Nanofermentation: Scalable Low Cost Nanomaterial Synthesis

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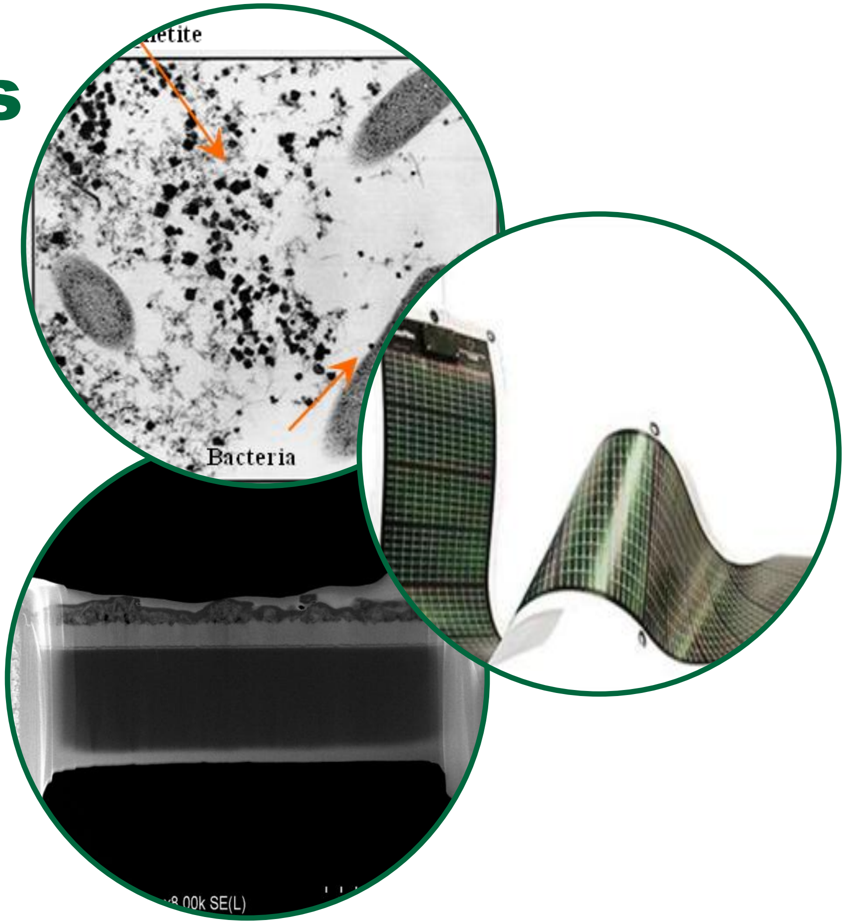
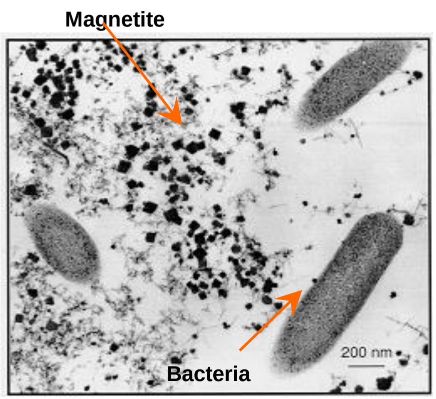


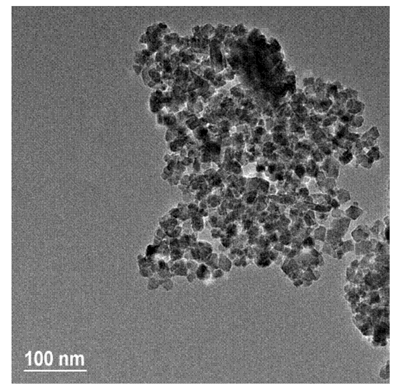
Bio-Synthesis of Nanomaterials

- ***Nanofermentation*: Why are we interested in bacterial synthesis of nanoparticles?**
  - Great potential in terms of low-cost mass production of size controlled (10 nm to 100 nm) nanomaterials
- **Bacteria first discovered in oil and gas deposits in 1992**
  - Strains of thermophilic anaerobic bacteria produce *extracellular particles* of magnetite
  - In 2006, ORNL discovered size and shape control
    - Addition of specific control agents control size and shape of final material
      - Combined (in-situ) particle synthesis with surfactant
    - ***Named 2006 R&D 100 and Micro/Nano-25 in 2006***

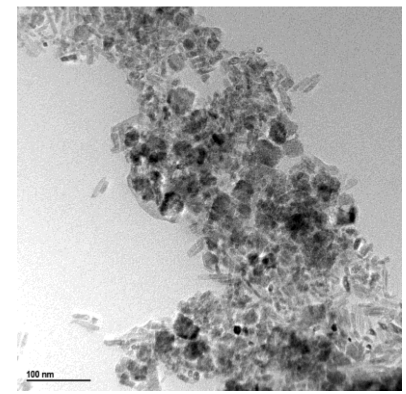


Novel

Scalable



Control size



Control Shape

- **How does process work?**
  - In fermentor, bacteria replicate every 3 hours until they reach an optimal population density (e.g., scale invariant), low temperature (4 – 70ºC), ambient pressure, pH values of 6.5 – 9
  - Bacteria act like a catalyst transforming precursors to nanomaterials (nucleation at cell membrane)
  - Low temperature , inexpensive salts for precursors and cheap fuel (glucose) drive low cost
    - (~$60/kg, 30 nm) compared to $1340/kg (99.5%, 25 nm) magnetite

"Game changing" approach to Nanomanufacturing

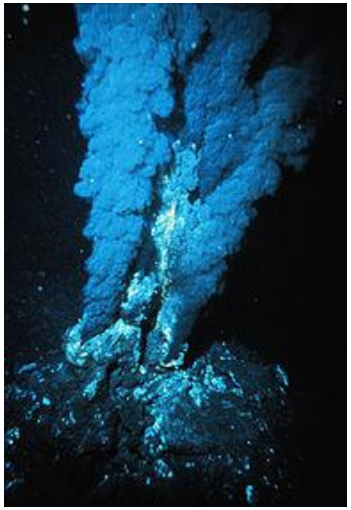
- ***Very scalable***
  - 50,000 gal fermentor provides 500 kg/month
  - *Equivalent to 10.8 MW of PV material /year*
- ***Energy efficient***
  - Organometallic synthesis occurs at 500°-600° C [Roca et al., 2006]
  - Sol-gel requires 250° - 400° C annealing under vacuum [Xu et al, 2007]
  - Nanofermentation occurs between 10° and 60° C [Phelps et al., 1998], *glucose is primary fuel!*
- ***Potential for very low cost***
  - Inorganic process: >$500,000/kg (CIGS), ~50% of raw materials used [Kaelin, 2005]
  - Nanofermentation: <$8,000/kg (CIGS), ~100% of raw materials used
- ***Highly refined final product***
  - In-situ integration of synthesis and surfactant yields highly dispersed materials
    - No other process can do this
  - 'One-pass' generation of multi-component compounds
    - Other techniques require multiple processes, increased cost and decreased control
- ***Environmentally-friendly process***
  - Chemical approaches require environmentally unfriendly solvents to control size [Sun, 2004]
  - Nanofermentation is a naturally occurring biological process.
    - Nature's been doing it for hundred of millions of years
    - We've just a) relocated where it's occurring and b) modified some of the parameters to control the product

Steps in the process: Find Bacteria

Explore deep mines in search of deep underground bacteria

Use ROVs for extract bacteria from deep sea sediments

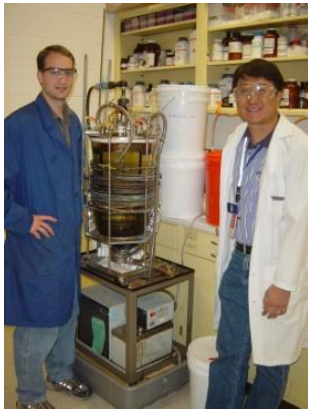
Extract bacteria from oil and gas exploration rigs



Extract bacteria from caustic springs in Yellowstone

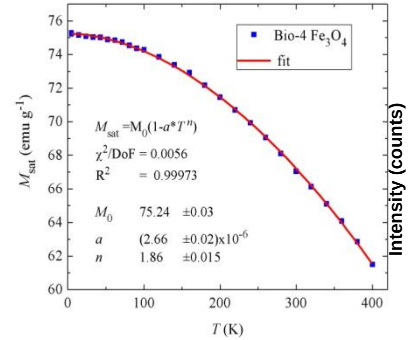
Develop procedure on test tubes

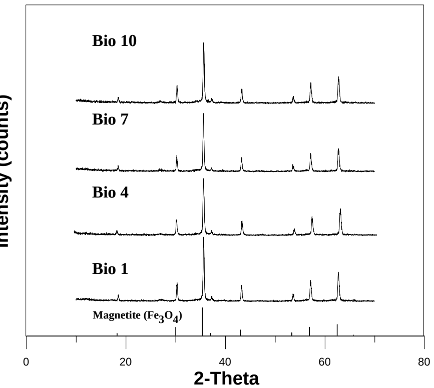
- **Transport bacteria to the lab**
- **Develop procedure, at a test tube level, to understand conditions by which bacteria can facilitate the growth of target materials with target size and shape.**
- **Scale up: Go from test tubes to bottles to demonstrate process is working at multiple scales**



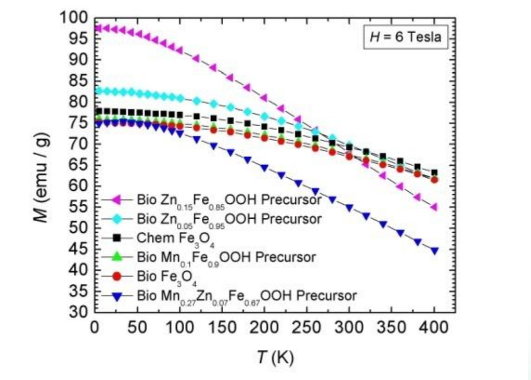
Magnetic Material Quality

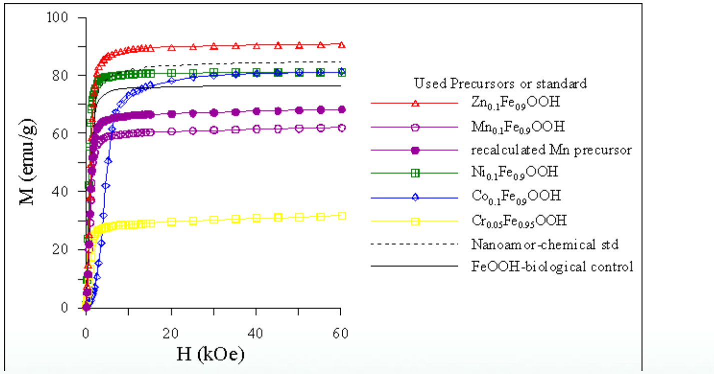
- Good match (x-ray diffraction, SQUID) between published magnetite particles and ORNL bio-synthesized particles
  - Goya (2003)
    - Ms = 77.8 emu/g (T=5K), 65.4 emu/g (T=300K)
  - Bio-synthesized
    - Crysal size – 35.1 nm
    - Ms = 76.9 emu/g (T=5K), 67.5 emu/g (T=300K)





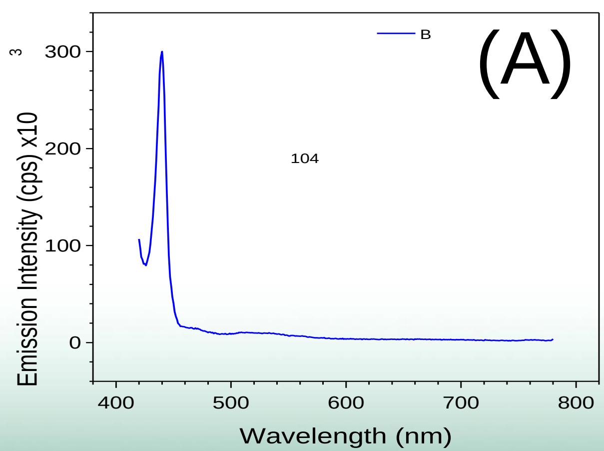
- ***What about metal-substituted magnetite?***
  - Discovered bacteria can synthesize wide range of metal-substituted magnetites: $Fe_{3-x}Co_xO_4$, $Fe_{3-x}U_xO_4$, $Fe_{3-x}Cr_xO_4$, $Fe_{3-x}Ni_xO_4$, $Fe_{3-x}Pd_xO_4$, $Fe_{3-x}Zn_xO_4$, $Fe_{3-x}Gd_xO_4$, $Fe_{3-x}Mn_xO_4$, $Fe_{3-x}Nd_xO_4$

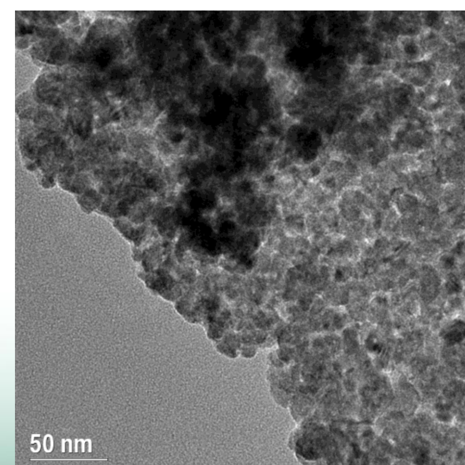




Bacterial Synthesis of Quantum Dots

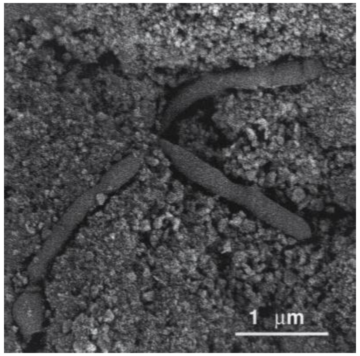
- **Until recently, focus of nanofermentation was on magnetic materials**
  - **Did not realize bacteria could facilitate production of other nanomaterials**
- **In 2007, discovered bacteria could synthesize quantum dots**
  - **Quantum dots are a critical material for photovoltaics, thermoelectric, solid state lighting…**
- **Preliminary synthesis and analysis looks very promising**
  - **Very scalable in terms of production of materials**
  - **Potential for low cost**
    - **CdS (2.8 nm) is somewhat harmful to bacteria so production cost ~$50/g**
    - **ZnS (6.5 nm) is much less toxic to bacteria and has potential for ~$1/gram**
    - **CIGS (~5 nm) can control stochiometry at ~$3/gram**





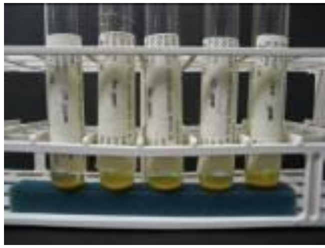
Recent Accomplishments
Bio-Synthesis of CdS and CIGS Nanoparticles

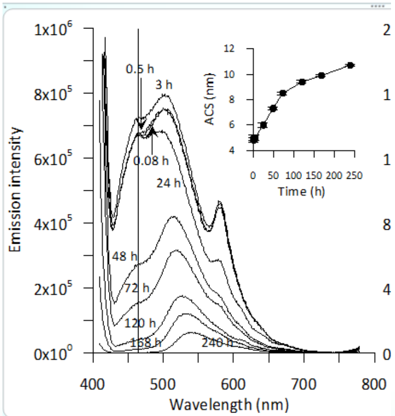
- **Successfully used bacteria to synthesize CIGS and CdS nanoparticles**
  - **Demonstrated feasibility and scaling from 10 mL to 30 L batches**
    - **> 3 orders of magnitude**
  - **Verified no degradation in material quality (PL and TEM) and production rate as a function of scale**
    - **Target was 3 g/L/month; achieved 6.8 g/L/month**
  - ***Quantified cost at $2667/kg (much less than ~$500K/kg from Lux). Materials for PV would be pennies per watt.***



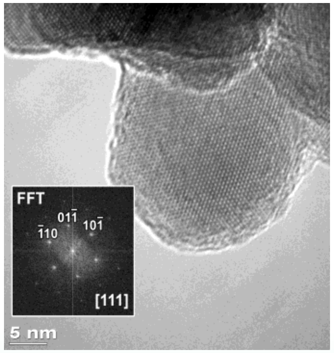
Bacteria

10 mL to L





Photoluminescence



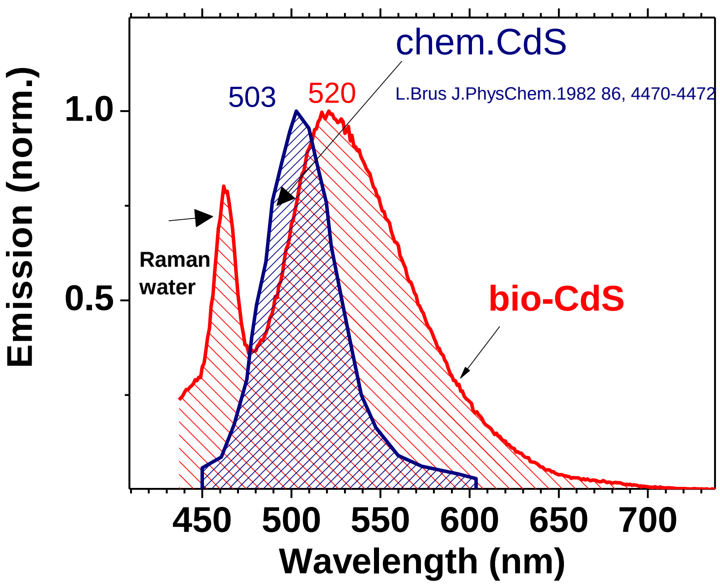
TEM of CIGS

Scale Up

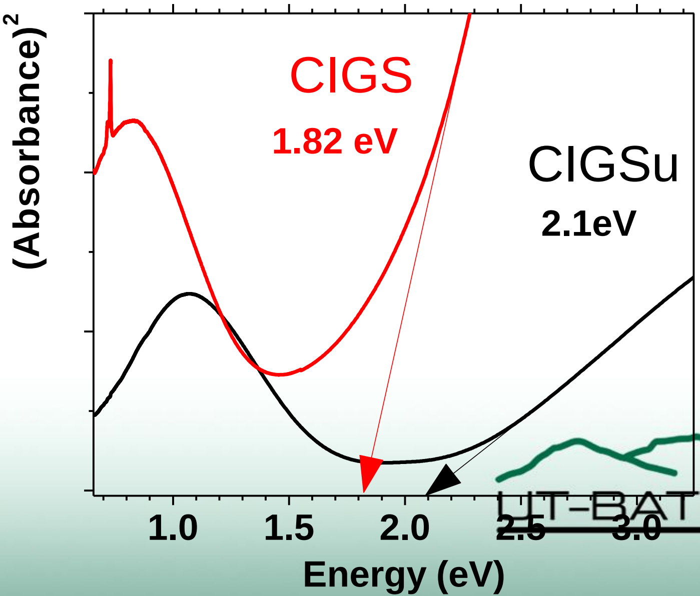
L to 30 L

Nanofermentation Activities
Verify Optical Properties

- ***Optical properties of CdS nano - particles***
  - Emission of Bio CdS in deionized water is comparable to chemically synthesized CdS in water
  - Bio CdS nanoparticles show broader size distribution

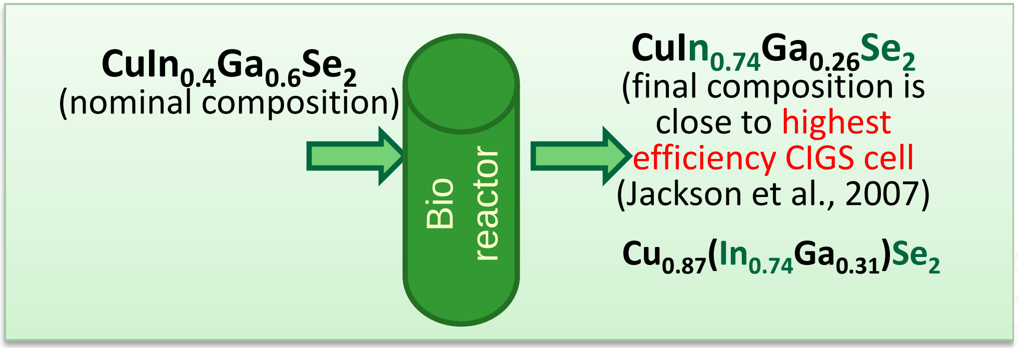


- ***Optical properties of CIGS nano-particles***
  - Absorption spectroscopy of Se and S- based CIGS confirmed correct optical band gap values:
  - Emission of Bio-CIGS, CIGSu (work in progress)
  - *No commercially available CIGS for comparison*

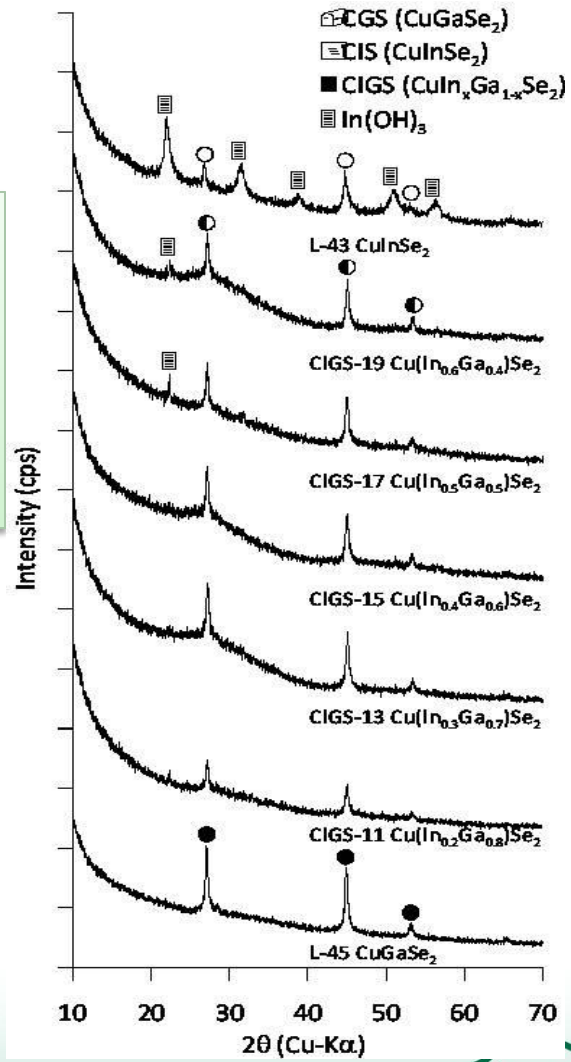


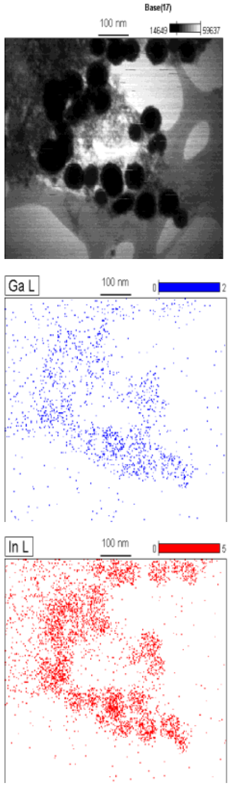
Nanofermentation Activities Stoichiometry Control

- **Demonstrated**
  - Stoichiometry of the particles is getting close to optimal



- **To be demonstrated**
  - Understand the mechanism to control nanoparticle composition. (The composition of materials going in does not match composition of nanoparticles harvested out bioreactor)





Material Development

- ***Develop and demonstrate the synthesis of new materials***
  - **Synthesize and analyze materials**
    - Demonstrate control over size, shape, morphology…
    - Investigate what the limits are in terms of materials (see table below for example materials)

Application	Target materials	Synthesis status
Magnetic oxide	Pure & Cr, Mn, Co, Ni, Zn, Nd, Gd, Tb, Ho, Er, U-doped magnetite ($\square_x Fe_{3-x}O_4$)	Demonstrated
Solid State Lighting	CdS and ZnS	Demonstrated
Solar cell (sulfide)	$CuIn_{0.5}Ga_{0.5}S_2$	Demonstrated
Solar cell (Selenide)	CdSe, $CuIn_{0.5}Ga_{0.5}Se_2$ (candidate:*Bacillus selenitireducens*)	Demonstrated
Solar cell (telluride)	CdTe	*Potential**
Structural	Titanium and Iron based metals	*Potential**
Battery cathode	$LiFePO_4$, $LiMnO_2$, $LiCoO_2$, $LiMgO_2$, $LiNiO_2$, $LiFeO_2$	*Potential**
Thermoelectrics	$Ca_4Co_3O_9$	*Potential**
Biomedical	**?**	***?***