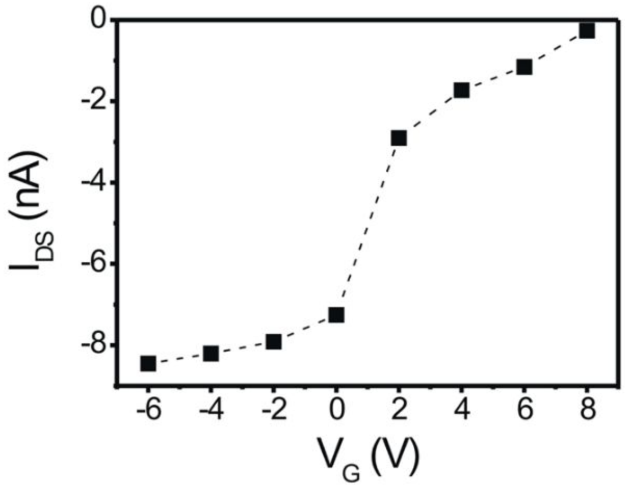




Add short blurb about what is going on

Prior Results: "Living Electronics"





On this slide, mention three things briefly:

1.) the measurements on the nanowires themselves, which show that they have voltage-dependent conductivity
2.) The way that they produce current and interface with solid substrates
3.) The potential applications for this - microbial sensors for materials

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Cultivation Experiment (detailed)

Group A	10mM NaS_2O_3, Inoculated
Group B	20mM NaS_2O_3, Inoculated
Group C	10mM NaS_2O_3, Sterile
Group D	20mM NaS_2O_3, Sterile

- *Shewanella* was cultivated in a chemically-defined liquid growth medium containing buffer salts, vitamins, minerals, amino acids, lactate as an electron donor and thiosulfate as an electron acceptor
- Four different groups were used in varying combinations of inoculation and thiosulfate
- Incubated at 30C with agitation and checked after 14 days
- After incubation, 0.2mL of a sterile preparation of 75% deionized water and 25% suspended MoO_3 (by volume) was added to each bottle
- No initial changes were visible in the bottles after addition of MoO_3

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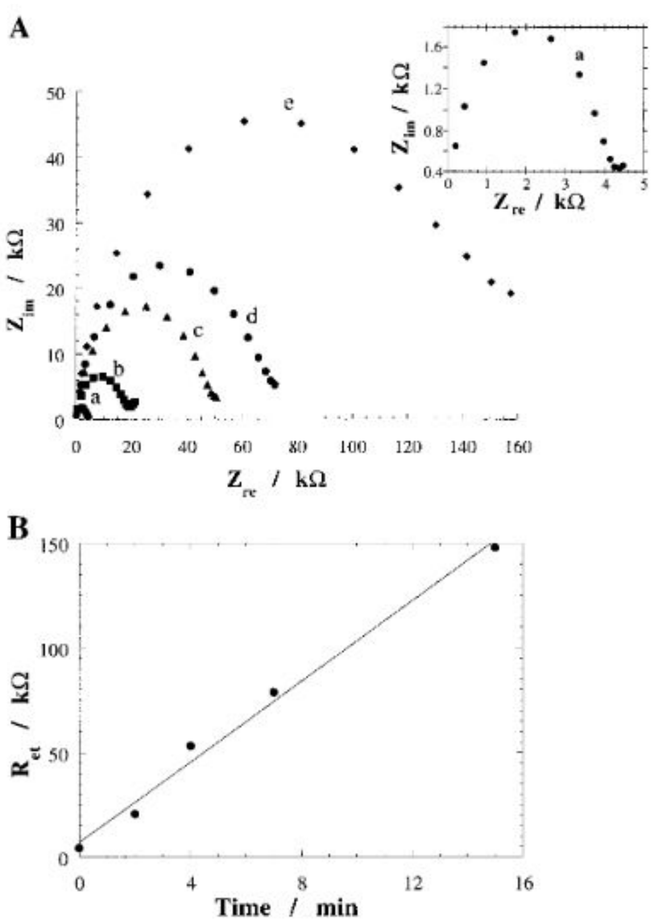
Introduction

Background (EIS)



- At left: Diagram from a paper by Patolsky et. al. (1999)
- "The precipitate accumulates on the electrode support by the nonelectrochemical biocatalyzed process. **Therefore, the insulating layer is anticipated to become thicker as time proceeds**. Curves b-e of Figure 2A show the Faradaic impedance spectra of the HRP-monolayer electrode in the presence of H2O2 , 5mM, at different time intervals. **The semicircle diameters of the impedance plots increase as the time intervals for precipitation are longer**, Figure 2B."
- "It is evident that upon the accumulation of the insoluble product on the electrode surface, **the interfacial electron transfer is retarded and the capacitance is decreased**"