Metal-like transport in proteins: A new paradigm for biological electron transfer and bioelectronics

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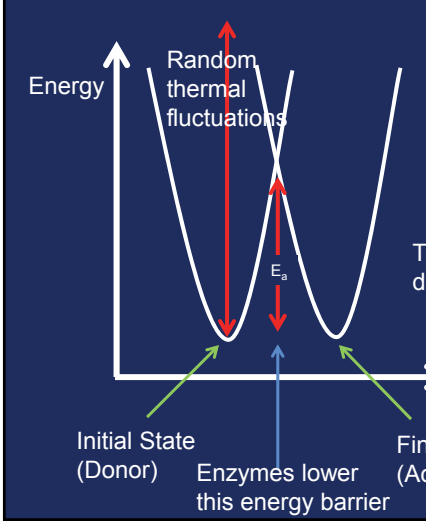
Biological Electron Transfer

Electron transfer reactions occur via tunneling or hopping, and can be driven by thermal fluctuations

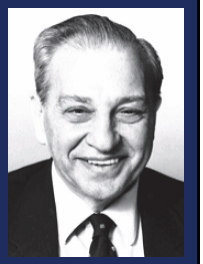


Thermal activation energy

$$\Delta G^* = \frac{(\Delta G^0 + \lambda)^2}{4\lambda}$$

Thermodynamic driving force

Reorganization energy



R.A. Marcus
Nobel Prize in Chemistry, 1992

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Proteins are Electronically Insulating

Within the context of this present analysis, it is apparent that proteins are large band gap materials, approaching 3 eV and there is no possibility of "metallic-like" conductivity even at the highest doping levels, that is, on D/A

(*Angew. Chem. Int. Ed.*, 2008, 47, 6758 – 6765)

transfer within the molecule. Delocalized coherent transport is dismissed in biomolecules due to their lack of periodicity, random fluctuations, and limited conductance values from experiments.

(Shinwari et. al. *Adv. Funct. Mater.* 2010, 20, 1865–1883)

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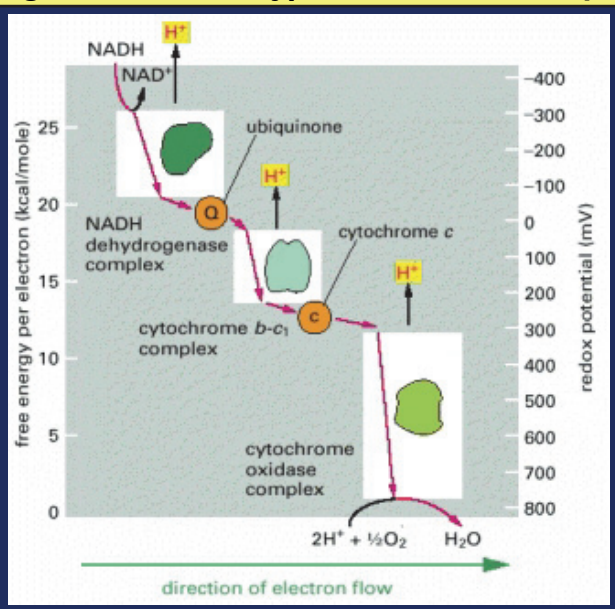
Redox gradient driven *typical* electron transport chain

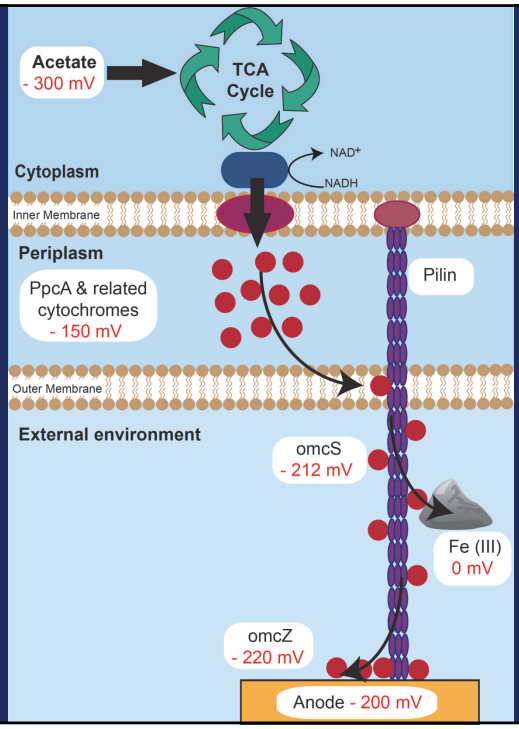


(Alberts B, Johnson A, Lewis J, et al., Molecular Biology of the Cell. 4th edition, 2002)

Surprising electron transport chain of ***Geobacter sulfurreducens***

Pili, omcS and omcZ are necessary for long-distance (> 1 µm) extracellular electron transfer

Both omcS and omcZ are farther apart and have lower redox potential than PpcA



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Why should we care about this?

Long-range (> 10 µm) conduction of electrons by microbial species has been invoked to explain a wide range of important redox phenomena that influence

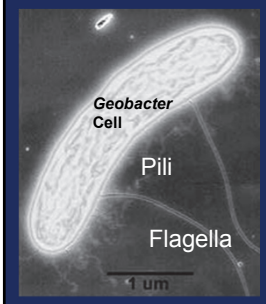
1) Carbon and mineral cycling in soils and sediments
2) Bioremediation
3) Corrosion
4) Carbon Sequestration
4) Anaerobic conversion of wastes to methane or electricity
5) Interspecies electron transfer via electrical connections

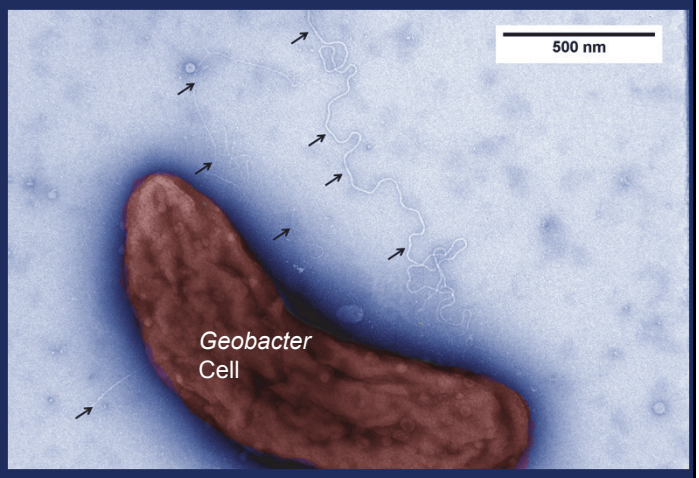
If the mechanism for this electron flow can be established, new paradigms will emerge in the field of microbial energetics and metabolism as well as in ecology and evolution.

This understanding will boost bioremediation and bioenergy technologies that can meet urgent global demand.

Do pili function as nanowires?

Single bacterium

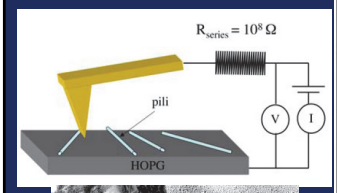


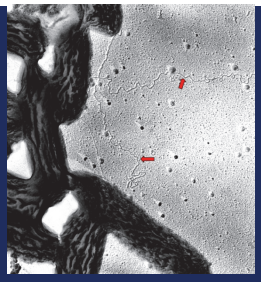


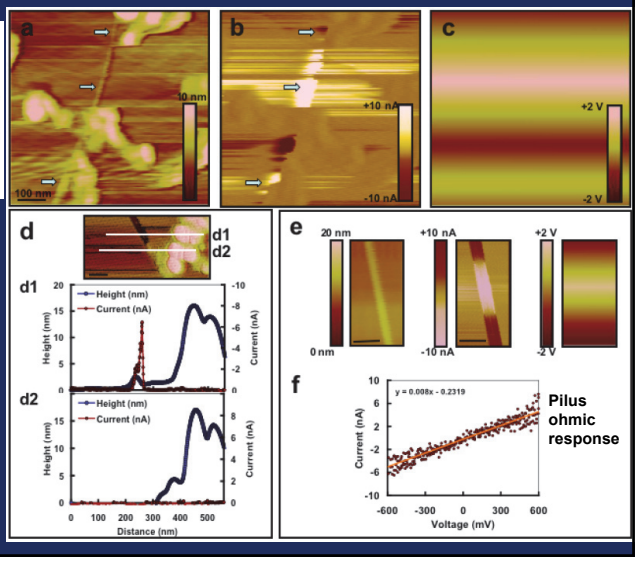
- Microbial nanowires are proteinaceous pili filaments secreted by *Geobacter*
- Pili are 2-5 nanometer wide but can grow up to tens of micrometer long
- Have been proposed to carry electrons from cell to distant electron acceptor.

Previous work suggested that pili might conduct electrons

- Genetic evidence suggested that pili are involved in electron transfer
- Conducting-probe AFM showed that pili are conductive along their width (2-5 nm) when chemically fixed and dried.



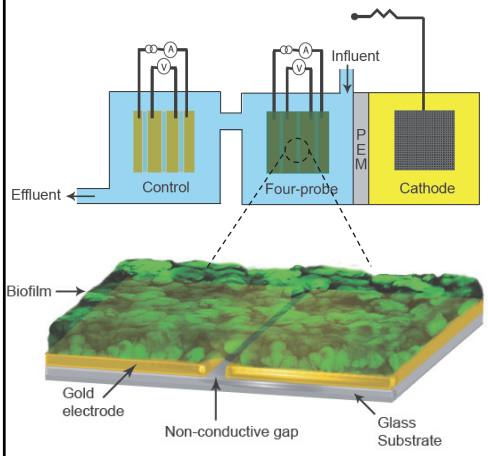




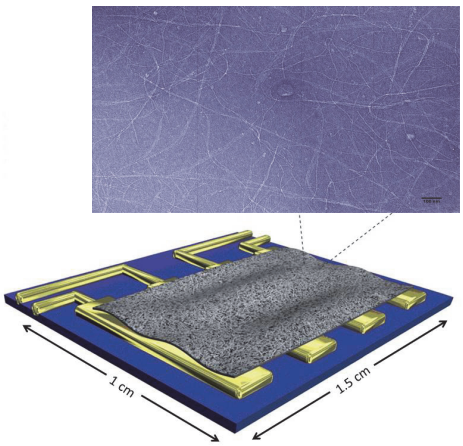
G. Reguera, K. D. McCarthy, T. Mehta, J. S. Nicoll, M. T. Tuominen, and D. R. Lovley 2005. Extracellular electron transfer via microbial nanowires. *Nature* 435:1098-1101.

Direct measurements of conductivity of living biofilms and microbial nanowires over centimeter-long distances

Multi-anode Microbial Fuel Cell



Microbial Nanowire Networks



Nikhil S. Malvankar et al., **Tunable metallic-like conductivity in microbial nanowire networks,** *Nature Nanotechnology*, 6, 573–579 (2011)

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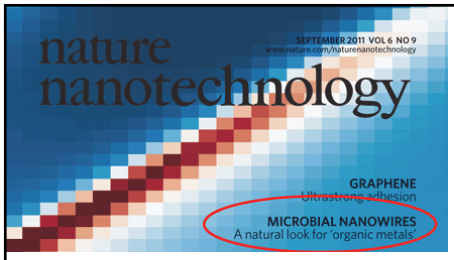
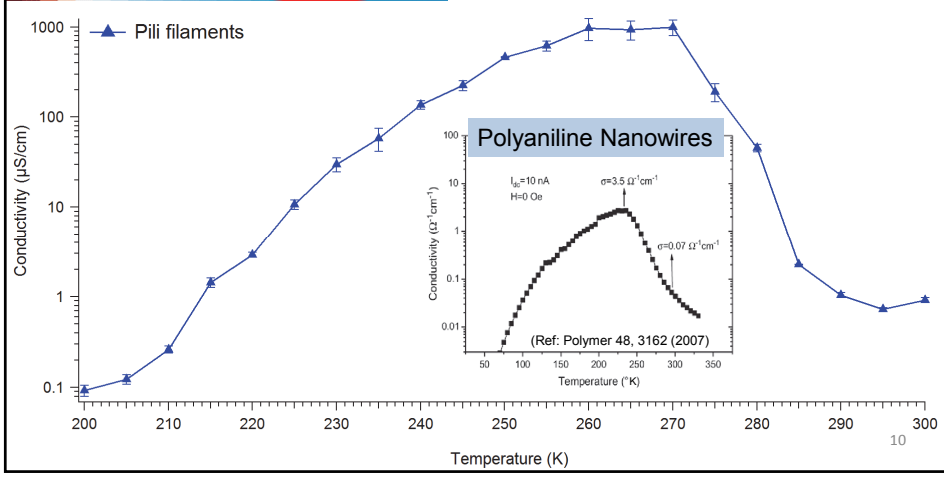


Microbial nanowires show electrical, structural and chemical properties similar to organic metals



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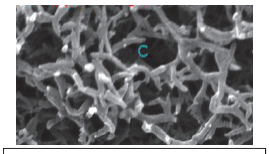
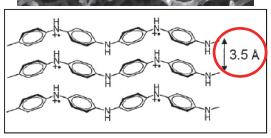
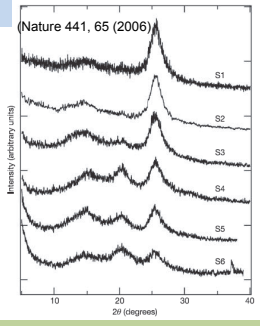
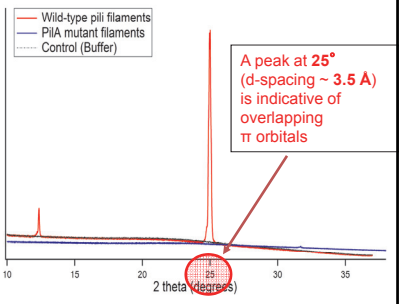
Polyaniline (PA)
Well known organic metal



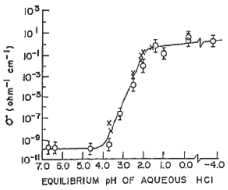


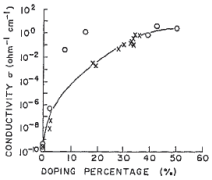
X-ray Diffraction of PA (left) and Pili (right)

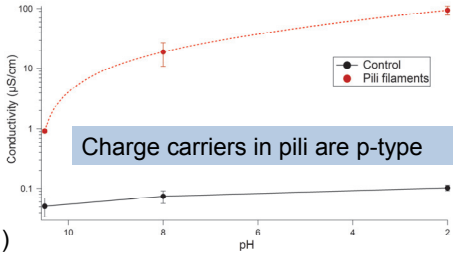




Proton doping in Polyaniline (left) and Microbial Nanowire (right)





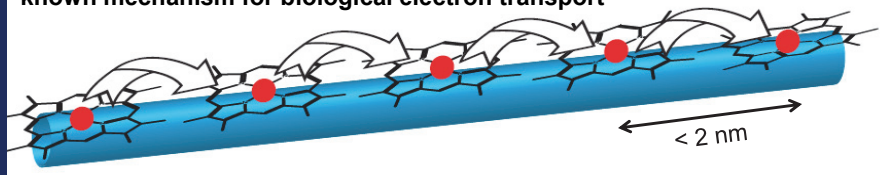


Charge carriers in pili are p-type

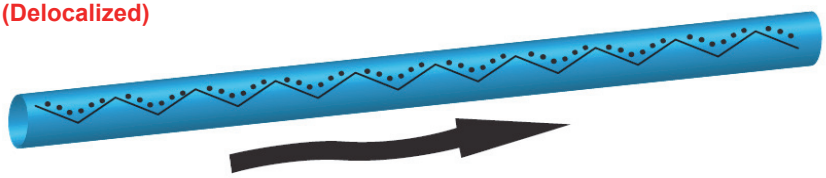
(Ref: Alan MacDiarmid, Nobel Lecture, 2001)

Metallic-like conduction is significantly different than previously considered modes of biological electron flow

Hopping or tunneling among *localized* charge carriers (cytochromes) is the known mechanism for biological electron transport



In metallic-like conduction, charges are spread across the molecules (Delocalized)



Nikhil Malvankar and Derek Lovley. **Microbial Nanowires: A new paradigm for Biological electron transfer and bioelectronics**, *ChemSusChem*, 5, 103, 2012.

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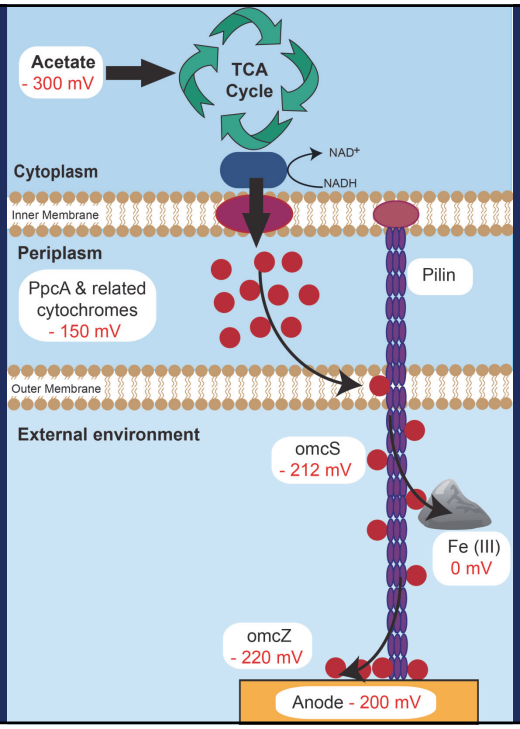
Metal-like conductivity of pili can explain the surprising electron transport chain of *Geobacter*

Delocalized electrons in pili can move under ordinary thermal condictions without any need for large redox gradient

How do electrons delocalize in pili?



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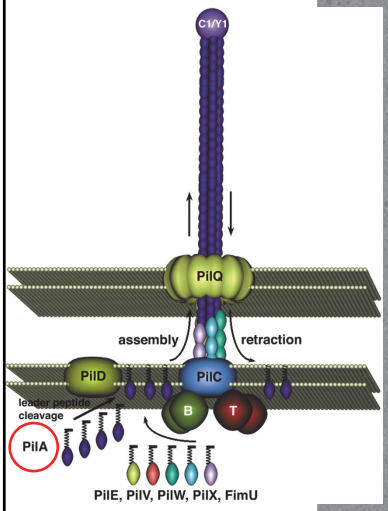
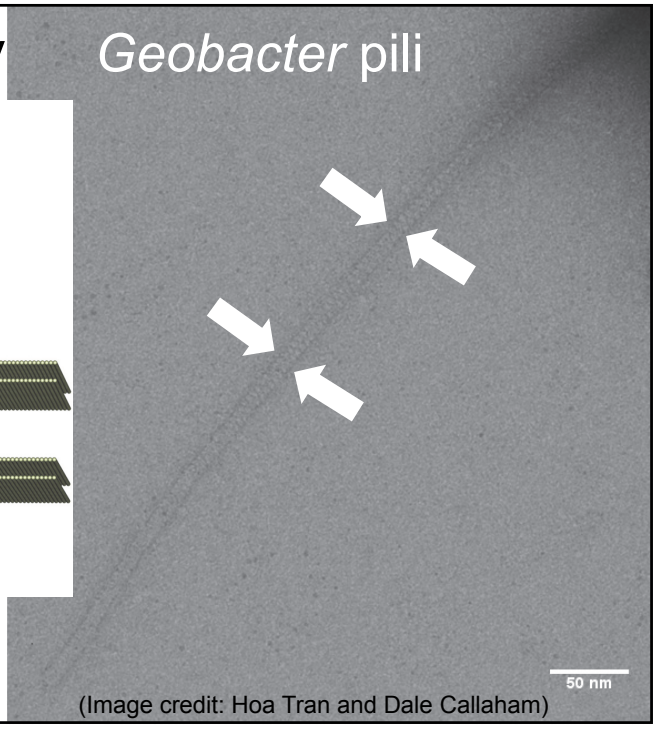
Pili assembly



Mattick, J.S. Annu Rev Microbiol, 2002. **56**: p. 289-314.

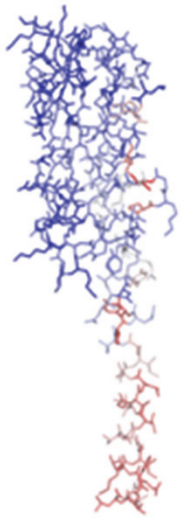
Geobacter pili



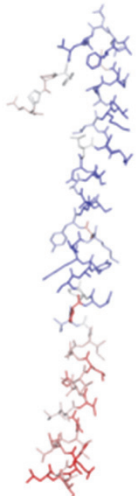
(Image credit: Hoa Tran and Dale Callaham)

Geobacter pilin is 3 times shorter than _Pseudomonas_

Pseudomonas pilin



Geobacter pilin



(Nikhil S. Malvankar, Unpublished data)

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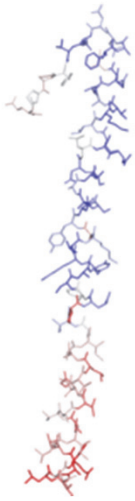
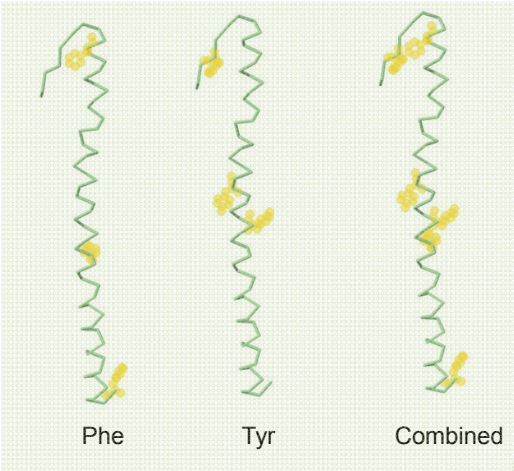
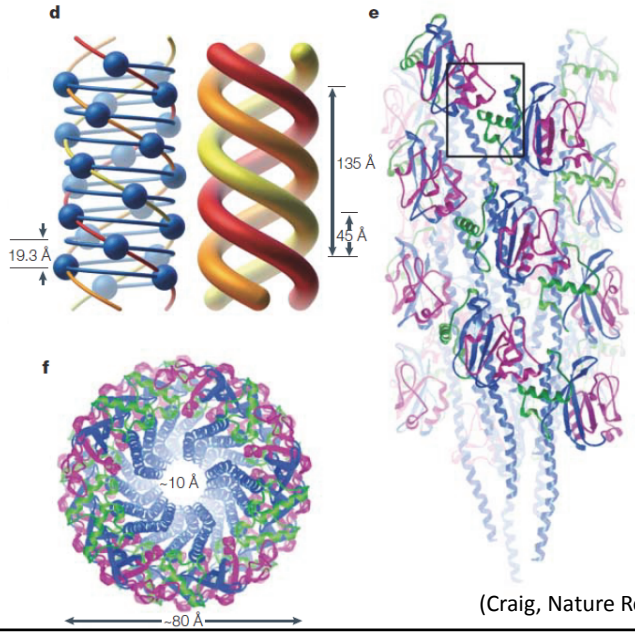
Geobacter pilin Predicted structure



Aromatic Amino Acids highlighted



Pilus assembly



(Craig, Nature Rev. Microbiol. 2003)

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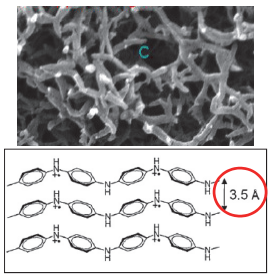
Well known organic metal



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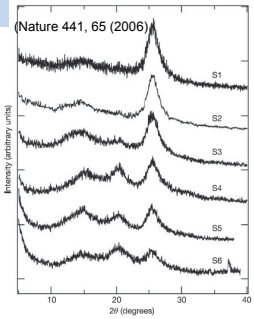

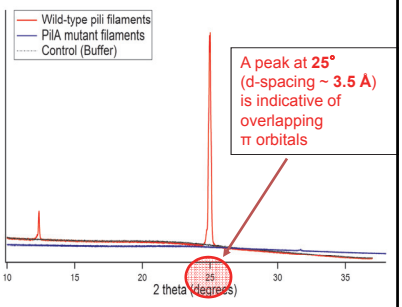

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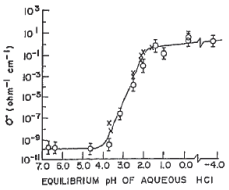
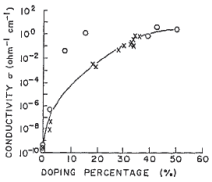
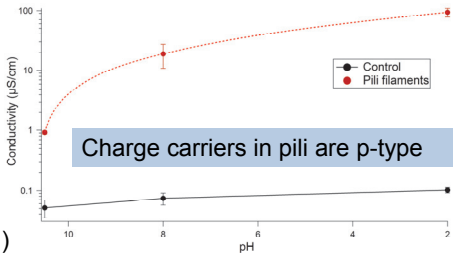


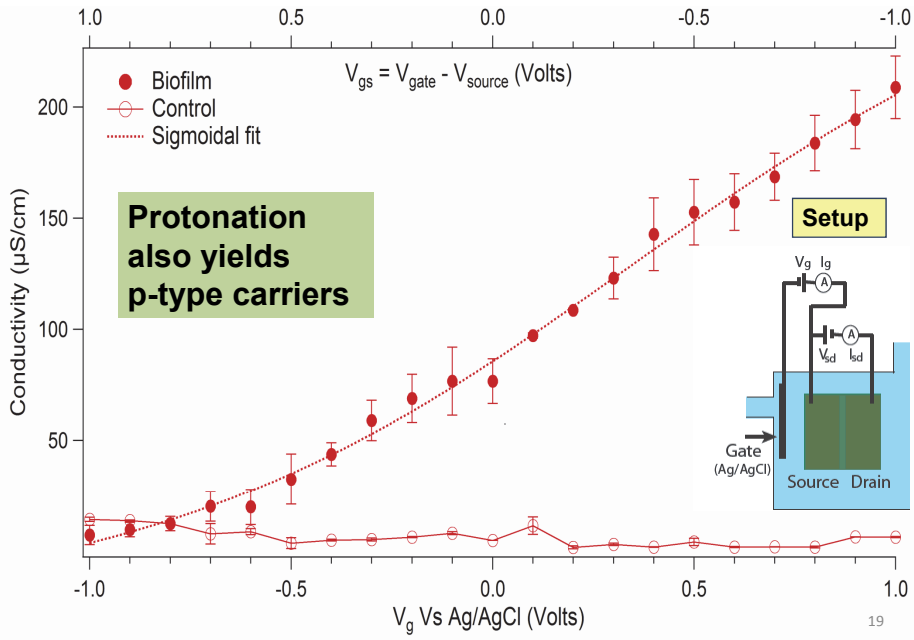




Charge carriers in pili are p-type

(Ref: Alan MacDiarmid, Nobel Lecture, 2001)

Electrochemical gating indicated that Charge carriers are p-type



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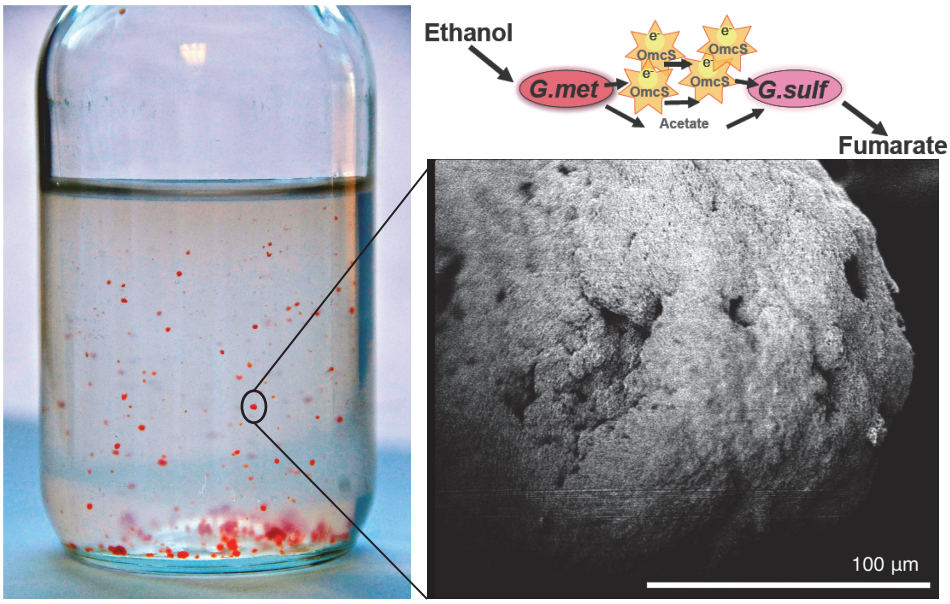
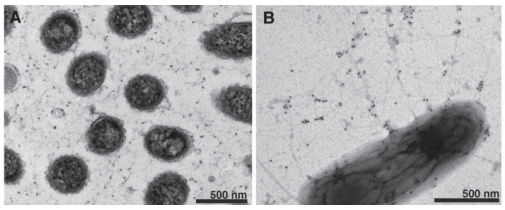
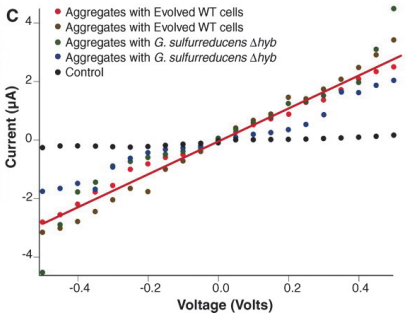
Aggregate of syntrophic co-culture of *G.sulfurreducens and G.metallireducens*

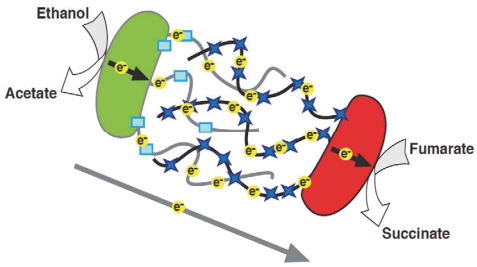


***Science* 330, 1413-1415 (2010)**

Pili are important for cell-to-cell electron transfer in evolved syntrophic co-culture







Bacterial co-culture is electrically conductive.

Science **330, 1413-1415 (2010)**

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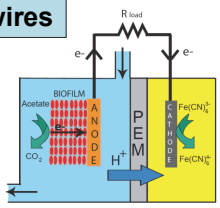
Microbial Nanowires: A new paradigm for biological electron transfer and bioelectronics

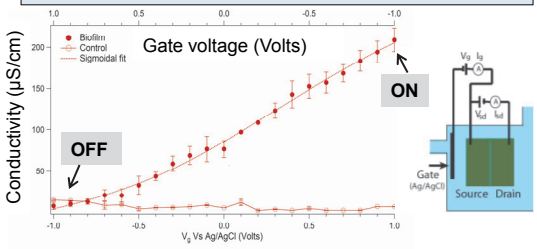
Protein-based nanomaterials are inexpensive and environmentally-sustainable
They can work under unusual aqueous and acidic environments

Applications of Microbial Nanowires

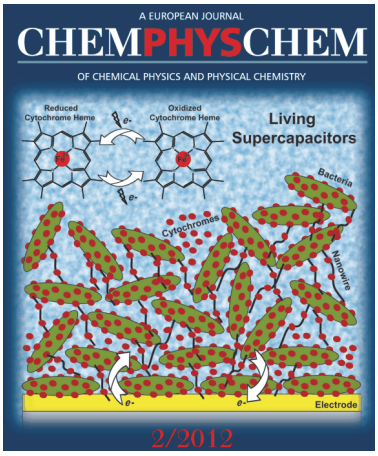
Microbial Fuel Cells with improved current and power density



Transistors with 100-fold ON-OFF ratio



High-performance Supercapacitors



Next Big Questions

1) Structural basis for electron delocalization
X-ray, electron diffraction?

2) Molecular basis for metallic-like conductivity
Replacing aromatic AA diminishes conductivity

3) How to enhance pili conductivity –
Replace with unnatural amino acids

4) Build devices with unique functionalities
Applications?

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Acknowledgements

Collaborators:
Prof. Derek Lovley (UMass Microbiology)
Prof. Mark Tuominen (UMass Physics)
Prof. Madeline Vargas (Biology, Holy Cross)

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DOE GENOMIC SCIENCE
SYSTEMS BIOLOGY FOR ENERGY AND ENVIRONMENT

Thank you !

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