

Rational Design of Electrodes in Electrochemical Energy Devices

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Electrochemical Devices

- Energy transfer and storage

Stationary power supply



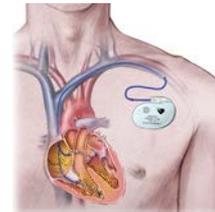
Portable Electronics



Toys



Medical



Vehicles



Grid-scale energy storage

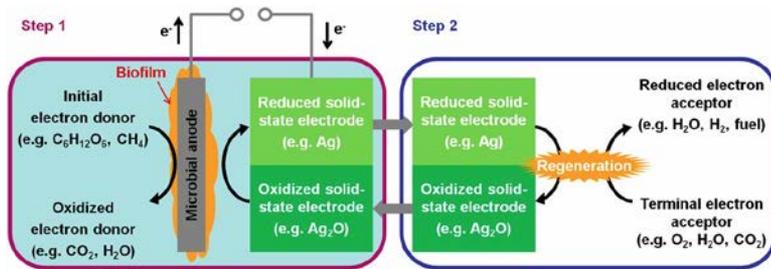




Electrochemical Devices

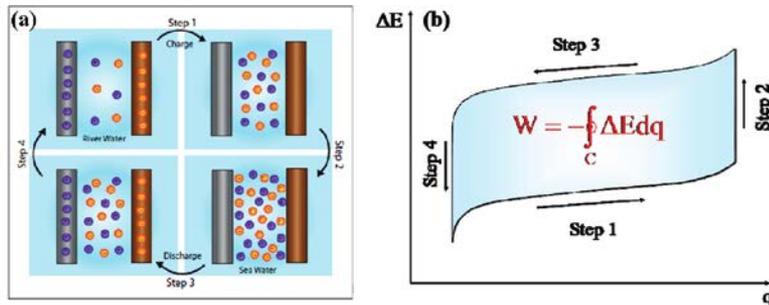
- Energy recovery

Waste organic matter



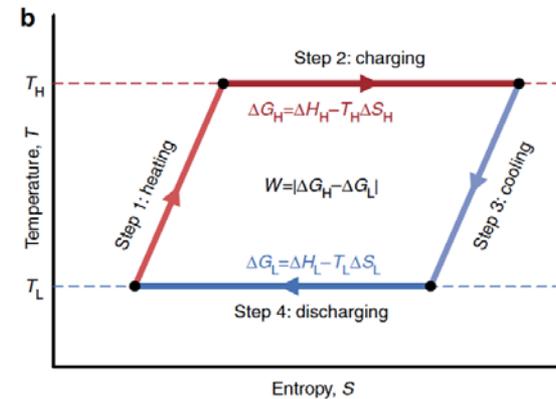
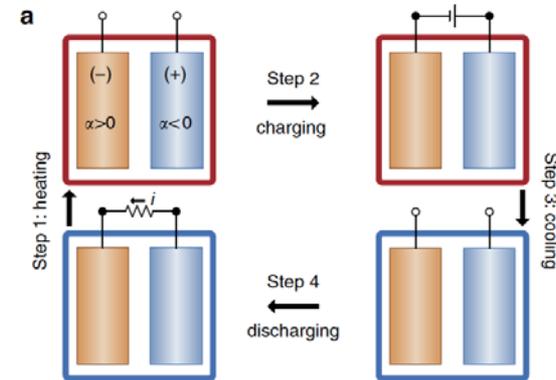
(X. Xie, et al. *PNAS*. 2013, 110: 15925-15930)

Salinity gradient



(F. Mantia, et al. *Nano Lett.* 2011, 11: 1810-1813)

Temperature gradient (waste heat)



(S. Lee, et al. *Nature Comm.* 2014, 5: 3942)



Rational Design of Electrodes: Roadmap

Understand the system

- Mechanism: redox reaction; bulk/surface
- Electrolyte: organic/aqueous; concentration
- Operation condition: pH; temperature; pressure



List the criteria

- Stable: mechanically, chemically, biologically
- Electron transfer: conductivity; interface
- Chemical transfer: diffusion; porous structure



Design

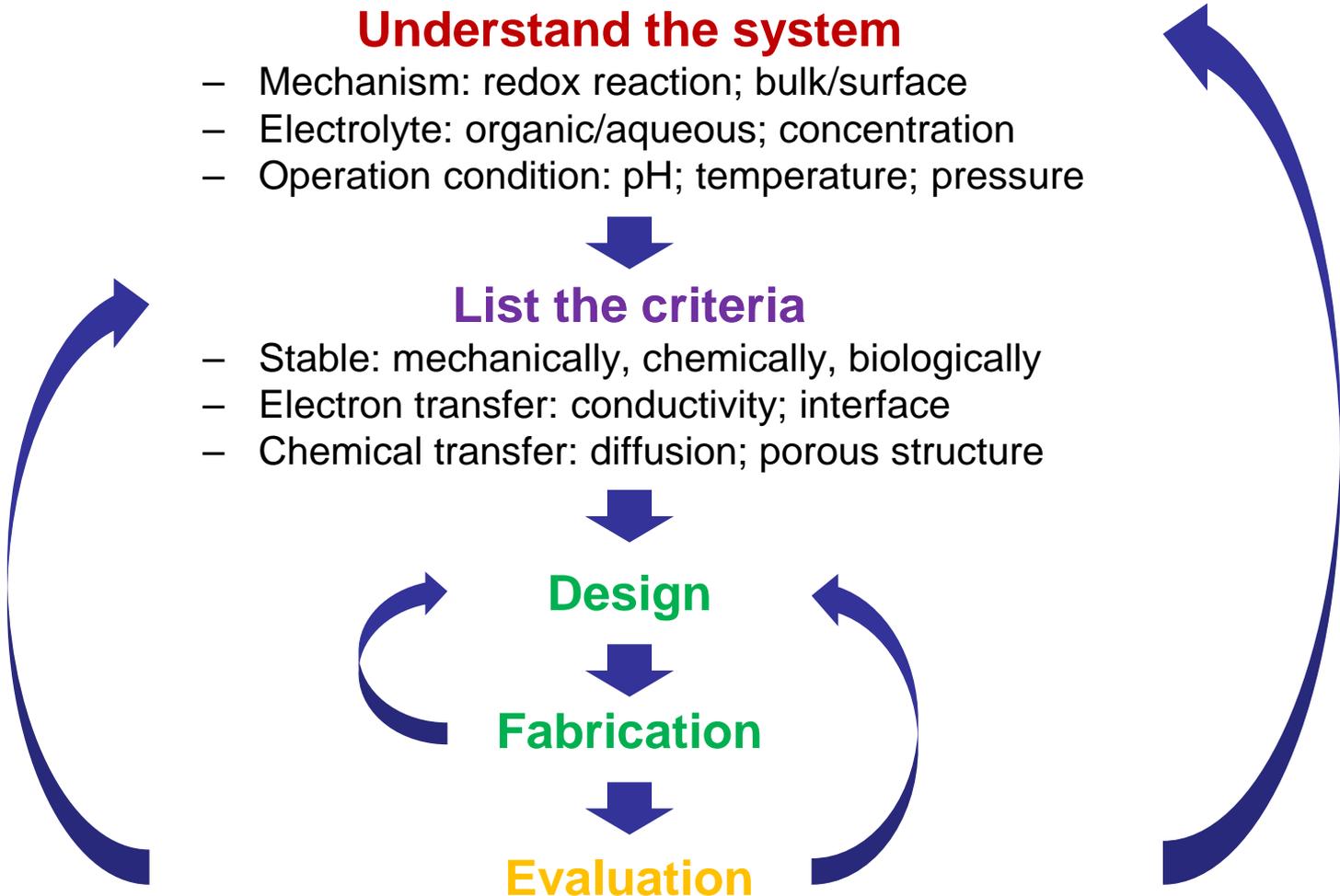


Fabrication



Evaluation

- Performance: current; power; cycling; long-term
- Cost: material; processing; life-span





Example

Design of Electrodes for Microbial Electrochemical Systems

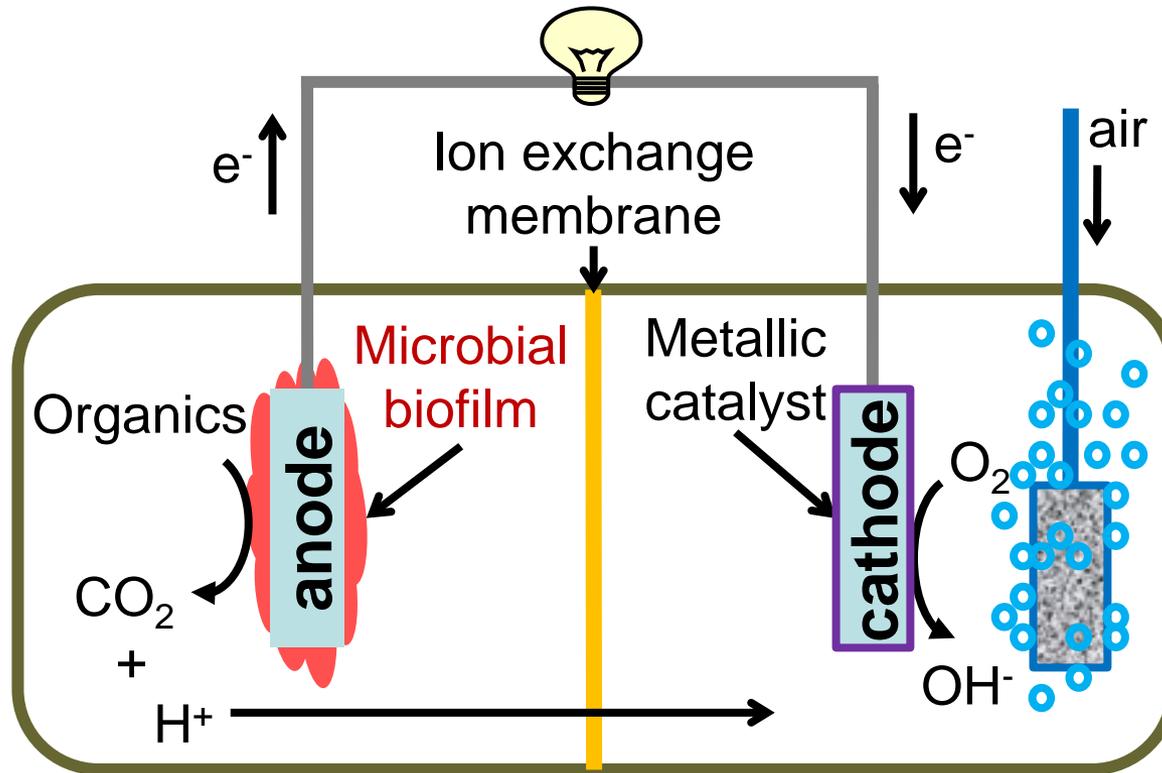
References:

- X. Xie, et al. *Nano Lett.* 2011, 11: 291-296
- X. Xie, et al. *Energy & Environ. Sci.* 2012, 5: 5265-5270
- X. Xie, et al. *ACS Nano.* 2014, 8: 11958-11965
- X. Xie, et al. *Energy & Environ. Sci.* 2015: Advance Article



Microbial Electrochemical Systems

- Energy: **chemical** → **electricity**
- Microbial fuel cells





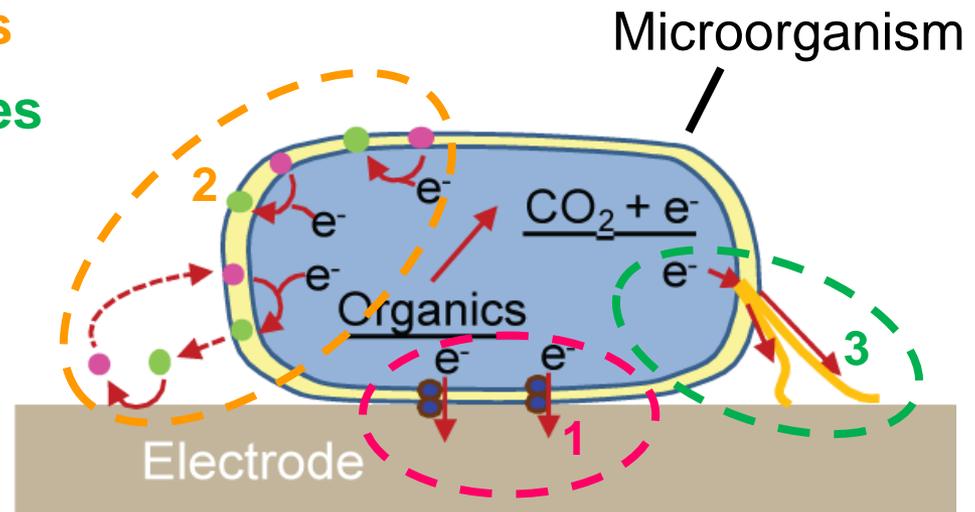
Bioelectrodes: Mechanism

- **Electrons: microorganisms → electrode**

Three pathways for extracellular electron transfer

1. **Direct membrane contact**
2. **Electron mediators**
3. **Microbial nanowires**

-  Microorganism
-  Electron transfer protein
-  Electron shuttle (reduced)
-  Electron shuttle (oxidized)
-  Microbial nanowire



Living catalysts: 10-100 μm thick

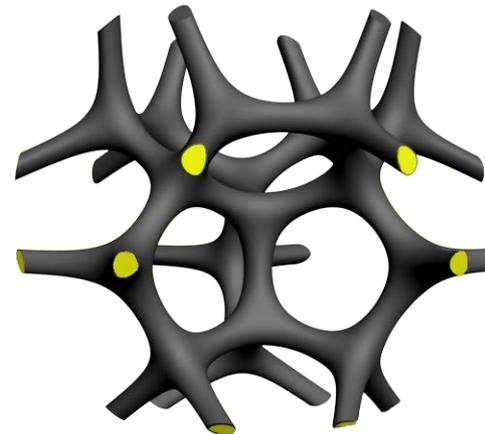
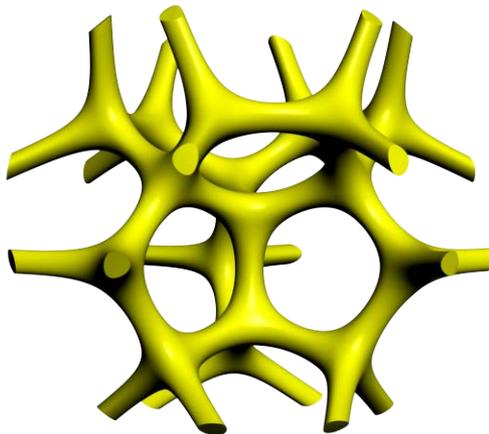


Bioelectrodes: Criteria & Design

- **Conductive**
- **Stable (chemical & bio)**
- **Biocompatible**
- **Macroscale porous structure**
- **Affinitive electrode surface**

More microbes for
electron transfer

More efficient
electron transfer





Carbon Nanotube (CNT)-Textile Synthesis

- A simple and scalable process



CNT powder

+ water + surfactant

sonication
→



CNT ink



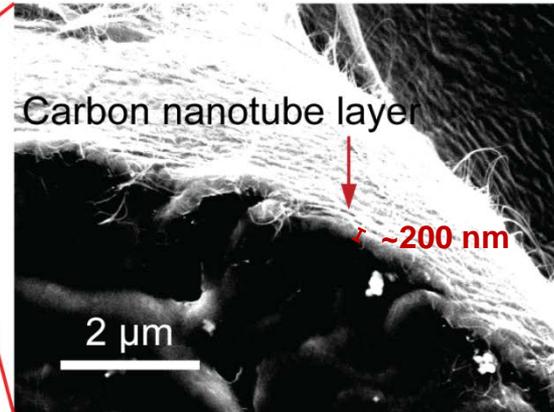
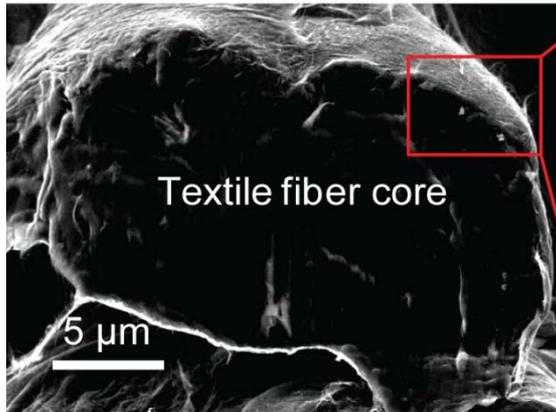
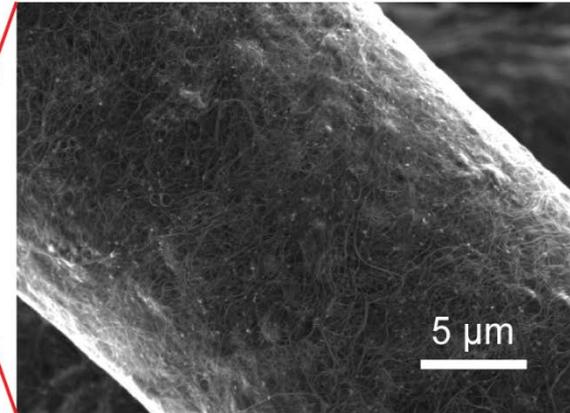
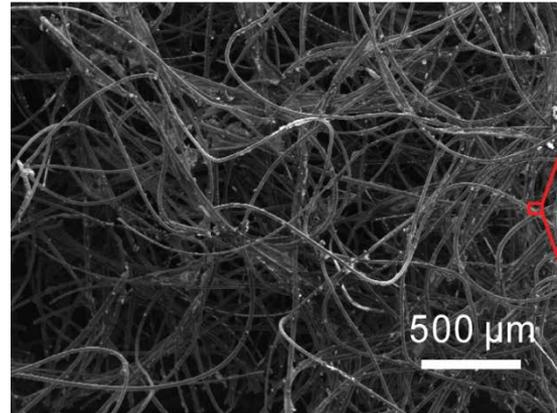
dry
→





Hierarchical Structure of CNT-Textile

**Macroscale
porous
textile**

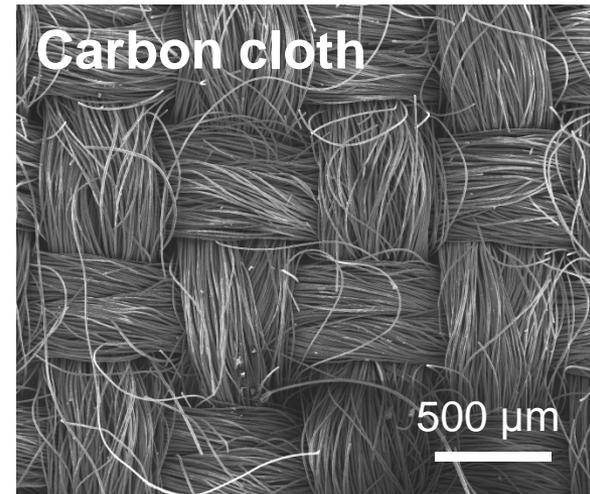


**Microscale
porous
CNT
coating**



MFC Experimental Setup

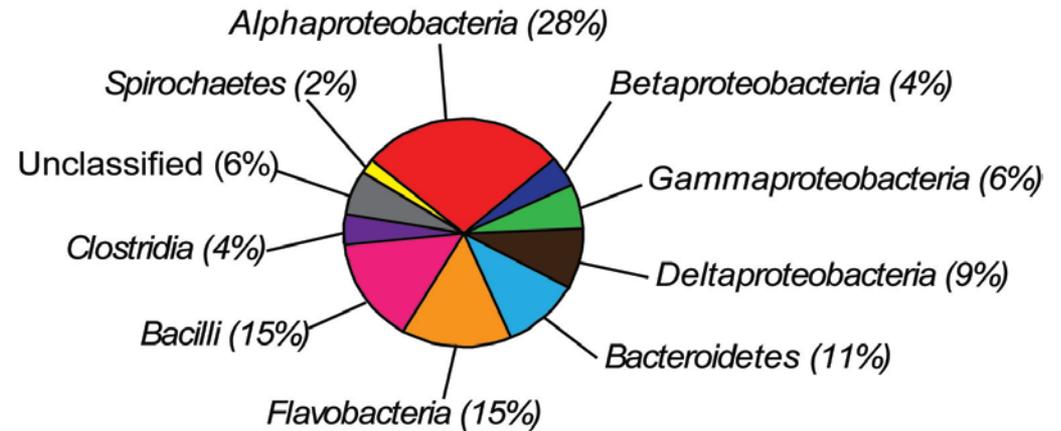
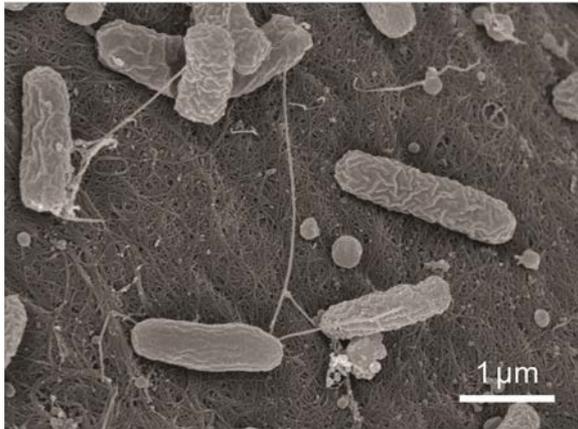
- H-shaped classic reactor
- Anode
 - **Carbon cloth** vs. **CNT-textile**
- Cathode
 - Pt on Carbon cloth
- Separator
 - Anion exchange membrane
- Feeding
 - Glucose (1 g/L)
- Inoculum (bacteria source)
 - Wastewater from Palo Alto Regional Water Quality Control Plant





Biocompatibility

- Microorganisms on CNT-textile



Evidence of colonization on CNT surface in MFCs



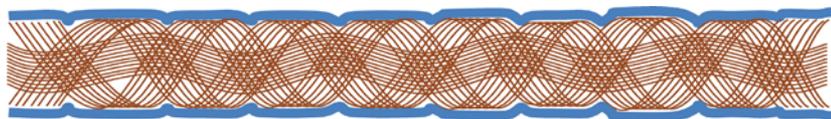
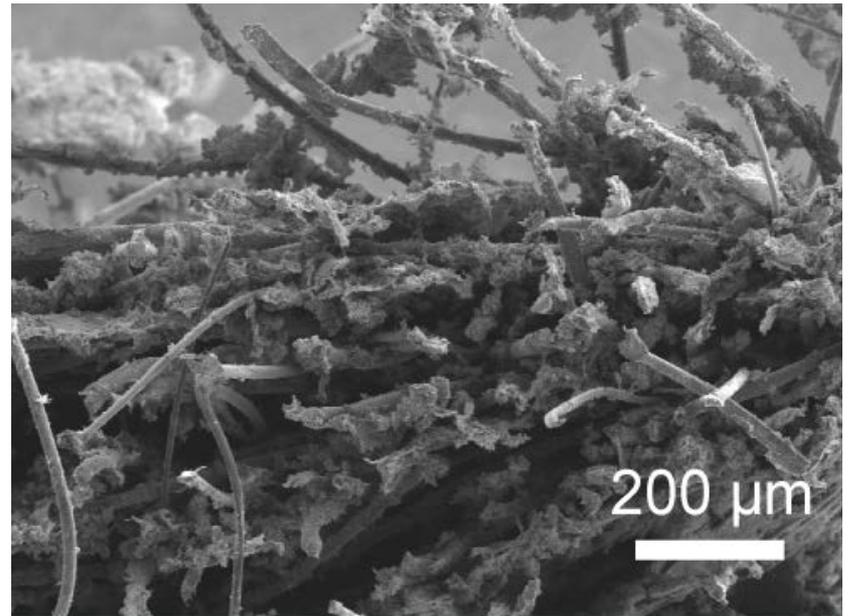
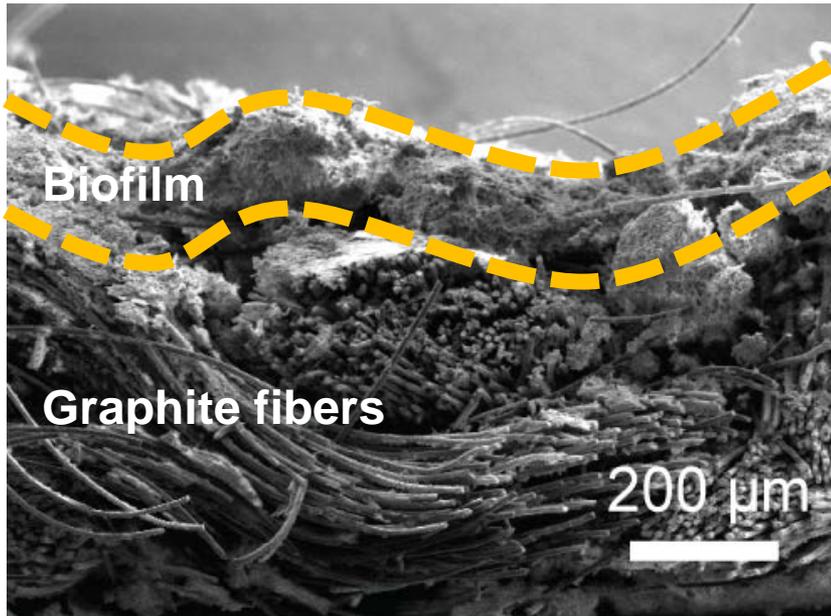
Macroscale Porous for Internal Colonization

- Cross-section of the anodes after 50 days of operation

Carbon cloth

vs.

CNT-textile

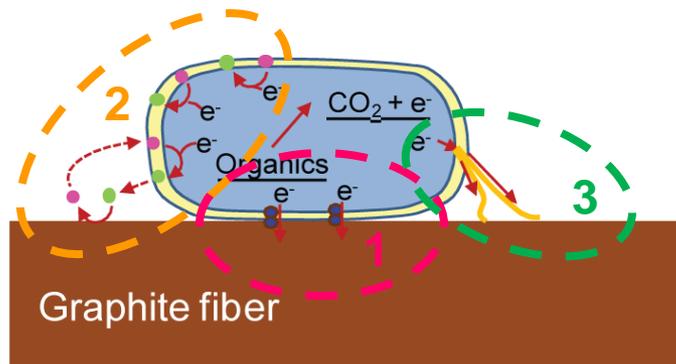
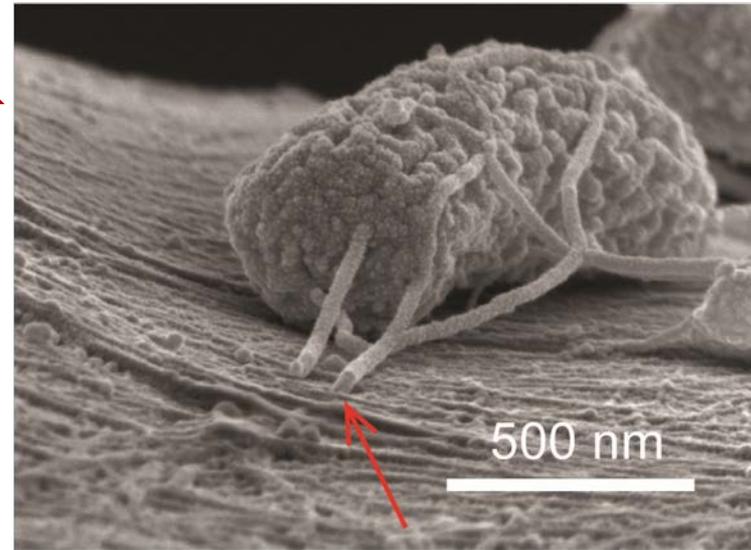


Biofilm-electrode interfacial area increased



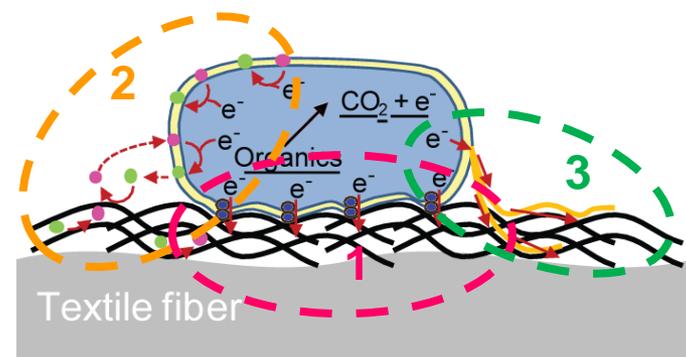
Affinitive Electrode Surface

- Rough and soft
 - 1 Direct membrane contact ↑
- Microscale porous
 - 2 Electron mediators ↑
 - 3 Microbial nanowires ↑



Carbon cloth

vs.



CNT-textile



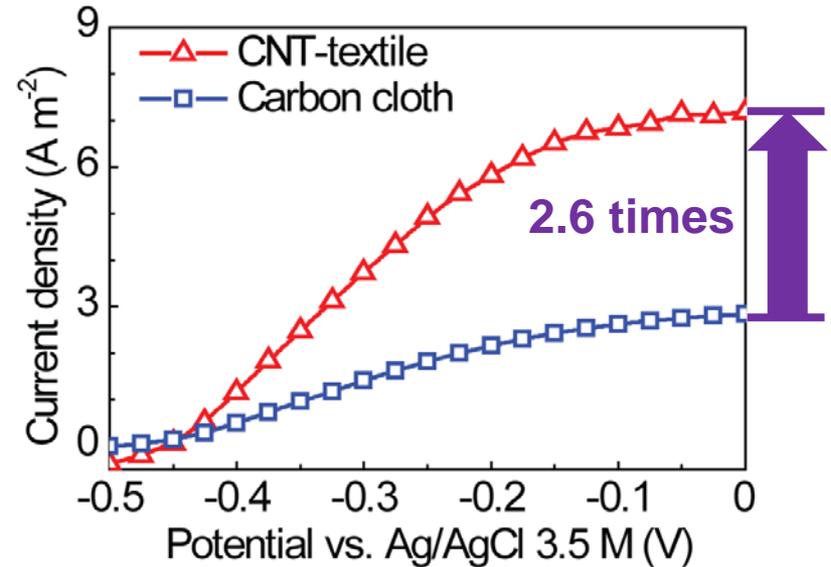
Maximum Current Output

- Linear staircase voltammetry (LSV)

Carbon cloth (2.8 A/m²)



vs. **CNT-textile (7.2 A/m²)**



Internal colonization

Affinitive electrode surface

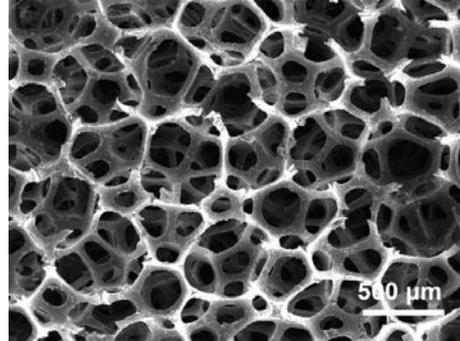


CNT-Sponge

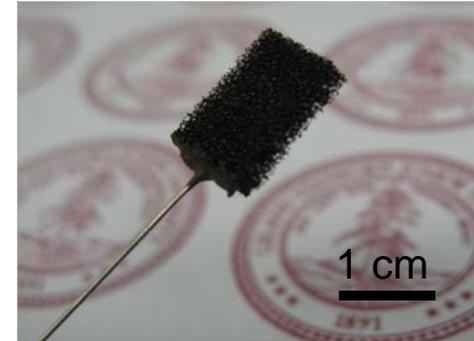
Fabrication



3D Framework



Isotropic

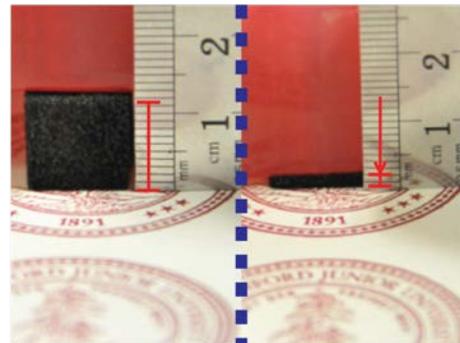


- **Mechanical properties**

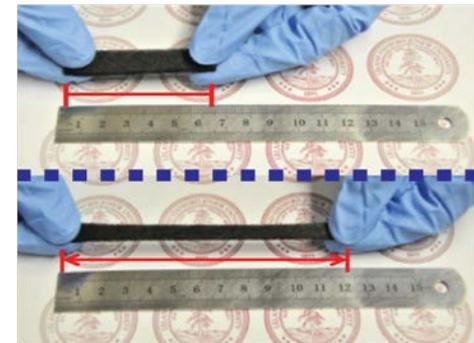
Flexible



Compressible



Stretchable

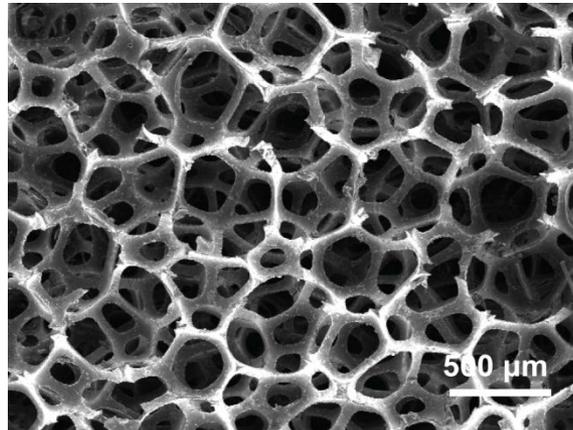
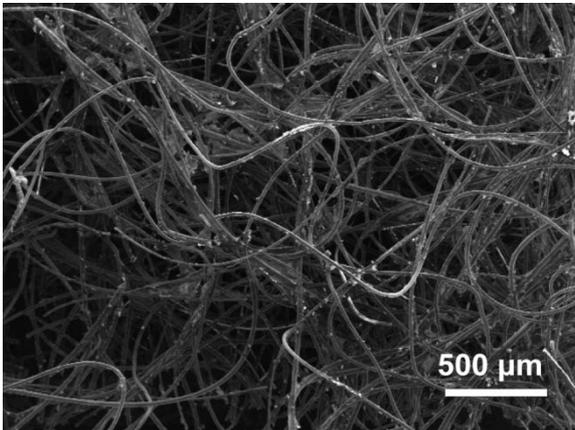


Macroscale Pores of CNT-Sponge

CNT-textile

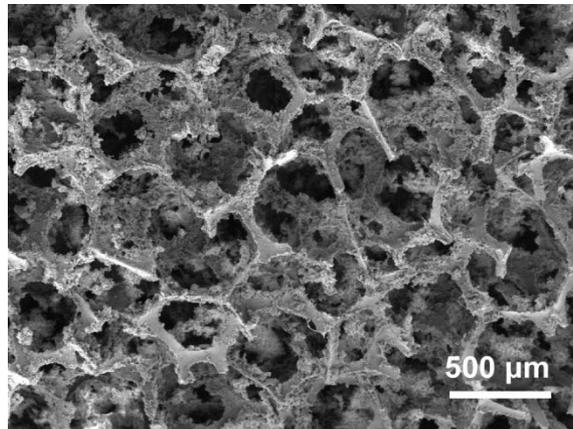
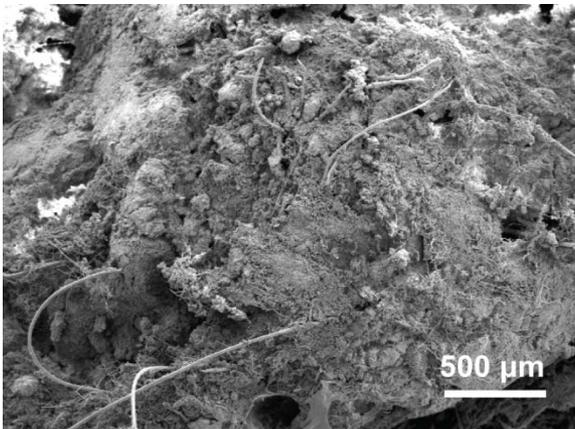
vs.

CNT-sponge



Uniform

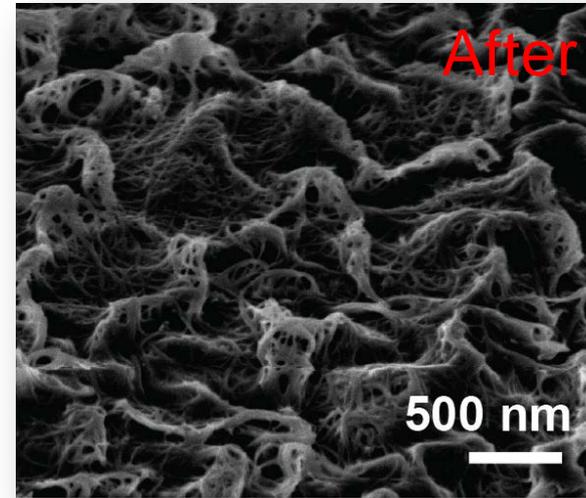
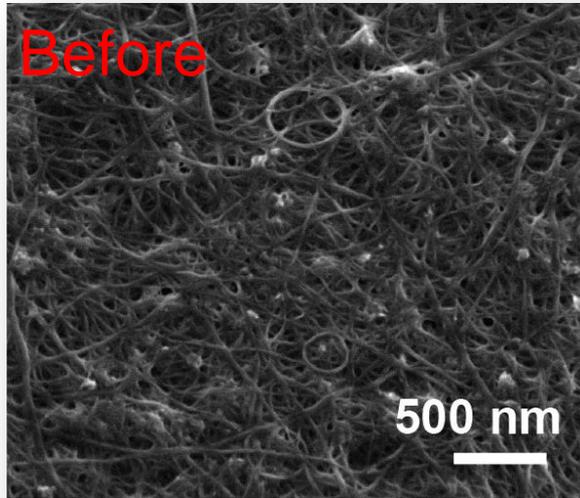
Tunable



After 1-year
operation in
MFCs



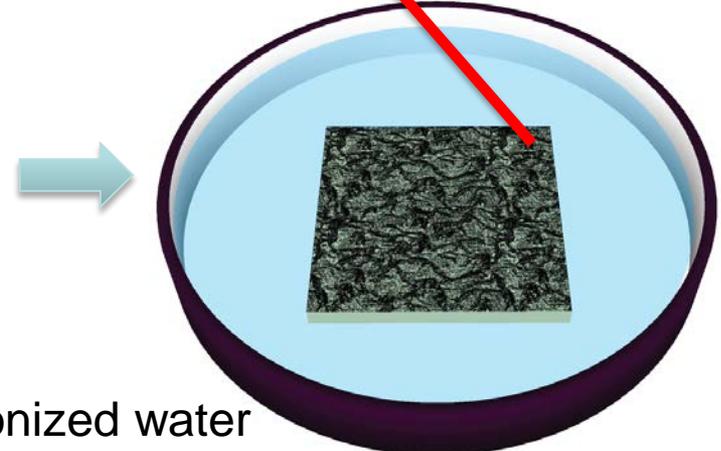
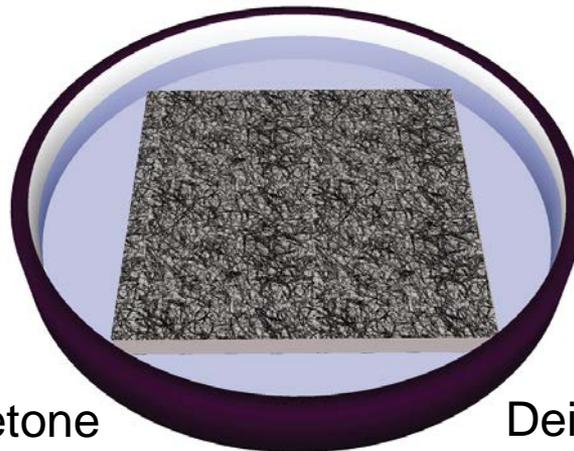
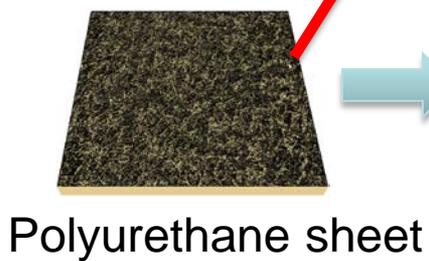
Mesoscale Crinkling CNT Coating



CNT-coated
substrate

Expansion in solution 1

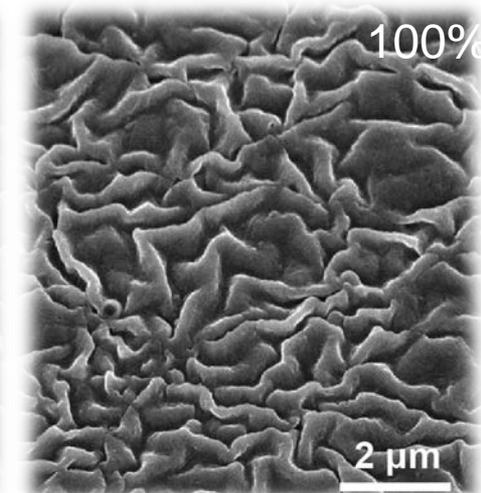
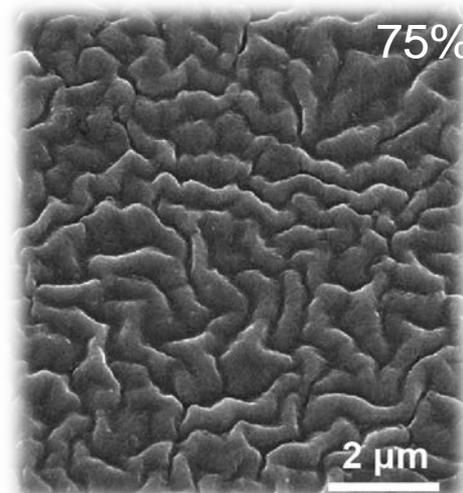
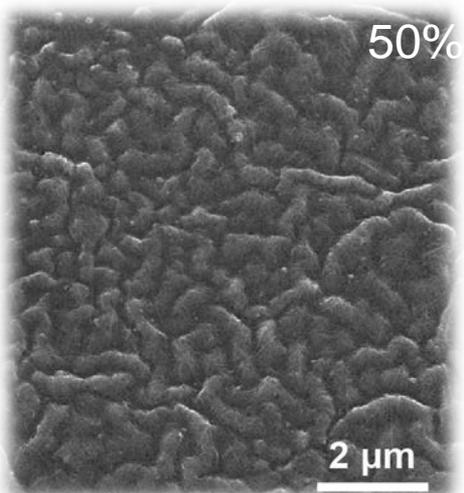
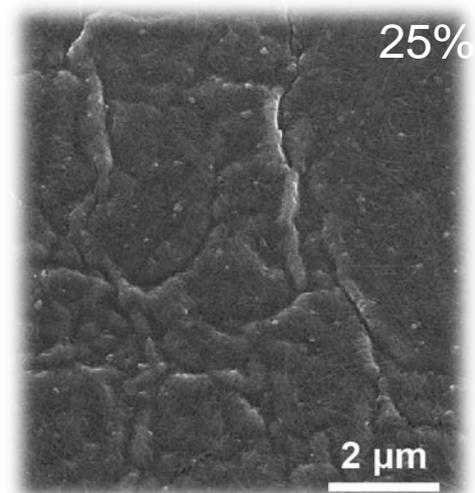
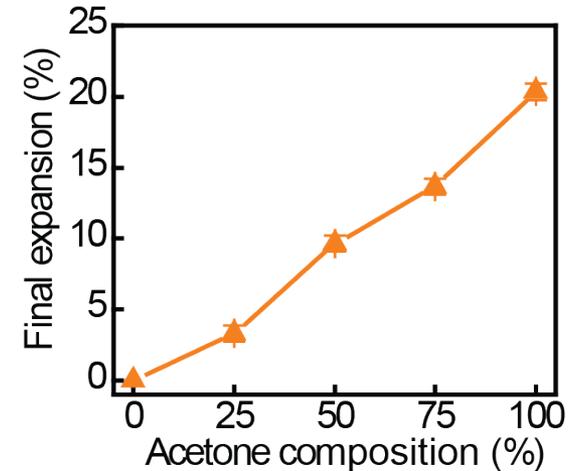
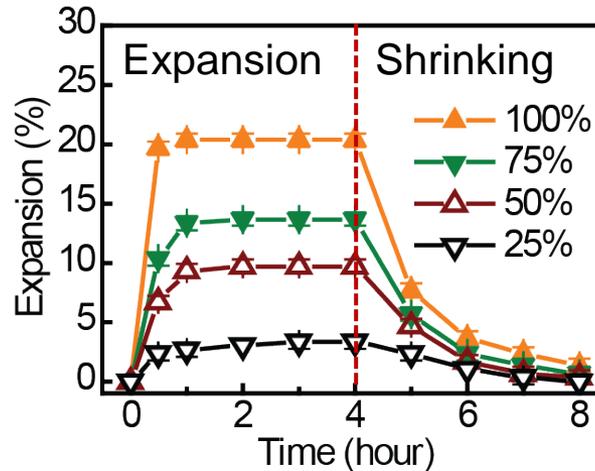
Shrinking in solution 2





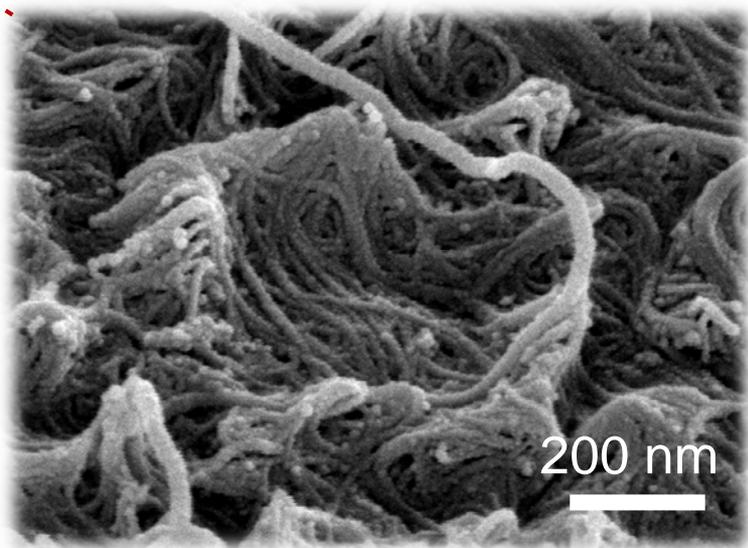
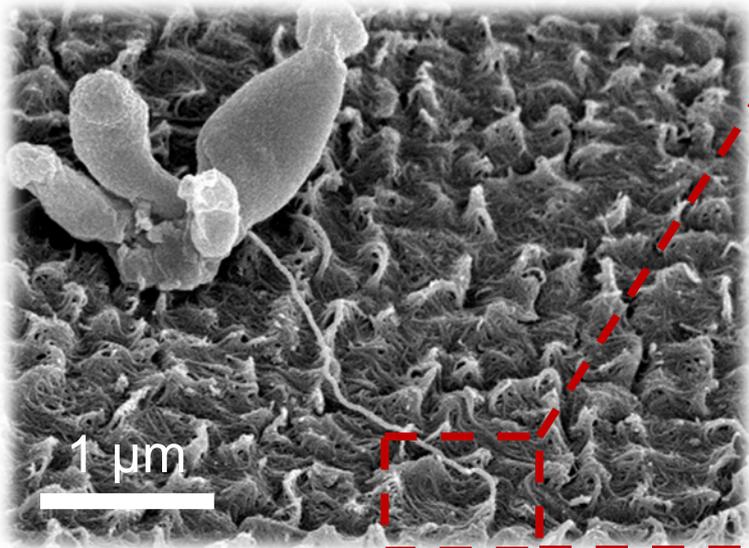
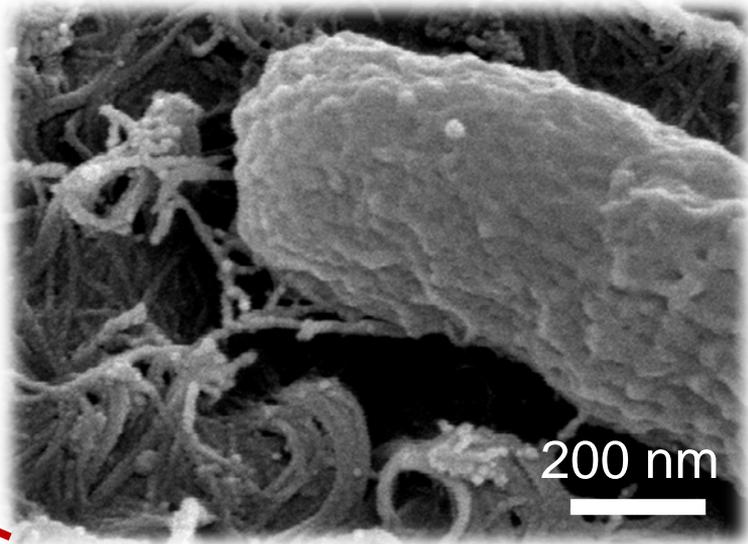
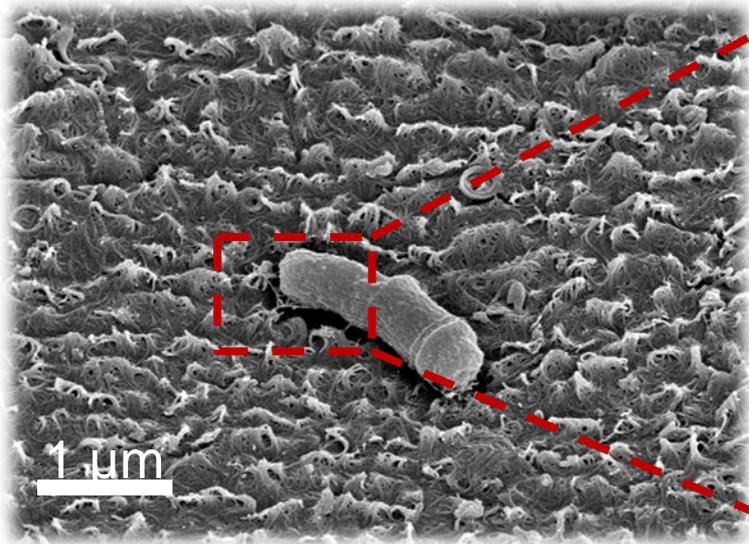
Crinkling Morphology: Controllability

Varying
acetone
concentration





Microorganisms on Crinkling CNT Coating



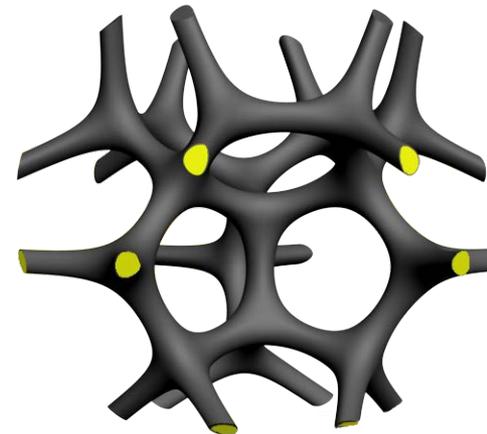
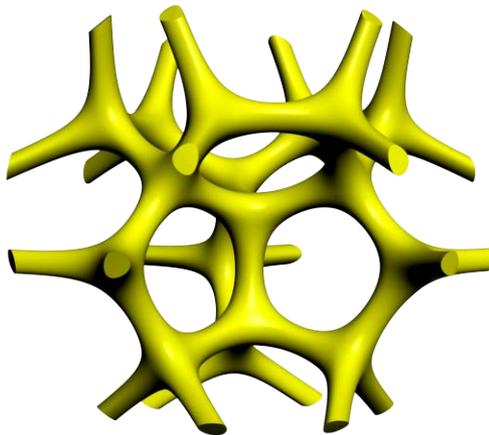


Bioelectrodes: Criteria & Design

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- **Macroscale porous structure**
- **Affinitive electrode surface**

More microbes for
electron transfer

More efficient
electron transfer





Take Home Messages

- Market of electrochemical devices is growing.
- New applications are emerging.
- Electrode design is critical.
- Nanotechnology is a powerful tool.

Thank You & Question